Flotation of mixed copper oxide and sulphide minerals with xanthate and hydroxamate collectors

K. Lee, D. Archibald, J. Mc Lean, M.A. Reuter

ABSTRACT

Sherwood Copper’s Minto Mine processes a high grade copper–gold deposit in Yukon, Canada. The ore mined is from a primary copper sulphide deposit with separate additional deposits of copper oxides. In conjunction with Ausmelt Chemicals, Minto is currently investigating options to recover copper oxide and sulphide minerals using flotation by blending their primary sulphide ore with oxide ores. The blend used in this laboratory scale investigation was 70% sulphide ore and 30% oxide ore on a weight basis. The copper sulphides present in the blend were bornite and chalcopyrite, while the oxides were malachite and minor azurite.

From previous flotation investigations of mixed copper oxide and sulphide minerals using xanthate and hydroxamate collectors it was hard to distinguish the impact of the alkyl hydroxamate collector on sulphide recovery as the sulphide and oxide minerals occurred naturally together. In the case of the Minto operation the copper oxide and sulphide minerals occur in separate ore deposits and can be treated separately or blended together. This investigation has shown that using n-octyl hydroxamates (AM28 made by Ausmelt Limited) in conjunction with traditional sulphide collectors can successfully simultaneously recover copper sulphides and oxides by flotation from blended oxide ores. The copper sulphide recovery did not decrease when processing the blended ore compared to treating the sulphide ore independently. At a blend of 70% sulphide ore and 30% oxide ore, the rougher scavenger copper recovery was as high as 95.5%. The copper recovery from the blended ore using a mixture of collectors was shown to be superior to the recovery obtained using only xanthate after controlled potential sulphidisation.

1. Introduction

Many copper sulphide mines around the world have significant copper oxide ore reserves associated with the larger primary copper sulphide deposit. The traditional techniques for processing oxide ores, either by leaching – SX/EW or flotation have caused many problems for these operations. Leaching – SX/EW requires capital expenditure to construct a dedicated plant to process oxide ore. Until recently, flotation of copper oxides would normally have been conducted in distinct campaigns to produce a copper concentrate which may not be saleable under existing contracts. With the introduction of n-octyl hydroxamate as a complementary collector to traditional sulphide collectors, flotation plants can now process blends of sulphide and oxide minerals to produce saleable concentrates.

Generally copper oxide minerals do not respond well to traditional sulphide copper collectors and require alternative flotation techniques to concentrate the copper oxides. The classical method involves controlled potential sulphidisation (CPS) to sulphidise the surface of the oxide minerals by the addition of a sulphidisation agent, such as sodium hydrogen sulphide (NaHS). When NaHS is used for CPS the pulp redox potential (Eh) is reduced to a target value between −450 and −550 mV (versus a standard hydrogen electrode) (Soto and Laskowski, 1973; Jones and Woodcock, 1978). Other normal sulphidisation reagents used in this process are sodium sulphide (Na2S) and ammonium sulphide ((NH4)2S).

In principle CPS works well in a controlled environment of the laboratory for copper oxide minerals. When practised in a plant operation, CPS can often produce a variable response in oxide copper recovery. The main drawback of CPS is that the optimum dose of the sulphidisation agent is highly dependent on the time of conditioning, procedures of mixing and other variables, leading usually to poor reproducibility in a plant situation (Castro et al., 1974a,b). Insufficient addition of the sulphidisation reagent will cause poor recoveries and an excess will cause the depression of oxide copper minerals (Lee et al., 1998). For mixed oxide and sulphide ores, CPS is unsuitable for simultaneous flotation of copper.
oxide and sulphide minerals, as the sulphides are usually heavily depressed by the sulphide ions from NaHS additions necessary to sulphidise the oxide copper.

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 (Nagaraj, 1987; Deng and Chen, 1991). All of these collectors showed promise in the laboratory tests but they had limited success when applied to a plant situation (Lee et al., 1998). 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 over the copper oxides (Deng and Chen, 1991).

The application of alkyl hydroxamate as a metal oxide mineral collector has been studied since the early 1940s. Popperle (1940) first patented the use of hydroxamic acids or their salts as collectors for ore flotation. Much research followed with the development of a number of different hydroxamate collectors. In the former USSR, a hydroxamic acid collector named as NM-50 was used as a collector for wolframite, cassiterite and rare metal ores (Gorlovskii et al., 1969). In the United States flotation of chrysocolla and hematite with n-octyl hydroxamates and some applications in platinum group metal flotation were studied (Nagaraj, 1987; Deng and Chen, 1991). All of these collectors showed promise in the laboratory tests but they had limitations when applied to a plant situation (Lee et al., 1998). 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 over the copper oxides (Deng and Chen, 1991).

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the addition of the collector or frother. The first three concentrates were collected for 0.5 min each, concentrations 4 and 5 were collected for 1 min each and concentrate 6 was collected for an additional 6 min. The total PAX addition to the test was 14 g/t and the total of MIBC was 48 g/t. Once the flotation kinetics was examined, further cleaning tests were conducted to examine upgrading. An additional 1 g/t PAX and 10 g/t MIBC were used in the cleaning stage.

Similar tests were carried out for the oxide composite. The pH of the pulp for flotation was the natural pH of the ground ore, at approximately pH 7.5. The rougher scavenger flotation test was conducted over several stages to estimate the required hydroxamate dose. Before each stage of flotation, a 2 min conditioning time was allowed after the addition of the collector or frother. The concentrates were collected over a 4 min time period. The overall AM28 dosage was up to 1200 g/t and 50 g/t of MIBC. After establishing satisfactory rougher scavenger flotation conditions, cleaning tests were conducted to examine upgrading. An additional 100 g/t AM28 and 50 g/t MIBC were used in the cleaning stages.

Based on the information gathered from sulphide and oxide composite tests, several conditions were trialled on the blend composite. Two collectors were used for the blend composite experiments, namely, PAX and AM28. Addition of PAX was used to float the sulphide copper and AM28 to float oxide copper at the same time. The pH of the pulp for flotation was the natural pH of the ground ore, at approximately pH 8.1. The conditioning and flotation times to collect each concentrate were the same as used in the sulphide batch flotation tests. Based on results from the oxide batch tests, the overall hydroxamate dose was reduced to 420 g/t to account for the reduction of oxide content. Several rougher scavenger tests were conducted, with the stage of flotation at which the hydroxamate was added and the dose amount being varied. Addition of PAX and MIBC to the flotation test was in the same format as was used in the sulphide composite tests. Cleaning experiments were conducted to examine upgrading of the rougher scavenger concentrate. During the cleaning stage an additional 25 g/t AM28, 1 g/t PAX and 10 g/t MIBC were added.

As a comparison experiment to the xanthate and n-octyl hydroxamate tests on the Minto blend composite, an additional test was carried out using the CPS method. The pulp redox potential (Eh) at each stage of the experiment was reduced using NaHS to a target value between −450 and −550 mV (versus a standard hydrogen electrode); the actual Eh at the beginning of each stage of flotation varied between −470 and −483 mV (versus a standard hydrogen electrode). This is consistent with other sulphidizing studies (Soto and Laskowski, 1973; Jones and Woodcock, 1978). The total amount of NaHS, PAX and MIBC added during the experiment was 1575 g/t, 80 g/t and 48 g/t, respectively.

### 2.5. Chemical analysis of products

Composite head samples and solid flotation products were assayed for total copper and acid soluble copper by inductively coupled plasma – optical emission spectroscopy (ICP-OES) using standard methods. The total copper digestion method used aqua regia while the acid soluble copper digestion used sulphuric acid.

From the head assay results shown in Table 2 it can be seen that the sulphide ore has a low acid soluble assay compared to the total copper assay. As a result when examining the copper assays for the blended ore products, the acid soluble copper assay relates to the copper minerals associated with the oxide ore. Therefore the difference between the two assays equates to the copper associated with the sulphide minerals.

### 2.6. Mineralogy and QEMSCAN analysis

Optical microscopy was conducted on the head samples of both sulphide and oxide ores from Minto to quantify the copper occurrences and rock mineralogy. Quantitative analysis was carried out on the Minto blend for feed, combined concentrate and tail samples for selected experiments.

### 3. Results

#### 3.1. Mineralogy

**3.1.1. Optical microscopy**

_Sulphide Composite_: The copper was present in the composite as bornite and chalcopyrite containing magnetite inclusions. The mineralisation was hosted by foliated granodiorite or gneiss. Higher-grade mineralisation often occurs in quartzo-feldspathic gneiss, biotite quartz feldspar gneiss and siliceous gneiss which are similar to the foliated granodiorite apart from the added minerals implied in their description and more intense foliation.

_Oxide Composite_: The copper was present in the composite as malachite and azurite and is dominated by composite particles of quartz and pinkish feldspar, plus minor to subordinate black mica (biotite). Closer examination of a polished thin section showed that the composite consisted of plagioclase, quartz, k-spar, biotite and epidote. Accessory minerals include sphene, magnetite, zircon and limonite-goethite.

**3.1.2. QEMSCAN analysis on Minto blend composite**

QEMSCAN was used to quantitatively determine the mineral abundance, elemental deportment of copper and liberation characteristics on feed, concentrate and tail samples from the Minto blend composite (70% sulphide:30% oxide). The samples were split into five sized fractions, −38, +38, +63, +106 and +150 μm and each fraction was mounted into a polished block. The block was mapped and the results combined to determine mineral 

<table>
<thead>
<tr>
<th>Ore type</th>
<th>Total copper (Cu)</th>
<th>Acid soluble copper (Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphide</td>
<td>3.7</td>
<td>0.2</td>
</tr>
<tr>
<td>Oxide</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Blend</td>
<td>3.6</td>
<td>1.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mineral group</th>
<th>Minerals included in the group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcopyrite</td>
<td>Chalcopyrite, covellite and other Cu sulphide species</td>
</tr>
<tr>
<td>Bornite</td>
<td>Bornite</td>
</tr>
<tr>
<td>Malachite</td>
<td>Malachite and minor azurite (optical analysis indicates that the majority of the copper oxides is malachite)</td>
</tr>
<tr>
<td>Chlorite</td>
<td>Chlorite</td>
</tr>
<tr>
<td>Fe sulphides</td>
<td>Pyrite and Pyrrhotite</td>
</tr>
<tr>
<td>Quartz</td>
<td>Quartz and high silica phases</td>
</tr>
<tr>
<td>Feldspar</td>
<td>Feldspar</td>
</tr>
<tr>
<td>Micas</td>
<td>Biotite, muscovite and phlogopite</td>
</tr>
<tr>
<td>Fe oxides</td>
<td>All Fe oxide phases, magnetite, hematite and limonites</td>
</tr>
<tr>
<td>Fe Ti oxides</td>
<td>Rutile and ilmenite</td>
</tr>
<tr>
<td>Carbonates</td>
<td>Ca carbonate and Fe carbonate</td>
</tr>
<tr>
<td>Apatite</td>
<td>Ca phosphate</td>
</tr>
<tr>
<td>Fe (Cu)</td>
<td>Goethite phase with minor amounts of Cu</td>
</tr>
<tr>
<td>Hydrouxides</td>
<td>Predominantly Cu silicates (fine intergrowth between Cu and Micas) including chrysocolla and Cu phosphates</td>
</tr>
<tr>
<td>Others</td>
<td>All other phases not included above and occurring in trace form</td>
</tr>
</tbody>
</table>
abundance, particle size distribution and liberation characteristics of the major copper species. For data simplification, the mineral species were grouped as listed in Table 3. The mineral abundance (mass%) for the feed, concentrate and tail for the blend composite is summarised in Table 4 and Fig. 1.

From the copper deportment analysis of the Minto blend composite, it was observed that most of the copper in the feed was associated mainly with bornite, chalcopyrite and malachite. A total of 2.6% of the copper was associated with goethite and other copper silicates which are not amenable to flotation and were not recovered by n-octyl hydroxamate. The elemental deportment of copper is shown numerically in Table 5.

QEMSCAN can determine liberation characteristics based on the area of the target particle compared to the perimeter of the particle and where it is associated with secondary minerals or touching other particles. Therefore where the ratio of a copper particle area to perimeter is high, this represents a completely liberated mineral grain and the locking-liberation characteristics of the minerals are quantified according to the criteria shown in Table 6. The liberation characteristics for the feed, concentrate and tail samples according to the locking-liberation characteristics criteria are shown in Table 7.

3.2. Batch flotation tests

The flotation response for the sulphide composite ore using conventional xanthate flotation reagent is illustrated in Fig. 2.
the rougher scavenger tests the copper recovery achieved was 98.8% at a concentrate grade of 37.3% Cu. These values are comparable to results achieved at the Minto processing plant under normal operating conditions with sulphide minerals. The concentrate can be upgraded further by additional cleaning stages. Fig. 3 represents the concentrate grade–recovery relationship when the concentrate from the rougher scavenger test was upgraded with one additional cleaning stage. The concentrate grade was increased to 46.5% Cu at 96.2% recovery by this cleaning step.

Several tests were carried out on the Minto oxide composite and the results were used to estimate the required hydroxamate dose for the blend composite. Figs. 4 and 5 summarise two similar tests where the total hydroxamate dose was 1200 g/t. Test A was performed at an initial hydroxamate collector dose of 400 g/t followed by successive 100 g/t additions, with a total flotation time of 37 min. Test B was performed with an initial hydroxamate collector dose of 600 g/t followed by further additions of hydroxamate collector. For stages 2 and 3, 200 g/t of hydroxamate collector was added and stages 4 and 5, 100 g/t of hydroxamate collector was added. The overall flotation time for Test B was 19 min. In both tests the relationship between copper grade and recovery increased significantly when the hydroxamate dose was greater than 800 g/t. The overall copper recovery by flotation is understated in this case because the mineralogical examination found copper bearing goethite minerals which are not amenable to flotation (Lee et al., 1998). A reduction in overall flotation time improved the copper concentrate grade by reducing the time for gangue to report to the concentrate as entrainment. Comparing Test A and B in Fig. 5, it is evident that there was an improvement in overall concentrate grade from 11.1% to 25.3%.

For the blend composite experiments the flotation products and tail samples were assayed for total and acid soluble copper. From the initial head assays (as shown in Table 2) the acid soluble copper assay relates to copper associated oxide ore. This relationship was supported by the optical examination of blend composite head sample, which showed that approximately one third of the copper was associated with copper oxide minerals. Therefore the recovery of sulphide and oxide components can be calculated.
In the initial blend composite experiments the hydroxamate collector (AM28) was added midway through the experiment, after the third concentrate. PAX was added at the beginning of the flotation experiment. It can be seen in Fig. 7 that for Test C, the first three concentrates did not contain any oxide copper. This shows that the copper oxide minerals were not recovered with xanthate at the concentration used and that only after AM28 was added to an experiment did the oxide minerals begin to float. For Test D the hydroxamate collector and PAX were added at the beginning of the flotation experiment (Fig. 8). Similar overall copper recoveries and faster flotation kinetics were obtained. The grade–recovery relationship improved for the blend composite when hydroxamate was added at the beginning of the flotation experiment, as shown in Fig. 9.

The total and acid soluble copper assays of the tail from Test D were 0.19% and 0.16% Cu, respectively. This shows that the residual copper found in the tail was mainly associated with copper oxide minerals. The total copper, sulphide copper and oxide copper recoveries of 95.5%, 98.2% and 89.4%, respectively. Comparing this result with the sulphide composite experiments, the sulphide recoveries were very similar at 98.8% (sulphide composite) and 98.2% (blend composite). Thus the sulphide copper recovery did not decrease when treating the sulphide composite separately or as a blend with oxides.

Test D was repeated and the concentrate from the rougher scavenger test was cleaned using one stage. The concentrate was upgraded from 19.3% Cu at 95.5% copper recovery to 35.1% Cu at 93.2% recovery. Quantitative mineralogical analyses were conducted on samples of the first cleaner concentrate and rougher tail as described previously. Table 5 shows that 18.6% of the copper found in the tail was associated with Fe (Cu) Hydroxide minerals, i.e. as copper bearing goethite. Since goethite is not amenable to flotation the copper recovery which can recovered by flotation was understated. Copper associated with goethite will report in both total and acid soluble assays. The deportment of copper in the tails sample has been summarised in Table 5 and shows that most of the copper found in the tails was associated with copper sulphide minerals.

Fig. 10 compares the grade–recovery relationship between the three composite samples. It can be seen that the Minto blend...
composite grade–recovery relationship lie between the Minto oxide and sulphide minerals. By blending the oxide and sulphide ores together, the grade–recovery relationship improves as there is less floatable gangue found in the sulphide ore. Bornite has a higher copper content compared to the oxide copper minerals found in the Minto oxide composite. Therefore as bornite was recovered from the Minto blend composite experiment the copper grade would improve over treating the oxide ore separately.

A CPS experiment was conducted on the Minto blend (Test E) as a comparison for the other blend experiments. It can be seen in Fig. 11 that the addition of NaHS has suppressed the flotation of copper sulphide minerals. After 3.5 min only 11.5% of sulphides had floated and it was only at the last stage of the experiment that the copper sulphides significantly started to float. During the last stage of the experiment, the longer flotation time may have caused a significant amount of the NaHS to oxidise with the flotation gas (air), thereby reducing the suppression effect on the copper sulphide minerals.

4. Conclusion

An advantage of treating sulphide/oxide blends is that many operations have commitments to produce a concentrate at a minimum sulphur and copper content, which may not be achieved if the ore types are treated independently. Traditional sulphidisation flotation techniques, which are widely used on copper oxide ore, can not be used in sulphide/oxide blends for simultaneous sulphidisation of copper sulphide minerals. This investigation showed that for a Minto composite blend of 70 wt% sulphide and 30 wt% oxide, the rougher scavenger copper recovery was 95.5%. The concentrate grade and copper recovery after 1 stage of cleaning was 33.9% Cu and 78.5%, respectively. AM28 successfully recovered malachite and minor azurite, which were present in Minto's oxide ore. The sulphide recovery for the blend composite was not adversely affected. Lower copper sulphide recovery is one of the main concerns for many operations in blending oxide ores with their main sulphide ores, and such a loss can be reduced by the use of alkyl hydroxamates like AM28.

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References


