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Original Article

Flotation of oxide copper ore with sodium oleate from the Sepon mine, Lao PDR

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Abstract

The flotation of oxide copper ore with sodium oleate was investigated to determine the optimum pH and dosages of chemical reagents. From the mineralogical analysis using X-ray diffraction, malachite was the major mineral and the gangue minerals were mostly silicates such as quartz and kaolinite. As a result this ore was characterized as oxide copper. This result related well with the chemical analysis using XRF which indicated that copper was the main element with some minor constituents. Oxide copper ore flotation with 800 g/ton sodium oleate at pH 9 yielded 14.4% Cu with 83.3% recovery in a rougher circuit. To enhance the flotation performance, in terms of %Cu, optimum dosages of sodium silicate, quebracho, and pine oil were examined. At the optimum dosages, the grade increased to 20.1% Cu with 76.4% recovery. To upgrade the rougher concentrate, sodium oleate was added in the cleaner stage and without any reagents added in the recleaner stage. The best performance was achieved in this rougher-cleaner-recleaner circuit with 70.7% recovery of 26.9% Cu. This finished concentrate complied with the copper market standard.

Keywords: flotation, malachite, oxide copper ore, reagent dosage, sodium oleate

1. Introduction

Copper (Cu) is a malleable and ductile metal which is a good conductor of heat and electricity (International Copper Study Group, 2017). Copper metal is primarily concentrated and extracted from copper ores. There are different types of copper ores: sulfide and oxide ores are found in copper deposits. Chalcopyrite is a major sulfide ore while malachite is the oxide one. Malachite [$Cu_2CO_3(OH)_2$] is a compound of copper carbonate hydroxide in the context of mineralogy which is formed mainly by weathering of sulfide ores in the vicinity. There are many copper mines operating in ASEAN countries, including the Phubia and Sepon mines in Lao PDR. The Phubia mine has produced copper concentrate mainly from sulfide ores using solely the flotation technique. On the other hand, copper metal has been produced from oxide ores by flotation, leaching, solvent extraction and electrowinning at the Sepon mine. The Sepon mine of Lang Xane Mineral Limited is one of the largest mines in Lao PDR. This mine has ore resources of about 25.5, 10.4, 10.7, and 2.0 million tons from the Khanong, Thengkham North, Theng kham South, and Phabing projects, respectively (Cromie, 2010). The ores of Thengkham North consist mostly of malachite with an average head grade of about 10% Cu. The flotation concentrate must have 25% Cu to comply with the copper standard in the metal market (Anon, 2006). Therefore, it is interesting to utilize a mineral processing technique to produce a final concentrate at the indicated grade. Specifically, froth flotation is widely used to float both sulfide and oxide copper ores. Sulfide ores are generally floated with sulfhydryl collectors such as xanthate or dithiophosphate. On the other hand, flotation of oxide ores involves two basic methods including anionic flotation using oxyhydryl collectors such as fatty acid and its salts, and sulfidization with sulfide or sulfite prior to flotation with sulfhydryl collectors (Bulatovic, 2010). However, malachite does not respond well with sulfhydryl collectors (Li, Rao, García, Li, & Song, 2018). Therefore, oxyhydryl collectors such as hydroxamates (Marion, Jordens, Li, Rudolph, & Waters, 2017; and Lee, Archibald, McLean, & Reuter, 2009) and

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carboxylates (Choi, Choi, Park, Han, & Kim, 2016; and Li, Rao, García, Li, & Song, 2018) have been used to study malachite flotation.

The purpose of this research was to study the effects of the types and dosages of chemical reagents on oxide copper flotation. Various types of reagents include pH modifier, oxyhydryl collector, inorganic dispersant and depressant, organic depressant, and frother. Moreover, a staging flotation method using a rougher-cleaner-recleaner circuit was utilized to enhance the flotation performance. Ultimately, the grade of the final concentrate obtained from an optimum flotation must achieve the specifications for copper.

2. Materials and Methods

2.1 Materials

An oxide copper ore was collected from Sepon mine, Savannakhet, Lao PDR. This run-of-mine (ROM) ore was crushed and ground using a roll crusher and rod mill, respectively. The ground ore was then sampled using a Jones riffle. The ore samples were prepared for mineral and chemical analyses and for the froth flotation study. X-ray diffraction (XRD) was used to analyze the mineral composition while X-ray fluorescence (XRF) was utilized to analyze the chemical composition. The flotation study was conducted using a Denver machine (Denver D-1, Serial no.7627-001) with a cell volume of 1000 mL operating at a fixed agitation speed of 1000 rpm in all experiments.

A variety of industrial-grade chemical reagents were used in the flotation of oxide copper ore: hydrochloric acid (HCl) and sodium carbonate (Na_2CO_3) were used as pH regulators. Sodium silicate (Na_2SiO_3) was added as inorganic dispersant and depressant while quebracho was applied as an organic depressant. Sodium oleate was the main collector. Pine oil was also put into the flotation cell as a frother. All reagents were diluted to 10% weight solution except pine oil which was used directly. Tap water was used in all tests.

2.2 Characterization

The ROM ore sample was characterized for its mineral and chemical composition. The mineral composition was analyzed using the XRD technique linked with an Intel Pentium IV Processor. The measuring conditions were: Cu K-alpha (λ=1.5406 Å) radiation at 30 KV and 10 mA; start and stop angles at 5 and 60 degrees; scanning speed of 0.2 sec/step with increments of 0.02; and detection with a scintillation counter. The ground sample (<75 μm) was packed into a hole on a plastic plate. After that the packed sample was taken to the X-ray with the above-mentioned conditions. The intensity of the detected signals was then plotted as a function of 2θ. Finally the intensity peaks were selected, searched, and matched with those of the standard minerals that complied with the International Centre for Diffraction Data using a computer program named EVA.

The chemical compositions of all samples from the flotation products (feed, slime, concentrate, and tailings) were analyzed using a handheld X-ray fluorescence device (Vanta™ XRF analyzer, Olympus Corporation, Tokyo, Japan. The measuring conditions were set in Geochem2 mode. In this mode there are two X-ray beams: beam number 1 radiated at 40 KV while beam number 2 radiated at 10 KV with a measuring time of 30 min/beam. All of the products were ground to a passing size of 75 μm. Each of the ground products was filled into the sample cup covered with 4 micron Prolene® film. After that, the filled cup was X-rayed in the above mentioned conditions.

2.3 Flotation

Processing of the oxide copper ore was carried out by the froth flotation method.

1. The ROM ore was crushed using a roll crusher to 100% passing size of 6 mm.
2. The crushed ore (1000 g) was ground using a rod mill with eight stainless steel rods for 10 min until 65% passed 75 μm.
3. The milled product was divided equally into four samples using a Jones riffle.
4. The milled product (250 g) was put into the flotation cell together with 900 mL of tap water to make a slurry of the ore.
5. The fine particles in the slurry were de-slimed by agitation for 5 min in the cell and then allowed to settle for 2 min and the suspended particles were rinsed.
6. The chemical reagents were sequentially added to the de-slimed suspension: HCl and/or Na_2CO_3 to the desired pH for 5 min, Na_2SiO_3 for 2 min, quebracho for 2 min, sodium oleate for 5 min, and pine oil for 3 min at the required amounts of all reagents. The copper concentrate floatation was then collected in 5 min.
7. The effect of suspension pH on flotation was investigated at pH 6, 6.66, 8, 9, and 10. The pH was adjusted using HCl or Na_2CO_3 or both.
8. The effect of sodium oleate was evaluated at doses of 400, 600, 800, 1000, and 1200 g/ton ore on the flotation at the optimum pH.
9. The effect of Na_2SiO_3 was studied at various doses of 50, 100, 150, 200 and 250 g/ton on the flotation at the proper dose of sodium oleate.
10. The effect of quebracho was tested at doses of 100, 250, 500, 750 and 1000 g/ton on the flotation of the well-dispersed and depressed suspension.
11. Pine oil at doses of 0, 25, 50, 75, and 100 g/ton were used to float a rougher concentrate from the suspension with sodium oleate at the appropriate dose.
12. The rougher concentrate was cleaned with 800 g/ton of sodium oleate at pH 9.
13. The concentrate was recleaned without adding reagents to increase the final concentrate grade. All products were filtrated, dried, weighed, and analyzed using the Vanta handheld XRF Analyzer.

The flotation performance was evaluated using grade (%Cu) and recovery (%R) as parameters. The %R was calculated using the two-product formula on the basic product grades and weights such as: $\%R = (c \times C)/(f \times F) \times 100$, where c and f are grades of concentrate and feed and C and F are weights of those corresponding products.

3. Results and Discussion

3.1 Mineral composition

The XRD technique was carried out on the ROM ore to identify the major and gangue minerals. The XRD pattern confirmed that malachite [$Cu_2CO_3(OH)_2$] was the major mineral (Figure 1). The gangue minerals contained in this ore were silicate minerals such as quartz (SiO_2) and kaolinite [$Al_2Si_2O_5(OH)_4$] with a small amount of marcasite (FeS_2). Therefore, this ROM ore was characterized as oxide copper. From the mineral processing viewpoint, this ore was categorized as a sparingly soluble mineral that responded well with a fatty acid and its salts such as oleic acid and sodium oleate (Fuerstenau & Han, 2003).

3.2 Chemical composition

The chemical composition of the ROM ore was analyzed using the Vanta handheld XRF Analyzer. The results of the analysis indicated that Cu (10.5%) was the main element, and the other constituents were 17.8% Si, 7.95% Mg, 5.86% Fe, 3.72% Al, 0.86% K, 0.76% Mn, 0.73% Ca, 0.18% S, 0.17% Ti, 0.11% Zn, and 51.16% light elements (Table 1). These results corresponded well with the mineralogical analysis.

Table 1. Chemical composition of the ROM ore.

Elements	Percent
Si	17.8
Cu	10.5
Mg	7.95
Fe	5.86
Al	3.72
K	0.86
Mn	0.76
Ca	0.73
S	0.18
Ti	0.17
Zn	0.11
Light elements	51.16

3.3 Effect of suspension pH on oxide copper ore flotation

The effect of suspension pH on flotation of oxide copper ore with 1000 g/ton sodium oleate and 100 g/ton pine oil is shown in Figure 2.

The grade and recovery of oxide copper ore were significantly affected by suspension pH adjusted by sodium carbonate or soda ash (Figure 2). As the pH increased from 8 to 9 by adding soda ash from 1600 to 2400 g/ton ore, the recovery decreased from 83.9% to 77.2% but the grade increased from 12.6% to 14.1% Cu. However, a further increase of soda ash caused a decrease in both the recovery and grade. It was also clear that the flotation of malachite with sodium oleate was greatly affected in the alkaline pH range. This was due to carboxylic acid which is highly ionized to carboxylate ions that are responsible for the flotation at the alkaline pH values (King, 1982). Therefore, the optimum dose of soda ash used in the following studies was 2400 g/ton which corresponded to a suspension pH of 9.

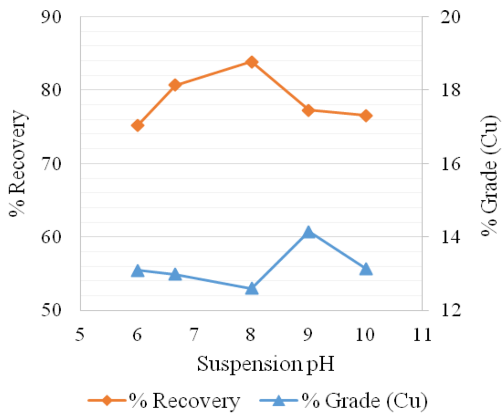

Figure 2. Flotation grade and recovery of oxide copper ore as a function of suspension pH with 1000 g/ton sodium oleate and 100 g/ton pine oil.

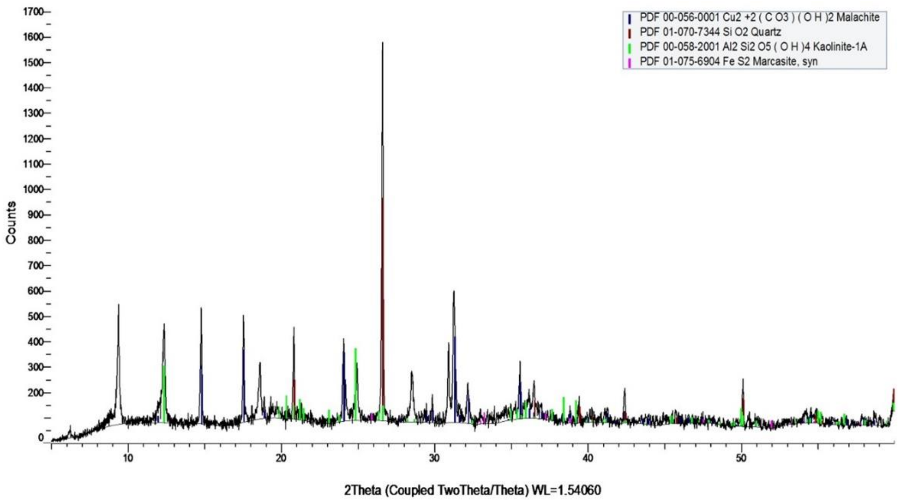

Figure 1. XRD pattern of the ROM ore.

3.4 Effect of sodium oleate doses on oxide copper ore flotation

The effect of sodium oleate doses on oxide copper ore flotation at pH 9 with 100 g/ton pine oil is illustrated in Figure 3.

As the dose of sodium oleate increased from 400 to 800 g/ton, both the grade and recovery increased markedly from 12.7% to 14.4% Cu and from 59.2% to 83.3% respectively. Further increases in the dose resulted in decreases in both grade and recovery. This was probably due to entrapment of gangue minerals in the closely textured froths. These froths are generated not only when overdoses of pine oil are used but also in the case of sodium oleate. It is already known that this carboxylate salt also has a frothing property in addition to the collecting property (King, 1982). As a result, 800 g/ton of sodium oleate was considered as the appropriate dose in the next flotation studies.

3.5 Effect of sodium silicate doses on oxide copper ore flotation

Bulatovic (2010) suggested that sodium silicate can be applied as an inorganic reagent to disperse and depress silicate minerals in the flotation of oxide copper and copper cobalt ores. In order to increase the flotation performance, sodium silicate was used in this study. The effect of sodium silicate on oxide copper ore flotation at pH 9 with 800 g/ton sodium oleate and 100 g/ton pine oil is depicted in Figure 4.

It is apparent that the grade slightly increased as the dose of sodium silicate increased to 100 g/ton ore, but the recovery sharply decreased as the dose increased. Therefore, the proper dose for the next flotation studies was 100 g/ton. An excess dose of sodium silicate was possibly the cause of the detrimental flotation of malachite. It seemed that the sodium silicate depressed not only the silicate minerals but also the carbonate ones such as malachite. Fuerstenau & Han (2003) indicated that calcite is the most sensitive to sodium silicate addition especially at pH 7–10 for example.

3.6 Effect of quebracho doses on oxide copper ore flotation

The effect of quebracho on oxide copper ore flotation at pH 9 with 100 g/ton sodium silicate, 800 g/ton sodium oleate, and 100 g/ton pine oil is presented in Figure 5.

It is clear that the grade increased dramatically as the dose of quebracho increased, whereas the recovery decreased significantly. The effectiveness of quebracho to depress calcareous minerals such as calcite was well demonstrated by Fuerstenau & Han (2003). By the same token, the alkaline-earth gangue minerals found in this oxide ore were also expected to be depressed with quebracho. However, a complete understanding of its behavior has not been realized. In any case, the reasonable dose of quebracho is about 500 g/ton in terms of both grade and recovery enhancement.

3.7 Effect of pine oil doses on oxide copper ore flotation

As discussed previously, sodium oleate functions not only as a collector but also as a frother. It would be expected that there is a synergistic effect of sodium oleate and pine oil on oxide copper ore flotation. Consequently, the effect of pine oil on the grade and recovery of copper concentrate was investigated at pH 9 with 100 g/ton sodium silicate, 500 g/ton quebracho, and 800 g/ton sodium oleate (Figure 6).

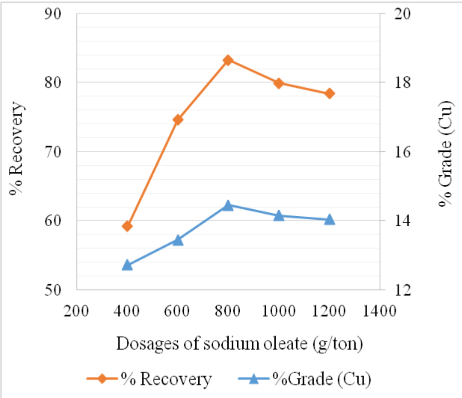

Figure 3. Flotation grade and recovery of oxide copper ore as a function of sodium oleate doses at pH 9 with 100 g/ton pine oil.

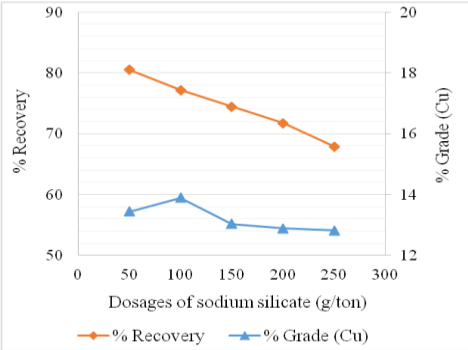

Figure 4. Flotation grade and recovery of oxide copper ore as a function of sodium silicate doses at pH 9 with 800 g/ton sodium oleate and 100 g/ton pine oil.

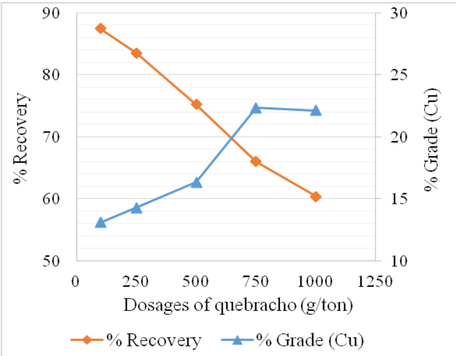

Figure 5. Flotation grade and recovery of oxide copper ore as a function of quebracho doses at pH 9 with 100 g/ton sodium silicate, 800 g/ton sodium oleate, and 100 g/ton pine oil.

The optimum dose of pine oil was found to be 25 g/ton yielding 20.1% grade with 76.4% recovery. Compared

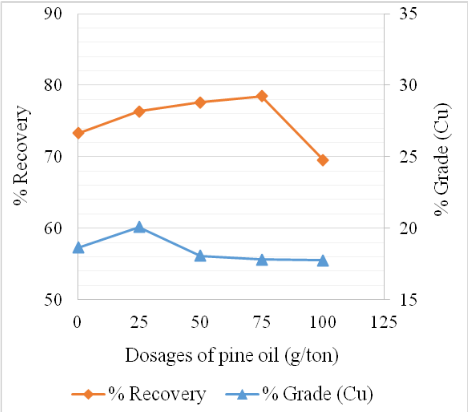

Figure 6. Flotation grade and recovery of oxide copper ore as a function of pine oil dosages at pH 9 with 100 g/ton sodium silicate, 500 g/ton quebracho, and 800 g/ton sodium oleate.

to the 100 g/ton pine oil giving 17.7% grade with 69.5% recovery, the lower dose gave better flotation performance. This was the appropriate dose used in the next stage of this flotation study.

3.8 Rougher, cleaner. and recleaner flotation

According to previous studies on the effects of chemical reagents on oxide copper ore flotation in a rougher circuit, the optimum doses of 100 g/ton sodium silicate, 500 g/ton quebracho, 800 g/ton sodium oleate, and 25 g/ton pine oil working at a suspension pH of 9 were used in staged flotation. This flotation that included rougher, cleaner, and recleaner stages was used to upgrade the final concentrate to comply with the copper market standard. It was observed that the rougher and cleaner concentrate grades were less than 25% Cu (Table 2). Therefore, the cleaner concentrate was recleaned without the addition of chemical reagents. Eventually a finished product from the recleaner stage met the specification for the copper market.

Figure 7 illustrates the grade and recovery of rougher, cleaner, and recleaner flotation of oxide copper ore at pH 9 with 100 g/ton sodium silicate, 500 g/ton quebracho, 800 g/ton sodium oleate, and 25 g/ton pine oil. As the %recovery decreased from 76.4 to 70.7, the %grade increased strikingly from 20.1 to 26.9 using the rougher-cleaner-recleaner flotation. This staged flotation enhanced the copper grade of the required finished product.

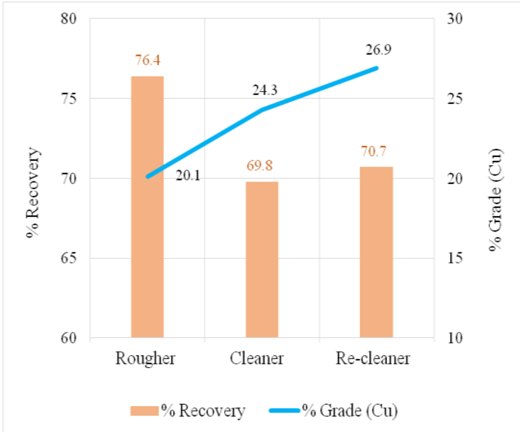

Figure 7. Grade and recovery of rougher, cleaner and recleaner flotation of oxide copper ore at pH 9 with 100 g/ton sodium silicate, 500 g/ton quebracho, 800 g/ton sodium oleate, and 25 g/ton pine oil.

4. Conclusions

The flotation of oxide copper ore with 800 g/ton sodium oleate at pH 9 yielded 14.4% Cu with 83.3% recovery in the rougher circuit. To enhance the flotation performance in terms of copper grade, the optimum doses of sodium silicate, quebracho, and pine oil were further examined. It was found that the grade slightly increased as the dose of sodium silicate increased to 100 g/ton, but the recovery sharply decreased with higher doses. However, the grade increased dramatically as the dose of quebracho increased, whereas the recovery decreased significantly at the dose of 500 g/ton. Because sodium oleate also functioned as a frother, 25 g/ton of pine oil was shown to be enough to generate an adequate amount of froth for this oxide copper flotation. With those optimum

Table 2. Rougher, cleaner and recleaner flotation of oxide copper ore at pH 9 with 100 g/ton sodium silicate, 500 g/ton quebracho, 800 g/ton sodium oleate and 25 g/ton pine oil.

Flotation stages	Products	Wt. (%)	Grade (%)	Recovery (%)
Rougher	Feed	100	11.2	
	Slime	15.1	9.07	12.2
	R-Concentrate	42.6	20.1	76.4
	Tailing	29.6	3.92	10.3
Cleaner	Feed	100	10.8	
	Slime	15.2	8.85	11.5
	Tailing	38.8	5.75	19.3
	C-Concentrate	30.3	24.3	69.8
	Middling	5.66	9.18	4.79
Recleaner	Feed	100	10.9	
	Slime	15.4	8.75	12.3
	Tailing	36.2	4.73	15.6
	Middling 1	6.72	6.90	4.23
	RC-Concentrate	28.7	26.9	70.7
	Middling 2	4.00	10.5	3.86

doses of chemical reagents, the grade increased to 20.1% Cu with 76.4% recovery. In order to upgrade the rougher concentrate, 800 g/ton of sodium oleate was added in the cleaner stage at pH 9 without any reagents added in the recleaner stage. The best flotation performance was achieved in the rougher-cleaner-recleaner circuit with 70.7% recovery of 26.9% Cu. This finished concentrate complied with the copper standard in the metal market.

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