Abstract— The flotation response of blended chrysocolla-sand samples using n-octanohydroxamate collector was investigated. Wet grinding, salinity, frother type and depressants were examined. A Copper recovery of 99.1% was achieved after wet grinding at pH 10, while the best copper grade was achieved after wet grinding at pH ~7. Using 80 g/t of a strong frother (IF4500A) did not result in a significant improvement in overall copper recovery, but it did lead to a faster recovery rate than when no additional frother was added. Sodium silicate as a depressant led to an improved concentrate grade, whereas using a tannic acid as a depressant did not significantly affect either recovery rate or grade. Using a short period flotation time resulted in higher copper grade and a lower iron grade. XPS was employed to characterise the surface composition and coverage of conditioned sand samples in the absence of chrysocolla.

Keywords—mineral processing; flotation collectors; oxide ores; chrysocolla; hydroxamate.

I. INTRODUCTION

The recovery of oxide copper minerals from, predominantly, sulfide ore bodies is a significant issue in the copper mining industry today. Chrysocolla is a copper oxide mineral that represents a large copper resource. This is usually stockpiled as it is not amenable to conventional thiol collection techniques [1]. Chrysocolla is prone to dissolution, lacks mechanical strength and possesses strongly hydrophilic surface groups [2, 3]. Parker et al. [4] and Hope et al. [5,7] have used vibrational spectroscopy, X-ray photoelectron spectroscopy and electrochemical techniques to study the surface of interaction of hydroxamates with copper oxide minerals, including chrysocolla. The chrysocolla structure and properties have been reported to exhibit rough surfaces and edges with numerous surface protrusions. Chrysocolla is a hydrated hydroxy silicate of copper and aluminium. The chemical composition of chrysocolla is generally accepted as $\text{Cu}_2\text{Al}_x\text{(OH)}\text{yH}_2\text{Si}_2\text{O}_5\text{nH}_2\text{O}$, with $x<1$.

Hydroxamate collectors have been found to have potential for the recovery of copper oxide minerals, including chrysocolla. Lee et al. [6] reviewed the recovery of oxide copper ore using alkyl hydroxamate and observed that alkyl hydroxamates are a superior collector for well-defined copper oxide minerals. Herrera-Urbina et al. [3] undertook Hallimond tube studies of chrysocolla and reported that the amount of copper solubility from chrysocolla increased sharply below pH 6 but remained relatively constant above this value. They also concluded that optimal recovery of chrysocolla by flotation using n-octanohydroxamate required minimizing the dissolution of copper, recommending dry grinding of the ore, followed by short conditioning times prior to flotation at approximately pH 6.5. As loss of copper from the mineral was not significant above pH 6.5, the recovery rate at pH >9.5 was not significantly different from recovery at pH 6.5 [3]. In 2011, Hope et al. [6] used a 2.5 L stirred flotation cell to investigate Clifton chrysocolla – Gosford sand flotation using n-octanohydroxamate as the collector. Dry grinding was employed to grind the chrysocolla sample before conditioning and flotation. The copper recovery exceeded 97% under the conditions employed. Iron was also collected (~70% recovery). The copper grade was only slightly below pure chrysocolla in the initial float, and declined in subsequent floats.

In this research, the flotation response of chrysocolla-sand mixtures using n-octanohydroxamate collector is reported, as a function of wet grinding, pH, salinity, blend chrysocolla-sand grinding, rest time, frothers, depressants and flotation period.

II. EXPERIMENTAL

A. Chemicals and materials

The chrysocolla sample used in the flotation studies was sourced from Clifton district, Arizona. The colour varied from dark blue green to bluish green with some isolated black and brown impurity visible to the eye. The sand sample used in the flotation studies originated from Gosford, NSW. AM2, the commercial octanohydroxamate variant was provided by Axis House Australia, (~25% $\text{C}_8\text{H}_{17}\text{O}_2\text{N}$, ~25% $\text{C}_2\text{H}_7\text{O}_2\text{N} (\text{H, K})$, and ~50% water with a minor amount of potassium n-octanoate) was used as the flotation collector. The pH was adjusted, when required, with ~1M KOH solution. Frothers, weak to strong; IF50, IF6801B and IF4500A; were supplied by Chemicals and Mining Services, Pty Ltd. Sodium silicate (Na_2SiO_3) from Chem-supply and tannic acid (C_9H_7O_5) from Tall Bennett Group were used as depressants. Sea water was used during some grinding experiments, to investigate the impact of salinity on flotation. Flotation in the 2.5 L stirred cell was undertaken using tap water and compressed air. The chrysocolla sample initially was crushed to < 3.55 mm.
A Carpeo sample splitter (model SS manufactured by Warman Equipment) was used to split the chrysocolla sample to give about 43 g per flotation test. Approximately 43 g of chrysocolla sample was mixed with tap water to produce ~40% solids content. The pH was adjusted to the selected value with KOH solution before grinding to ~100 µm using a 5 kg sealed stainless steel laboratory rod mill manufactured by ESSA Australia. Sand was wet ground separately to approximately the same particle size. A Mastersizer X from Malvern was used to measure the particle size distribution. Representative samples with approximately 1% contained copper were prepared on a kilogram scale from the ground mineral and sand.

B. X-ray fluorescence techniques

An X-ray fluorescence (XRF) spectrometer from Thermo Scientific (NITON XL3t) was employed for measurement of copper, iron and trace metals. The concentrate and tail samples were separately prepared by mixing with tap water to produce ~30% solid content. AM2 collector at a level of 200 g/t was used for the first step, followed by addition of 50 g/t IF50 (frother) for the second, third and fourth concentration steps. Mixed frothers were also investigated by adding 20 g/t of IF50 for the first concentrate, followed by 20 g/t of IF6801B for the second concentrate, then two further collections with additions of 50 g/t AM2 and 20 g/t IF50.

The impacts of frothers and depressants on flotation response were also investigated. Wet grinding of chrysocolla at various pHs was undertaken to investigate the influence of copper dissolution. The chrysocolla samples were separately wet ground at pHs of approximately 4, 7, 9, 10 and 11 and used to prepare the 1% contained copper flotation charge. The flotation testing was undertaken at pH ~9.5. A four-stage sequential addition of AM2 (2% solution in 1% KOH) was employed: 400 g/t with 20 g/t IF50 (frother) for the first step, followed by addition of 100 g/t AM2 and 20 g/t IF50, then two further collections with additions of 50 g/t AM2 and 20 g/t IF50.

C. X-ray photoelectron spectroscopy

The Gosford sand and 99.99% pure silica samples were separately prepared by mixing with tap water to produce approximately 30% solid content. AM2 collector at a level of 600 g/t treated the resultant slurry. The pH was adjusted to ~9.5 using 0.1M KOH and stirred for 2 minutes. The sample was collected on filter paper and washed with KOH solution and water. The sample on paper was dried in a vacuum desiccator at room temperature.

X-ray photoelectron spectra were collected from conditioned particulate Gosford sand and 99.99% pure silica samples. The samples were mounted on fresh indium surfaces by applying only minimal pressure to minimise crushing. XPS data were obtained on an ESCALAB 250Xi spectrometer using monochromatised Al Ka X-rays focused to a spot size of 0.5 mm and electron analyser pass energy of 20 eV for narrow rage scans. A nominally 4.6 eV in lens low-energy electron beam was used for charge compensation, and binding energies were corrected using the C 1s hydrocarbon component at 285.0 eV as reference, and assuming that the electron beam-induced shift would be the same for all photoelectron peaks.

D. Flotation experiments

Batch flotation tests were conducted on a kilogram scale for 1% contained copper using a 2.5 L stirred flotation cell. ~1 L of water was added to the flotation cell to produce ~30% solid content in the cell. The flotation charge of mixed chrysocolla-sand was stirred at 500 rpm to give the conditioning period of 2 minutes. The pH was adjusted to desired value and the collector and frother were added at the selected dosage. The pH needed to be re-adjusted after the reagent addition to ensure that flotation occurred at the target pH. Flotation was commenced by introducing a compressed air flow of 7 L/min. Several concentrate collections were taken sequentially to emulate plant operation and a flotation time of 2 min was selected for the first concentration, followed by 3 min intervals for each of the second, third and fourth concentration steps.

The effect of flotation time dependence has been investigated. Approximately 43 g of chrysocolla sample was separately wet ground at ~pH 9 before transferring and mixing with ~1 kg of dry sand. Flotation tests were undertaken at pH~9. A four-stage sequential addition of AM2 was employed...
consistently with the previous investigation. However, the total floating period process was set variously at ~3.5, 7 and 11 minutes in order to optimize the floating period.

III. RESULTS AND DISCUSSION

The surface topography and vibrational spectra of ground chrysocolla and sand samples used in the flotation studies were characterised and reported previously [5, 7]. The chrysocolla particles exhibited a rough surface that appeared to be independent of the particle size, with 100 µm particles having similar surface roughness to the <20 µm particles. The ground Gosford sand sample exhibited non-porous, sharp, compact and fractured structures and liberated iron oxide particles which exhibited magnetism. The Mastersizer software was employed to determine the actual particle size distribution achieved by grinding.

XRF analyses of the ground chrysocolla and sand sample are presented in table I. As the representative flotation charge of chrysocolla-sand sample contained approximate 43 g of chrysocolla and approximate 1 kg of sand, the flotation charge contained 0.86% of copper and 0.27% of iron.

| TABLE I. XRF METALS ANALYSIS OF GROUND CLIFTON CHRYSOCOLLA AND GOSFORD SAND SAMPLES |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Chrysocolla (metal w/w %) | Sand (w/w %) | Chrysocolla (metal w/w %) | Sand (w/w %) | Chrysocolla (metal w/w %) | Sand (w/w %) | Chrysocolla (metal w/w %) | Sand (w/w %) |
| Cu | 20.80 | Fe | 2.14 | Zn | 0.23 | Cu | 0.01 | Mn | 0.13 | Fe | 0.19 | Pb | 0.09 | As | 0.27 |

In Figure 1A, the copper recoveries after wet grinding at various pHs are presented. It is evident that the best copper recovery (99.1%) was achieved when the sample was prepared by wet grinding at pH ~10. Wet grinding chrysocolla at pH ~4 resulted in low copper recovery (attributed to copper dissolution) and grade. >60% of the copper was recovered in the first collection step, with the majority of copper recovered in the first two collection steps. It can be observed from the data that the copper was collected faster when the chrysocolla sample was ground at higher pH. The copper grade recovered generally decreased with an increase in the grinding pH. The best grade was observed when grinding was conducted at pH 7. Iron recovery is presented in Figure 1B, and it can be seen that the highest iron recovery (78.1%) was achieved when the sample was ground at pH ~4, with lowest recovery at pH ~7 (52.9%). Grinding at higher pH resulted in increasing iron recovery rate.

Figure 2 presents copper and iron grade-recovery curves for the sea water ground chrysocolla flotation tests. It is evident that saline water substantially affected the recovery kinetics of copper, with much less impact on the iron recovery. This may be due to complexation increasing the copper solubility.

In Figure 3, the flotation response of blended chrysocolla-sand grinding is compared to the response of a sample in which the chrysocolla sample was ground separately, then blended. Copper grade concentrate of the blended chrysocolla-sand grinding were observed to be significantly lower than the case which the chrysocolla sample was separately ground, indicating that copper is solubilised during grinding and nucleates on the sand. This nucleates on the sand surfaces of copper ions may form the complex with hydroxamate collector.
which resulted in entraining of sand particles floating. As the result of low copper recovery and grade concentrate from the blend grinding process, it is evident that the blend grinding affected the mechanism of the copper recovery and grade as more sand was collected.

As a result of a low grade concentrate being observed from the mixed chrysocolla-sand grinding experiments, X-ray photoelectron spectroscopy (XPS) was employed to characterise the surface of mixture sand-hydroxamate sample to elucidate the mechanism of the sand flotation. The sand at the bottom and the deposit at the top of a sand conditioning slurry were collected and investigated. XPS spectra from the sand of the conditioned sample revealed that the surface comprised 27.3 at.% Si, 50.2 at.% O and 19.3 at.% C. Ca, Mg and Fe were also detected in the minor concentrate at 0.7 at.%, 0.3 at.% and 0.7 at.% respectively. Cu was not detected. The Si: O ratio different from 1: 2 due to the different escape depths of the Si 2p and O 1s photoelectrons. The Si 2p spectrum was fitted with a single component of width 1.6 eV at ~104.1 eV. The N concentration was 1.5 at. %. At the start of the spectral suite, the N 1s component accounting for 70% of the N 1s intensity was at a corrected binding energy of ~402 eV, with a second component accounting for 30% of the intensity at 400.5 eV. At the end of the spectral suite, the two components were comparable intensity at corrected binding energies of ~400 and 401.4 eV, respectively. A binding energy near 401eV was broadly consistent with hydroxamate adsorbed to Ca, Fe and Mg. A lower binding energy component near 400eV, which increased in relative intensity with analysis time, has arisen from the hydroxamate alteration of degradation product. The overall N 1s intensity decreased with analysis time, consistent with some electron stimulated desorption. Hydroxamate was therefore being adsorbed onto the sand under these conditions.

The sample from the top of the sand conditioning cell was found to comprise 20.6 at.% Si, 39.1 at.% O, and 30.4 at.% C. Minor amounts of 1.4 at.% Ca, 1.5 at.% Mg and 0.3 at.% Fe were also detected. The additional impurity detected on the scum surface was Al at 1.5 at. %. Cu was not detected. The Ca and Mg concentrations were double those observed from the hydroxamate alteration of degradation product. The initial N concentration (5.2 at.%) was higher than at the sand surface, and the total N 1s intensity was significantly lower at the end of the spectral suite. It is likely that the hydroxamate was absorbed to the Al, Ca and Mg as well as to the Fe at the surface and this enabled flotation of the particles.

The XPS studies of the sand-hydroxamate surface composition indicated that the sand would have floated because of interaction of the hydroxamate collector with Ca and possibly Mg impurities as well as with the relatively low concentration of Fe from comminution of the sand. A high-purity (99.99%) SiO2 was also prepared and investigated in the same way in order to confirm that sand itself does not interact with the collector. The untreated pure SiO2 surface did not contain extraneous elements, apart from a very low concentration of N at ~0.25 at. %. The corrected 1s binding energy of that N was close to 400 eV, suggesting that it was extraneous N, possibly from the sample tube. The surface C concentration was ~15 at. %, which is relatively low for a specimen that has processed in air and contained in a polymer tube.

The composition of SiO2 surface treated with 600 g/t of AM2 collector included 18 at.% C, 0.5 at.% F, 0.4 at.% Mg, 0.3 at.% Cu, and 0.8 at.% N, as well as a low concentration of K. The K was probably due to residual KOH. The Cu, Mg and F originated from the tap water. The N 1s spectrum at the outset was fitted with two unresolved components; one at ~399.6eV and the other 1eV higher. It is confirmed that not much hydroxamate had absorbed on the surface (<1 at.%). The low N concentration was also consistent with previously finding that silica does not interact with nominally saturated solution of potassium hydroxamate at its unadjusted pH of 9.6.

Resting for 1 hr after grinding process resulted in substantial grade improvement, from ~15 % Cu for no rest time to ~25 % Cu (Figure 4). The copper recovery also slightly improved from 96% for no rest time to 98.5% for 1 hr rest time. The iron recovery decreased from 74.5% for no rest time to 59% for 1 hr rest time. As the copper recovery from the 1 hr rest time process was higher than normal process with no rest time, it implies that a quick release of copper ions into the solution when tap water was added has been alleviated by processing the chrysocolla sample at pH >6 (grinding at pH 9, resting 1 hr at pH 7.42 and floating at pH 9.5).
The impacts of frothers and depressants on flotation response were also investigated. The flotation conditions used for these investigations were consistent with those used elsewhere in this paper (four-stage sequential addition of AM2 and pH ~9.5).

Figure 5 demonstrates the flotation responses after adding various strength frothers. Adding a stronger type of frother slightly increased copper recovery rate, but decreased substantial grade. The flotation with no additional frother yielded 95.2% Cu, while the weak (IF50), moderate (IF6801B) and strong (IF4500A) frother gave yields of 96.4%, 97.2% and 97.9% Cu, respectively. However, a substantial decrease in the grade was observed from ~15% Cu for no additional frother to ~11% Cu for weak frother, ~3% for moderate frother and to ~4% Cu for strong frother type (Figure 5A). The strong frother also exhibited faster recovery kinetics for copper. Additional strong frother indicated a significant increase in the total iron recovery (Figure 5B). It is also evident that using mixed strength frother exhibited improvements in both recovery and grade, compared to the cases where only a single moderate or strong strength frother was employed.

Sodium silicate and tannic acid were investigated as depressants for sand and iron oxide recovery, respectively. A single dose of 200 g/t of sodium silicate or 50 g/t of tannic acid was added to the flotation cell before adding the first dose of AM2 collector and IF50 frother in a four stage sequential flotation test (pH ~9.5). A mixed depressant (200 g/t sodium silicate + 50 g/t tannic acid) experiment was also conducted.

Figure 6A shows that the use of sodium silicate results in improvement of copper recovery rate comparing to the non-depressant used. Tannic acid addition did not result in a significant decrease in iron recovery as expected, but shows significantly decreasing on both Cu and Fe grade concentrate. Mixed depressants resulted in significant change. In Figure 6B, Fe grade and recovery rate is significantly lower comparing to the no depressant case. It is evident that the mixture of depressants resulted in the flotation of substantial quantities of the sand. Conversely, iron recovery was depressed.

Figure 6: Effect of different types of depressants on the grade and recovery of chrysocolla concentrate, pH 9.5, with sequential addition of AM2.

The effect of flotation time dependence has been investigated. Figure 7 exhibits the graph results on the copper and iron recovery rate and grade concentrate. It is obvious that copper grade concentrate was significantly dropped when the flotation time was increased. Conversely, the iron grade concentrate was increased when the flotation time was increased.
CONCLUSIONS

A copper recovery of 99.1% was achieved in the bench-scale flotation experiment from a wet grinding process at pH 10, while the best copper grade was achieved from the grinding process at pH 7. Wet grinding chrysocolla at pH ~4 exhibited poor copper recovery and grade. In all experiments, the majority amount of copper was recovered in the first two collecting steps. Grinding the chrysocolla sample at a higher pH also resulted in faster copper recovery and an increase in the iron recovery.

Using sea water instead of tap water for grinding chrysocolla decreased both recovery rate and concentrate grade for both Cu and Fe. The flotation response of grinding blended chrysocolla-sand yielded a poor performance on both recovery rate and concentrate grade. It was observed that low copper grade resulted from the floating of sand particles. The surface of sand-hydroxamate mixture was investigated by using XPS. The XPS results exhibited the interaction of hydroxamate with the impurities on the sand surface leading to the flotation of sand particles. The copper recovery results from the 1hr rest period after wet grinding presented as high as the test with no rest time.

Investigation of the strength types of frother indicated that while adding a stronger frother slightly increased the recovery rate for both Cu and Fe, but it decreased in the grade of concentrate for both Cu and Fe. The stronger type of frother also exhibited a faster recovery rate on copper. Adding mixed frothers yielded higher grade and recovery rate by comparison with the single moderate or strong strength type of frother test.

The flotation response after adding sodium silicate as a depressant presented the majority effect that the grade concentrate for Fe exhibited a significant decrease by comparing to the test with non depressant addition. Adding tannic acid as a depressant aimed to eliminate the iron impurity in the copper concentrate but the result unexpectedly showed no significant decrease of iron in the copper concentrate. Using longer flotation time resulted in significantly low copper grade concentrate but increased in iron grade concentrate.

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REFERENCES