FLOTATION OF OXIDE COPPER ORE FROM SEPON MINE, LAO PDR WITH SODIUM OLEATE

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<td>Flotation, malachite, oxide copper ore, reagent dosage, sodium oleate</td>
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FLOTATION OF OXIDE COPPER ORE FROM SEPON MINE, LAO PDR

WITH SODIUM OLEATE

Original Article

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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 XRD, malachite is the major mineral. And gangue minerals are 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 indicating that copper is 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 rougher circuit. To enhance the flotation performance, in term of %Cu, optimum dosages of sodium silicate, quebracho and pine oil were examined. At the optimum dosages, the grade was increased to 20.1% Cu with 76.4% recovery. To upgrade the rougher concentrate, sodium oleate was added in cleaner stage and without any reagents added in 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 schedule in a metal market.

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 found in copper deposits. Chalcopyrite is a major sulfide ore while malachite is the oxide one. Malachite \([\text{Cu}_2\text{CO}_3(\text{OH})_2]\) is a compound of copper carbonate hydroxide in the context of mineralogy which formed mainly by weathering of sulfide ores in the vicinity. There are many copper mines operating in ASEAN countries, including Phubia and Sepon mines in Lao PDR. Phubia mine has produced copper concentrate mainly from sulfide ores using solely flotation technique. On the other hand, copper metal has been produced from oxide ores by flotation, leaching, solvent extraction and electrowinning in Sepon mine. The Sepon mine of Lang Xane Mineral Limited is one of the largest mines in Lao PDR. This mine has the ore resources about 25.5, 10.4, 10.7 and 2.0 million tons from Khanong, Thengkham North, Thengkham South, and Phabing projects respectively (Cromie, 2010). The Thengkham North’s ores consist mostly of malachite with an average head grade about 10% Cu. To comply with the copper schedule of a metal market the flotation concentrate must have 25% Cu (Anon, 2006). Therefore, it is interesting to utilize a mineral processing technique to produce the final concentrate as indicated grade. Specifically froth flotation is widely used to float both sulfide and oxide copper ores. Sulfide ores are generally floated with sulphydryl 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 sulphydryl collectors (Bulatovic, 2010). However, malachite is not respond well with sulphydryl collectors (Li,
Therefore, oxyhydryl collectors such as hydroxamates (Marion, Jordens, Li, Rudolph, & Waters, 2017; and Lee, Archibald, McLean, & Reuter, 2009) and carboxylates (Choi, Choi, Park, Han, & Kim, 2016; and Li, Rao, García, Li, & Song, 2018) have been used to study a malachite flotation.

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

2. Materials and Method

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 by using roll crusher and rod mill respectively. After that the ground ore was sampled using Jones riffle. The ore samples were prepared for mineral and chemical analyses and froth flotation study in respect. 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 by using Denver machine (Denver D-1, Serial no.7627-001) with a cell volume of 1000 ml operating at fixed agitation speed of 1000 rpm in all experiments.

A variety of industrial-graded chemical reagents were used in the flotation of oxide copper ore as follows: hydrochloric acid (HCl) and sodium carbonate (Na₂CO₃) were used as pH regulators. Sodium silicate (Na₂SiO₃) was added as inorganic dispersant and...
depressant while quebracho was applied as organic depressant. Sodium oleate was utilized as a main collector. And pine oil was put into the flotation cell as frother. All reagents were diluted to 10% weight solution except pine oil which is directly used. Tap water was utilized in all tests.

2.2. Characterization

The ROM ore sample was characterized for its mineral and chemical composition. The mineral composition was analyzed by using XRD technique linked with Intel Pentium IV Processor. The measuring conditions were as follows: Cu K-alpha (\(\lambda=1.5406\) A\(^0\)) radiation at 30 KV and 10 mA; start and stop angles at 5 and 60 degrees; scanning speed of 0.2 sec/step with increment of 0.02; detection with scintillation counter. The ground sample (\(-75\mu m\)) was packed into a hole on plastic plate. After that the packed sample was brought to x-ray with the above-mentioned conditions. The intensity of detected signals was then plotted as a function of 2\(\theta\). Finally the intensity peaks were selected, searched and matched with those of the standard minerals complied by the International Centre for Diffraction Data (ICDD) using computer program named EVA.

The chemical composition of all samples from the flotation products (feed, slime, concentrate and tailing) was analyzed using Vanta Handheld XRF Analyzer. The measuring conditions were set in Geochem2 mode. In this mode there are 2 X-ray beams: beam number 1 radiating at 40 KV while beam number 2 at 10 KV with measuring time of 30 min/beam. All the products were ground to the passing size of 75 \(\mu m\). Fill each ground product into the sample cup covered with 4 micron Prolene\textsuperscript{®} Film. After that, the filled cup was x-rayed with the abovementioned conditions.
2.3. Flotation

Processing of the oxide copper ore was carried out by froth flotation method described as following:

1. Crush the ROM ore by using roll crusher to 100% passing size of 6 mm.

2. Grind 1000 g of the crushed ore using rod mill, with 8 stainless steel rods, for 10 min to 65% passing 75 μm.

3. Divide the milled product equally into 4 samples using Jones riffle.

4. Put 250 g of the milled product into the flotation cell together with 900 ml of tap water to make the ore slurry.

5. De-slime fine particles in the slurry by agitation for 5 min in the cell then place for 2 min and rinse the suspended particles.

6. Add chemical reagents orderly to the de-slimed suspension and condition as following schemes: HCl and/or Na₂CO₃ to the desired pH for 5 min, Na₂SiO₃ for 2 min, quebracho for 2 min, sodium oleate for 5 min and pine oil for 3 min to the required dosages of all reagents, then float and collect the copper concentrate for 5 min.

7. Investigate the effect of suspension pH on flotation at pH 6, 6.66, 8, 9 and 10 adjusted by using HCl and/or Na₂CO₃.

8. Examine the effect of sodium oleate dosages of 400, 600, 800, 1000 and 1200 g/ton ore on the flotation at the optimum pH.

9. Study the effect of Na₂SiO₃ with various dosages of 50, 100, 150, 200 and 250 g/ton on the flotation at the proper dosage of sodium oleate.

10. Test the effect of quebracho dosages of 100, 250, 500, 750 and 1000 g/ton on the flotation of the well-dispersed and depressed suspension.
11. Pine oil with dosages 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 dosage.

12. Clean the rougher concentrate with 800 g/ton sodium oleate at pH 9.

13. Re-clean the concentrate without the reagents added in order to increase a final concentrate grade. All products were filtrated, dried, weighed and analyzed by using Vanta Handheld XRF Analyzer.

14. Evaluate the flotation performance by using grade (%Cu) and recovery (%R) as parameters. Calculate the %R using two-product formula on the basic of product grades and weights such as: \[ \%R = \frac{c \times C}{f \times F} \times 100 \], where \( c \) and \( f \) are grades of concentrate and feed, and \( C \) and \( F \) are weights of those corresponding products.

3. Result and Discussion

3.1. Mineral composition

XRD technique was carried out on the ROM ore to identify the major and gangue minerals. The XRD pattern in Figure 1 confirms that malachite \([\text{Cu}_2\text{CO}_3(\text{OH})_2]\) is the major mineral. And the gangue minerals containing in this ore are silicate minerals such as quartz \((\text{SiO}_2)\) and kaolinite \([\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]\) with small amount of marcasite \((\text{FeS}_2)\). This ROM ore can be characterized as oxide copper. In the mineral processing viewpoint, this ore is categorized as a sparingly soluble mineral responding well with a fatty acid and its salts such as oleic acid and sodium oleate (Fuerstenau & Han, 2003).

Figure 1: XRD pattern of the ROM ore.
3.2. Chemical composition

Chemical composition of the ROM ore was analyzed using Vanta Handheld XRF Analyzer. The analysis result shown in Table 1 indicates that Cu (10.5%) is the main element, and the other constituents are 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. This result is corresponding well with the above mineralogical analysis.

Table 1: Chemical composition of the ROM ore.

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.

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.

As shown in Figure 2, the grade and recovery of oxide copper ore are significantly affected by suspension pH adjusted by sodium carbonate or soda ash. As the pH increases from 8 to 9, by adding soda ash from 1600 to 2400 g/ton ore, the recovery decreases from 83.9 to 77.2% but the grade increases from 12.6 to 14.1% Cu. However, further increasing of soda ash dosage causes the decreasing of both the recovery and grade. It is also clear that the flotation of malachite with sodium oleate is greatly effected at the alkaline pH range. This is due to carboxylic acid is highly ionized to carboxylate ions responsible to
the flotation at the alkaline pH (King, 1982). Therefore, the optimum dosage of soda ash used in the following studies is 2400 g/ton corresponding to the suspension pH 9.

3.4. Effect of sodium oleate dosages on oxide copper ore flotation

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

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

As the dosages of sodium oleate increase from 400 to 800 g/ton, both the grade and recovery increase markedly from 12.7 to 14.4% Cu and 59.2 to 83.3% respectively. Further increasing of the dosages results in the decreasing of both grade and recovery. This may be caused by entrapment of gangue minerals in the closely textured froths. These froths are generated not only by using the overdoses of pine oil but sodium oleate as well. It is already known that this carboxylate salt also has a frothing property in addition to the collecting one (King, 1982). As a result, 800 g/ton sodium oleate is considered as an appropriate dosage in the next flotation studies.

3.5. Effect of sodium silicate dosages 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 dosages 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.

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

It is apparent that the grade slightly increases with the increasing dosage of sodium silicate to 100 g/ton ore, but the recovery sharply decreases with the dosages. Therefore, the proper dose used in the next flotation studies is 100 g/ton. An excess dose of sodium silicate may be the cause of the detrimental flotation of malachite. It is implied that sodium silicate depresses not only the silicate minerals but also the carbonate ones such as malachite studied. 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 dosages on oxide copper ore flotation

The effect of quebracho dosages 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.

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

It is clearly that the grade increases dramatically with the increasing of quebracho dosages, whereas the recovery decreases significantly. The effectiveness of quebracho to
depress calcareous minerals such as calcite is well demonstrated by Fuerstenau & Han (2003). By the same token, the alkaline-earth gangue minerals found in this oxide ore are also expected to be depressed with quebracho. However, a complete understanding of its behavior has not been realized now yet. Anyhow, the reasonable dosage of quebracho, considered in terms of both grade and recovery enhancement, is about 500 g/ton.

3.7. Effect of pine oil dosages on oxide copper ore flotation

As previously discussed, sodium oleate functions not only as a collector but also a frother. It would be expected that there is a synergistic effect of sodium oleate and pine oil on the oxide copper ore flotation. Consequently, the effect of pine oil dosages 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 as shown in Figure 6.

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.

Found that the optimum dose of pine oil is 25 g/ton yielding 20.1% grade with 76.4% recovery. Comparing to the 100 g/ton pine oil giving 17.7% grade with 69.5% recovery, the lower the dosage gives the better the flotation performance. This is an appropriate dosage used in the next staging flotation study.
3.8. Rougher, cleaner and recleaner flotation

According to previous studies of the effects of chemical reagents on oxide copper ore flotation in a rougher circuit, the optimum dosages of 100 g/ton sodium silicate, 500 g/ton quebracho, 800 g/ton sodium oleate and 25 g/ton pine oil working at suspension pH 9 were used in a staging flotation. This flotation including rougher, cleaner and recleaner stages was used to upgrade the final concentrate complying with the copper market standard. It was shown in Table 2 that the rougher and cleaner concentrate grades are less than 25% Cu. Therefore, the cleaner concentrate was re-cleaned without the chemical reagents added. Eventually a finished product from the recleaner stage meets the need of the copper market.

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.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Recovery</th>
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<tr>
<td>Rougher</td>
<td>Cleaner</td>
</tr>
<tr>
<td>20.1%</td>
<td>26.9%</td>
</tr>
</tbody>
</table>

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 are also shown in Figure 7. As the % recovery decreases from 76.4 to 70.7, the % grade increases strikingly from 20.1 to 26.9 by using the rougher-cleaner-recleaner flotation. This staging flotation does enhance 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 rougher circuit. To enhance the flotation performance, in term of copper grade, the optimum dosages of sodium silicate, quebracho and pine oil were further examined. Found that the grade slightly increased with the increasing dosage of sodium silicate to 100 g/ton, but the recovery sharply decreased with the dosages. However, the grade increased dramatically with the increasing of quebracho dosages, whereas the recovery decreased significantly at the dosage of 500 g/ton. Because sodium oleate also functioned as a frother, then 25 g/ton of pine oil was shown to be enough to generate adequate amount of froths for this oxide copper flotation. With those optimum dosages of chemical reagents added, the grade was increased to 20.1% Cu with 76.4% recovery. In order to upgrade the rougher concentrate, 800 g/ton sodium oleate was further added in the cleaner stage at pH 9, and 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 schedule in a metal market.

Acknowledgments

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Region 3, Chiang Mai, Thailand and Dr. Ponlayuth Sooksamiti for using theirs facilities in mineral and chemical analyses.

References


Table 1: Chemical composition of the ROM ore.

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<th>Elements</th>
<th>Percent</th>
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<tr>
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<tr>
<td>Cu</td>
<td>10.5</td>
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<tr>
<td>Mg</td>
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<td>Fe</td>
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<td>Al</td>
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<td>Mn</td>
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<td>Ca</td>
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<td>Zn</td>
<td>0.11</td>
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<tr>
<td>Light elements</td>
<td>51.16</td>
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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.

<table>
<thead>
<tr>
<th>Flotation Stages</th>
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<th>Wt. (%)</th>
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<td>Feed</td>
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<td></td>
<td>Slime</td>
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<td></td>
<td>R-Concentrate</td>
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<td>20.1</td>
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<tr>
<td></td>
<td>Tailing</td>
<td>29.6</td>
<td>3.92</td>
<td>10.3</td>
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<tr>
<td>Cleaner</td>
<td>Feed</td>
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</tr>
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<td>Middling 2</td>
<td>4.00</td>
<td>10.5</td>
<td>3.86</td>
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Figure 1: XRD pattern of the ROM ore.

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

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.
Figure 7: Grade and recovery of rougher, cleaner and re-cleaner 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.