A Multistage Sulphidisation Flotation Procedure for a Low Grade Malachite Copper Ore

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Abstract—This study was carried out to develop a flotation procedure for an oxide copper ore from a Region in Central Africa for producing an 18% copper concentrate for downstream processing at maximum recovery from a 4% copper feed grade. The copper recoveries achieved from the test work were less than 50% despite changes in reagent conditions (multistage sulphidisation, use of RCA emulsion and mixture, use of AM 2, etc). The poor recoveries were attributed to the mineralogy of the ore from which copper silicates accounted for approximately 70% (mass) of the copper minerals in the ore. These can be complex and difficult to float using conventional flotation methods. Best results were obtained using basic sulphidisation procedures, a high flotation temperature and extended flotation residence time.

Keywords—Froth flotation, Sulphidisation, Copper oxide ore, Mineralogy, Recovery

I. INTRODUCTION

This article concentrates on the development of the flotation procedure for an oxide copper ore in the RCA. Oxide copper ores are very common in the RCA. These are formed by atmospheric weathering of near surface sulphide deposits [1]. The most common treatment route for these ores is hydrometallurgy which involves flotation, heap leaching, solvent extraction and electrowinning [1]. For the flotation process, the two most common approaches are controlled potential sulphidisation (CPS) and the fatty acid flotation method [1]. Heap leaching involves trickling dilute sulphuric acid over a heap of copper ore, to form a pregnant copper sulphate solution. Copper is subsequently extracted from the solution using solvent extraction and electrowinning technologies. Froth flotation was introduced for treatment of these ores as weathering of gangue minerals made the clarification of solutions sent to electrowinning extremely difficult [1].

Secondary sulphide (supergene) ores, are resistant to sulphuric acid leaching. These ores consist of a mixture of copper carbonate, sulphate, phosphate, and oxide minerals and secondary sulphide minerals, dominantly chalcocite and other minerals such as digenite. For these ores bacterial oxidation and froth flotation may be the preferred treatment routes. Some supergene ores may be rich in native copper. Normally it will not be recovered in the flotation concentrate but will report to the tailings due to the dense nature of the particles. The tailings would then be treated via a gravity separation circuit where the density of the material is used to liberate it from the lighter silicate minerals. The gangue minerals present then become important as clay-rich native copper is difficult to recover.

The most common and main copper mineral present in the RCA ores is malachite. Many copper deposits are also low grade (2-4% copper) and may require excessive amounts of acid to leach, in some cases the presence of certain types of acid consuming gangue minerals (dolomitic, micaeous or siliceous) make it uneconomical to leach the ore as it is [1]. These ores would require a pre-concentration stage prior to leaching. Froth flotation is the most common form of concentration for all sulphide mineral ores and oxide minerals especially copper carbonates like malachite. Generally copper oxide minerals do not respond well to traditional sulphide copper collectors and require alternative flotation techniques to concentrate the copper oxides [2]. Sulphidisation as a technique to recover copper from oxide ore by flotation was investigated in this study.

II. FROTH FLOTATION THEORY

Oxides and silicates are the most abundant minerals in the earth's crust and their flotation behavior is important because of their inherent value and their common occurrence as gangue minerals in ores [3]. Flotation is a physio-chemical process which exploits the differences in the electrochemical properties of mineral surfaces. All minerals are soluble in water to some extent, which results in the formation of an ‘electrical double layer’ at the mineral surface. Flotation depends directly on the nature and properties of mineral-water interface. Two factors are important: (1) the interaction of water molecules with the mineral surface, both in liquid and gaseous environments, and (2) the electrical double layer at solid-water interface [4]. The addition of flotation reagents selectively renders the surfaces of mineral particles either hydrophobic or hydrophilic as a result of the ionic interactions and exchanges that can occur at the double layer. The hydrophobic particles become attached to air bubbles and are carried upwards through the slurry to a froth layer that forms at the top of the flotation cell. This froth layer is removed and
usually becomes the concentrate. Hydrophilic particles remain in the slurry in the flotation cell.

Most minerals are naturally hydrophilic i.e. polar in molecular structure and they need collectors to render them hydrophobic (non-polar in molecular structure). Collectors are heterogeneous compounds with a functional inorganic group and a hydrocarbon chain. There is a difference in electric charge on the ends of the inorganic group caused by an uneven distribution of polar bonds on its ends. The hydrocarbon chain is non-polar and has no difference in charge between its ends. The inorganic group is the portion which adsorbs on the mineral surface (provides hydrophobicity), in that way cause the mineral to attach itself to the bubble, fig 1. The most common mineral types that are recovered this way are sulphides and the widely used sulphide collectors are sodium and potassium salts of certain acids containing a hydrocarbon group. These are anionic collectors and include xanthates and dithiophosphates.

Frothers must be to some extent soluble in water, otherwise they would be distributed very unevenly in an aqueous solution and their surface-active properties would not be fully effective. The alcohols (OH) are the most widely used frothers, since they have practically no collector properties, and in this respect are preferable to other frothers, such as the carboxylic acids, which are also powerful collectors [6].

During froth flotation the ore is crushed and ground to a specific size sufficient for copper mineral liberation. The ore is then suspended in slurry and mixed with reagent or collectors. The collectors react with copper sulphide mineral particles to make them hydrophobic. The treated ore is introduced to a water-filled aeration tank and a frother (usually alcohol based) is added. Air is then induced and the air bubbles attached to the hydrophobic copper minerals are skimmed off. These skimming are generally subjected to a cleaner-scavenger cell to remove excess silicates and to improve the grade of the final product which is sent for downstream processing [6].

### III. FLOTATION OF OXIDE COPPER ORE

The two most common approaches to oxide copper flotation are:

- **Controlled potential sulphidisation (CPS)** using a sulphidiser like NaHS (Sodium Hydrogen Sulphide) or Sodium Sulphide.
- **Fatty acid flotation method**/the carboxylic acids process. This involves the use of palm oil or tall oil which is mixed with gas oil or diesel.

#### A. The Sulphidisation Process

This process was first applied on lead carbonate ores and is now the most currently used method to float copper oxide ores. It offers advantage over other processes like the fatty acid process as it is more selective and it is not limited to certain types of gangue minerals. Literature on actual plant practice shows that the flotation conditions used in the plants applying the sulphidisation process, do not differ very much in terms of reagent selection. A sulphidiser, such as sodium sulphide or sodium hydrosulphide was added to the flotation systems in slug doses with manual regulation like other reagents such as collectors, frothers and depressants [7]. This method of sulphidisation resulted in variable success and was endured until the development of the more efficient process called Controlled Potential Sulphidisation (CPS) [8].
employ multistage addition of sodium sulphide or sodium hydrosulphide as a sulphidising agent together with xanthate type collectors such as amyl-, isopropyl-, isobutyl and more recently allyl-n-amyl-xanthate better known under the trade name aeropromoter 3302 (A product of cynamid). Gas oil or a mixture of gas oil and fatty acid is sometimes added in order to strengthen the collection process. Dispersion of gangue is realised by conditioning the feed with sodium silicate.

Sulphidisation has been practised successfully but suffers several drawbacks which include:

- Difficulty in controlling the degree of the sulphidising agent. Dosage control is crucial since under-sulphidising may result in sulphidiser inefficiency and over-sulphidising may result in depression of the valuable mineral. This has lead to controlled potential sulphidisation which entails relating sulphidiser dosage level to electrode potential or mV (milli Volt).
- Different responses of the various oxide minerals to sulphidisation.
- The issue of odour associated with sulphidising agents.

**B. The Carboxylic / Fatty Acid Process**

A number of different collectors have been evaluated for oxide copper flotation without sulphidisation. They include organic complexing agents, fatty acids, fatty amines and petroleum sulphonates [9-10]. All of these collectors showed promise in the laboratory tests but they had limited success when applied to a plant situation [11]. The limitation of some of these collectors is their lack of selectivity over carbonate gangue minerals, such as dolomite and calcite. It has been reported that the gangue minerals even float preferentially when applied to a plant situation [11]. The limitation of some of these collectors is their lack of selectivity over carbonate gangue minerals.

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**IV. IMPROVING THE FLOTATION OF OXIDE COPPER ORE**

**A. The Direct Flotation Process**

Malachite can be floated using only amyl xanthate or ethyl xanthate under certain conditions of copper ion concentration. Unfortunately, positive results with those xanthates have only been obtained in the conditions of “Hallimond” cells, which are sufficiently quiescent to prevent the non-adherent collector coating to peel away.

Tall oils, which are by-products of the paper industry, are becoming popular because of their relative cheapness. They contain a high proportion of resin acids together with fatty acids such as oleic and linoleic acid. By fractional distillation it is possible to reduce their resin acid content and thereby lowering their excess frothing power. However, this may affect their selectivity towards malachite flotation. Fuel oil has to be added to tall oil in the proportion of 10:1. Any lower value of this ratio would lead to rapid decrease of the selectivity. 1 : 1mixtures of tall oil and stearic acid were also found to give results comparable to those of palm oil but with some loss of selectivity [12].

Another combination of collectors is that of hydrolised palm oil with naphtenic acids obtained from petroleum refining. Naphtenic acids present good collecting and frothing properties and are only influenced by the hardness of the water or lower temperatures. By using this type of collector together with hydrolsed palm oil, results equivalent to those of palm oil alone but at half the palm oil consumption required.

**B. The Use of Alkyl Hydroxamates / Chelating Reagents**

Alkyl-hydroxamates have also been shown to give high copper recoveries due to a more selective flotation of copper from slimes. Alkyl hydroxamates/chelating reagents were originally proposed for oxide copper flotation but have not been used commercially for various reasons such as lack of availability and costs [11].

A chelate- forming reagent must have at least two atoms that can be co-ordinated by the metal at the same time. Such atoms are usually oxygen, nitrogen, sulphur and phosphorus. The co-ordination species that provide these donor atoms are known as “ligands”. The principle of using chelating agents as collectors has excited a lot of research over the past fifty years. These compounds are often highly selective to certain metals and a number of them have been investigated with success in laboratory experiments [12]. When more than one atom of a single ligand molecule or ion interacts with a metal ion, it may be presumed to bend itself around a central atom to form a complex ring structure called a “chelate”. For the ideal flotation collector the functional groups should be part of a sufficiently long hydrocarbon chain (C6-C8) to impart hydrophobicity for the mineral on adsorption. Hydrocarbon positioning also affects the flotation properties of the chelating reagent.

Conventional collectors such as xanthates and thiophosphates typically do not perform well on oxidised surfaces, indicating that an oxide specific flotation collector is required to maximise recovery. Although there has been some success with saturated fatty acids, problems associated with lack of selectivity led to an investigation of hydroxamates as selective flotation reagents.

Hydroxamates are anionic collectors which have been...
known for many years. They are weak acids with pKa of between 9 and 10. Although these reagents are most effective at high pH (above 10), they have shown to improve metal recovery at pHs ranging from 7 to 10. Since AM 2 has limited solubility at pH 4-5 it is not able to form the reactive aggregate as it does at higher pH especially for copper recovery [13].

The novel structural features of hydroxamates make them highly effective as selective collectors of oxidised metal minerals. The hydrophobic tail promotes bubble attachment while the hydroxamate moiety is structured to selectively attach to the oxidised metal surface by chelation. The most effective hydroxamate reagent is AM 2 which has been developed by Ausmelt, Australia. AM 2 is a potassium n-octyl hydroxamate with a stabilised hydroxamate structure which results in strong selective surface chelation [13].

Extensive testwork in metallurgical laboratory particularly for copper has shown AM 2 as a scavenger or secondary collector, acting synergistically with conventional sulphide collecting reagents. For fully oxidised ores, AM 2 can be used alone and has shown excellent performance for difficult to float minerals such as chrysocolla [14-20]. Hydroxamate reagents are not widely used due to costs associated with them.

V. MATERIALS AND METHODS

A. Samples
Approximately 15 kg of ore was available for the test work. The ore sample was crushed in stages using a laboratory jaw and cone crusher to a size required for lab milling i.e. -1.7mm. The crushed ore was then blended and rotary split to 1kg representative sub-samples for the test work. During blending a 200g sub sample was extracted and pulverize for head analysis.

B. Head analysis
A head sample of the composite ore was assayed for total Cu, Co, Ca, Fe ,Mg, Al by ICP and acid soluble/oxide copper by AA. The sulphide copper was obtained by difference and this was to confirm the copper content in the ore.

C. Milling curve
A milling calibration curve was constructed to estimate the milling time required to achieve a grind of 75%-75µm, based on experience with similar ores. Three 1 kg samples were milled at 50% solids in a rubber lined rod mill for three different time intervals. The milled product was sized to determine the % passing 75 micron screen. The relationship between ore fineness and milling time is shown in fig 3. From fig 3, 18 minutes was required to achieve the required grind.

D. Particle size analysis on milled feed (size by assay)
Size analysis was conducted on the milled feed (75% - 75µm) from top size down to -25µm using the √2 sieve series. Each size fractions was assayed for total copper and oxide copper. The purpose of this was to determine the deportment of copper in the size fractions and to determine if a high grade fraction can be directed to final concentrate.

E. Laboratory flotation tests
All tests were conducted using the standard flotation procedure. Three hundred grams per ton sodium silicate was added in the mill as a dispersant for gangue. A 1 kg sample was rod milled at 50% solids and transferred into a 2.5 litre flotation cell. This was done immediately after milling to minimise any further oxidation or chemical reactions that may take place.

F. Experimental procedure
The milled slurry was diluted in a float cell to a density of approximately 35 % solids. This solid concentration was found to be high enough to maximise flotation capacity i.e. mass of concentrate produced per unit volume of cell. However, care was taken that it was not too high as to cause viscosity problems. The milled slurry was then agitated in a Denver D-12 machine running at an impeller speed of 1200 rpm to ensure homogenous suspension of solids. Reagents specific to each test were added and conditioned as required, thereafter air was manually induced using an air rotameter. The concentrates were collected by manually scraping the froth every 15 seconds using scraper blades.
TABLE I
FLOTATION REAGENTS USED

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Description</th>
<th>Type</th>
<th>Condition time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaHS</td>
<td>Sodium hydride sulphide</td>
<td>Sulphider</td>
<td>0</td>
</tr>
<tr>
<td>PAX</td>
<td>Potassium amyl xanthate</td>
<td>Sulphide collector</td>
<td>1-3</td>
</tr>
<tr>
<td>AMX</td>
<td>n-octyl hydroxamate</td>
<td>Oxide collector</td>
<td>3-6</td>
</tr>
<tr>
<td>Emulsion</td>
<td>Rheola, Rinka RCA</td>
<td>RCA oxide collector</td>
<td>3-6</td>
</tr>
<tr>
<td>Mixture</td>
<td>90% Diesel + 10% Tall oil</td>
<td>RCA oxide collector</td>
<td>3-5</td>
</tr>
<tr>
<td>Dow 200</td>
<td>Alcohol based frother</td>
<td>Frother</td>
<td>0.5</td>
</tr>
</tbody>
</table>

VI. RESULTS AND DISCUSSION

A. Head analysis

Head assay results are presented in Table 2. The total copper grade of the sample was 4.5% and 88% copper oxide. The 12% copper remaining could be sulphide, refractory or un-dissolved copper. The cobalt content was 0.5%. The silicate content of the ore was 28%, this could indicate that the gangue type in the ore is mainly siliceous, indicating that carboxylic acid collectors would be suitable for this ore.

TABLE II
HEAD ANALYSIS RESULTS

<table>
<thead>
<tr>
<th>Total copper (%)</th>
<th>Oxide copper (%)</th>
<th>Cu (%)</th>
<th>Al (%)</th>
<th>Si (%)</th>
<th>Ca (%)</th>
<th>Fe (%)</th>
<th>Total copper (%)</th>
<th>Mg (%)</th>
<th>Oxide copper (%)</th>
<th>Co (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>3.69</td>
<td>0.5</td>
<td>6.41</td>
<td>27.8</td>
<td>0.31</td>
<td>3.77</td>
<td>1.77</td>
<td>&lt;0.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

B. Particle size analysis

As presented in fig 5 (a), 38% of the total copper was distributed in the liberated size fraction (-25 µm) however another 38% was evenly distributed in the coarser size fractions (75 µm, 106 and 150 µm). This distribution was related to the mass of sample in these size fractions. The highest copper grade reported was 9% in the 212 size fraction, fig 5 (b). This was not high enough to indicate native copper. It was thus, not possible to isolate a high grade fraction to final concentrate.

Fig. 5 (a) Total copper distribution, milled feed size fractions

Figs 6 and 7 represent the copper and cobalt grade and recovery profiles. The total copper and cobalt recovery remained at less than 50% despite the changes in reagent conditions. The average copper grade achieved in the roughers was 11% copper at 37% recovery (Test 1- Test 6). Cobalt results were 1% cobalt in the rougher concentrate at 39% recovery. De-sliming did not improve copper recoveries because of the large losses to the slimes fractions.

However, it improved the selectivity of the sulphidiser resulting in relatively high copper and cobalt grades in the concentrate. The grades were 13% and 2.6% for copper and cobalt respectively. The cobalt results were improved by vigorous de-sliming as shown by Test 5 results. The copper was upgraded from 0.5% to 2.6% at 56% recovery.

Fig. 5 (b) Total copper distribution, milled feed size fractions

Fig. 6 Copper grade and recovery profiles

Fig. 7 Cobalt grade and recovery profiles
The copper and cobalt losses in Test 6 were less but recovery improvements were not significant. A single, open circuit cleaning upgraded the copper grade from 8% in the rougher to 15% in the cleaner concentrate. The cleaner losses were significant. The cobalt did not upgrade very well, the grades were 1% and 1.8% for the rougher and cleaner concentrates respectively.

Fig.8 Copper flotation kinetics

The base case test (Test 1) show slow copper flotation kinetics. Only 20% of copper was recovered in the first 6 minutes of flotation. This raises some concern on the type of copper minerals present as copper is known to have very fast flotation kinetics. The introduction of a RCA mixture (Test 2) to replace the emulsion did improve the initial kinetics to some extent, however the overall recovery improvement was not significant (from 31-34%). Increasing the sulphidiser dosage (Test 3) did not have a significant effect on the flotation kinetics and the overall recovery. This further confirms that the copper minerals concerned are very slow floating. Introduction of AM 2 did not improve kinetics as seen in the three first flotation stages and overall recoveries were comparable to the base case test since subsequent scavenger stages were similar. Test 8 resulted in the best overall recovery at 45% copper and 50% cobalt but with slower copper flotation kinetics with only 9% copper recovery in the first 6 minutes. The test employed relatively low sulphidiser levels and long flotation residence time (more scavenger stages) which could be beneficial to the recovery.

VII. CONCLUSION

The project highlighted the importance of understanding ore mineralogy in developing a flotation procedure since all copper oxide minerals present as copper is known to have very fast flotation kinetics. The introduction of a RCA mixture (Test 2) to replace the emulsion did improve the initial kinetics to some extent, however the overall recovery improvement was not significant (from 31-34%). Increasing the sulphidiser dosage (Test 3) did not have a significant effect on the flotation kinetics and the overall recovery. This further confirms that the copper minerals concerned are very slow floating. Introduction of AM 2 did not improve kinetics as seen in the three first flotation stages and overall recoveries were comparable to the base case test since subsequent scavenger stages were similar. Test 8 resulted in the best overall recovery at 45% copper and 50% cobalt but with slower copper flotation kinetics with only 9% copper recovery in the first 6 minutes. The test employed relatively low sulphidiser levels and long flotation residence time (more scavenger stages) which could be beneficial to the recovery.

REFERENCES


