

# THE INVESTIGATION OF CHRYSOCOLLA AND MALACHITE FLOTATION USING HYDROXAMATES

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## ABSTRACT

Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy, Atomic absorption spectroscopy (AAS) and X-ray Photoelectron spectroscopy (XPS) have been employed to characterise the surface layer and compound formation during the interaction of hydroxamate flotation reagents with chrysocolla and malachite surfaces. Scanning Electron Microscopy (SEM) has also been carried out to observe topography, structure and the composition of the near surface layer. The flotation response of a single mineral chrysocolla / quartz sand sample and mixed chrysocolla + malachite / quartz sand sample using n-octanohydroxamate collector have been investigated.

*Keywords: Alkyl hydroxamates, Mineral processing, Flotation collectors, Oxide ores*

## INTRODUCTION

Chrysocolla forms a large potential copper resource that has not been accessed due to difficulties associated with processing the ore. The flotation of this oxide copper mineral is an area of considerable interest to miners and processors, but difficulties encountered in progressing from micro flotation studies through to the processing plant have hindered the practical extraction of copper from the chrysocolla deposits. There have been a number of papers, patents and processes proposed for the flotation of chrysocolla, largely based on the results obtained from Hallimond tube experiments with some contact angle data (Aplan and Fuerstenau, 1984; Fuerstenau et al., 2000; Fuerstenau and Pradip, 1984; Herrera-Urbina et al., 2010; M. Barbaro et al., 1997; Peterson et al., 1965). It has been demonstrated that n-octanohydroxamate is a strong candidate for practical flotation of chrysocolla ore. Unfortunately, these laboratory studies have not been translated into practice. The nature of the chrysocolla structure, porosity and properties have been discussed in Parker et al., (2011).

We have obtained a porous chrysocolla sample from the Clifton district in Arizona in a quantity sufficient for us to undertake kilogram scale, near single mineral, sand extended flotation recovery experiments. This bulk sample has been ground to 85% passing 100  $\mu\text{m}$  to generate a fully liberated chrysocolla and blended with ground sand of similar size profile to provide a synthetic ore sample suitable for bench testing. We previously have used bench scale testing to investigate hydroxamate flotation of blended copper ores of malachite and sulfides from Minto (Lee et al., 2009). In this paper we report the results obtained from chrysocolla bench flotation testing as a function of copper content of a chrysocolla sand mixture, pH conditions, dosage of reagents and frother, extended condition time, NaSH/AM2 combination, ammonium hydroxide addition and mixed chrysocolla + malachite/sand

flotation with the n-octanohydroxamate flotation collector AM2. The malachite ore prepared in the manner described by Lee et al., (2009) was subjected to column flotation testing. The nature of the collector – mineral interaction is discussed and the role of the solution potential measured at a platinum electrode is considered.

## **EXPERIMENTAL METHODS**

### **Chemicals and materials**

The chrysocolla used in the flotation studies was from Clifton, Arizona. The colour varied from dark blue green to bluish green with isolated brown (impurity) staining visible to the eye (chrysocolla,  $(\text{Cu};\text{Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ , typical w/w% as oxides; Si, 44.83; Cu, 42.48; Al, 4.42; Ca, 1.12; Mg, 0.53) (RRUFF, 2011). Natural malachite and azurite samples were obtained from mine sites in the Democratic Republic of Congo and Canada. The collectors, potassium hydrogen n-octanohydroxamate (AM28),  $(\text{C}_8\text{H}_{17}\text{O}_2\text{N})_2$  (H, K) and the commercial variant, AM2 were provided by Axis House. A frother was used for the 2.5 L stirred flotation cell, either methyl isobutyl carbinol (MIBC) or the commercial product, Interfroth (IF50, from Chemicals and Mining Services Pty Ltd.). The pH was raised when required with hydroxide; tests were run with potassium or ammonium hydroxide. Sodium hydrosulfide hydrate (NaSH), (ACROS Organics) was used to simulate transition behaviour from sulfidisation to hydroxamate during flotation plant testing. Column flotation of malachite ore utilised de-ionized laboratory water and compressed air. Flotation in the 2.5 L stirred cell used tap water and compressed air and concentrate samples were collected from the froth overflow.

A 5 kg sealed stainless steel laboratory rod mill manufactured by ESSA Australia, model RM 250 x 300, with 10 stainless steel rods was used to grind minerals, ore and sand fractions. Chrysocolla was dry ground to approximately 100  $\mu\text{m}$  particle size, while Canadian

malachite ore (Lee et al., 2009) and the quartz sand samples were wet ground to the same approximate particle size. Particle sizes were measured by using Mastersizer X from Malvern. The Canadian malachite ore used for the column testing was stored in a freezer at -18° C until required. Sand samples were dried prior to mixing the chrysocolla (target mineral) and quartz (gangue) components to formulate the selected composition using a Carpeo sample splitter (model SS manufactured by Warman Equipment). Representative samples containing approximately 1% copper were prepared on a kilogram scale. The quartz / chrysocolla samples were floated by using a locally constructed laboratory scale 2.5 L stirred flotation machine.

### **Spectroscopy and electrochemistry**

Raman spectra were acquired by using a Renishaw System InVia spectrometer. The excitation wavelength was 632.8 nm from a HeNe laser. Raman spectra were calibrated using the 520 cm<sup>-1</sup> silicon band. Spectral manipulations such as baseline adjustment, smoothing and normalisation were performed by using Renishaw WiRE 3.2 software. Fourier transform infra red (FT-IR) spectra were acquired from a Thermo Nicolet- Nexus spectrometer equipped with EverGlo IR source optics which provides a stabilised signal. Spectra were acquired in the range of 4000 - 500 cm<sup>-1</sup> with 0.5 cm<sup>-1</sup> resolution and processed using OMNIC ESP software. The solid samples were prepared for investigation by mixing with potassium bromide (KBr), then ground and pressed into disks.

The pH and platinum electrode potential (Eh) measurements were used to investigate the interaction of the flotation reagent with the flotation sample. Measurements were undertaken during flotation testing in the bench scale stirred flotation cell and also while base titrating (KOH) AM28 treated, stirred sand / chrysocolla mixtures. Eh measurements during titrations were made with a Pine Wavenow USB potentiostat interfaced with a PC running Pine

Aftermath software V1.2.4361. The Pt electrode potentials recorded during titrations are reported against a Ag/AgCl (3.0 M KCl) reference electrode.

### *Analytical techniques*

#### **X-ray fluorescence spectroscopy**

An X-Ray Fluorescence (XRF) spectrometer from Thermo Scientific (NITON XL3t) was utilised for measurement of Cu, Fe and trace metals. The concentrate and tails samples from the flotation process were collected on filter paper, washed, dried in an oven at 60° C for 12 hours then fine ground for XRF measurement using Thermo Scientific analysis software.

#### **X-ray photoelectron spectroscopy**

X-ray photoelectron spectra were collected from a surface of particulate mineral concentrate specimens embedded in freshly exposed indium foil surface. The samples were obtained from flotation concentrates that had been washed and dried. XPS data were obtained on an ESCALAB 250Xi spectrometer using monochromatised Al  $K_{\alpha}$  X-rays focused to a spot size of 0.5 mm and an electron analyser pass energy of 20 eV for narrow range scans. Included in the binding energies employed for calibration were 83.96 eV for Au  $4f_{7/2}$  of metallic gold and 932.6 eV for Cu  $2p_{3/2}$  of Cu metal. The pressure in the analysis chamber was better than  $5 \times 10^{-9}$  mbar during spectral acquisition. Acquisition of photoelectron spectra required the use of a flood gun and binding energies were referenced to 285.0 eV for the hydrocarbon C 1s photoelectrons. The possibility of beam damage by the floodgun low energy electrons was monitored and spectra were obtained as quickly as possible, at the expense of signal-to-noise, in order to minimise any damage arising from the secondary electrons associated with the X-ray photoemission.

### **Scanning electron microscopy**

An FEI Quanta 200 Environment SEM was used to characterise topography of chrysocolla and sand samples. The surface layer of a chrysocolla sample was prepared by cutting with a diamond blade on a Buehler Isomet low speed saw lubricated with water. The sample surface was ground with silicon carbide abrasive paper progressively to P1200. The ground sample was then polished with water lubricated 6  $\mu\text{m}$  and 3  $\mu\text{m}$  diamond paste laps followed by sonication for 10 minutes in DDI water to dislodge small particles from the surface. The ground chrysocolla, sand and concentrate samples were prepared by pressing particles into a conductive carbon paste coating on a stub holder with a thin gold coating being evaporated onto the exposed particle surfaces to prevent charging during the investigation.

### **Atomic absorption spectroscopy**

An atomic absorption spectrometer (AAS) model spectra AA-10 from Varian with a Cu/Fe cathode lamp was used to measure the Cu and Fe content of Canadian malachite ore and concentrates. Samples were prepared by digesting the Cu and Fe sample in aqua regia, followed by fuming to dryness, then taken up in hydrochloric acid and diluted with DDI water as required.

### ***Flotation experiments***

#### **Column flotation**

Experiments undertaken with column flotation of a Canadian malachite ore were carried out without utilising any frother. The column used was 3 cm diameter and 24 cm long. A fritted glass disk with 20  $\mu\text{m}$  pores was located at the bottom of the flotation column approximately 2 cm above the air inlet. A flow meter was attached to control air flow and the flotation charge was 5 g of the ground wet malachite ore. AM28 was added at a dose level of 20 g/t, the slurry was conditioned for 1 minute on 10 mL/s flow rate. The pH was re-adjusted after

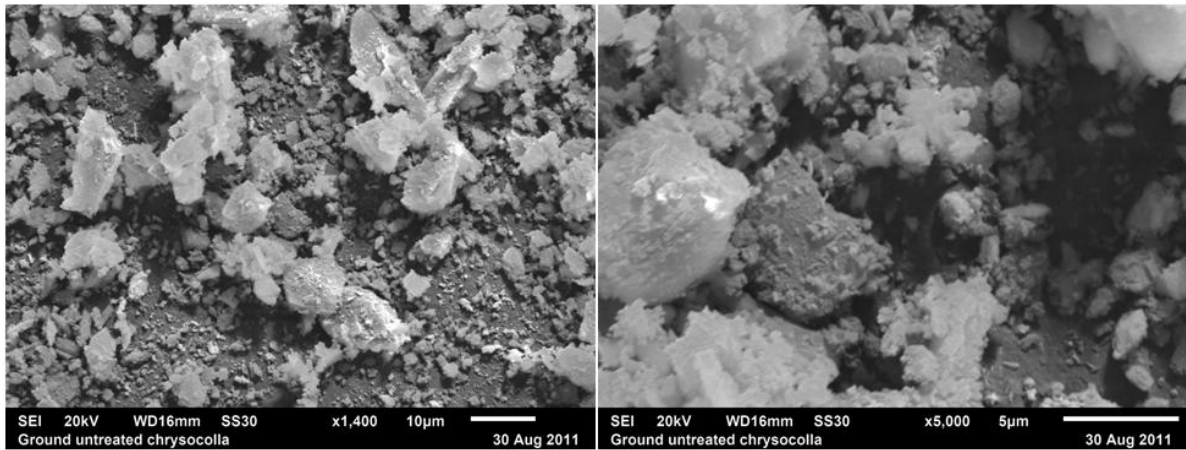
the reagent addition to ensure that flotation occurred at the target pH. The flotation time was 2 minutes with a 50 mL/s air flow rate. Concentrate fractions were washed, gravity filtered, dried and weighed. Atomic absorption spectroscopy of the total digest determined Cu and Fe content which was used to determine the percentage recovery.

### **Flotation machine bench tests**

Flotation experiments were conducted using the 2.5 L stirred flotation cell. The flotation charge of 84 g or 42 g of chrysocolla was chosen with approximately 1 kg of sand. The charge was mixed with 1 L of water and transferred to the flotation cell. The slurry was stirred at 660 rpm for 2 minutes. The solids content in the cell was then adjusted to 30% by addition of approximately 1 L of water and stirred at 500 rpm for 2 minutes. The pH was then adjusted to the desired value with hydroxide or hydrochloric acid solution and the collector and frother were added at the selected dosage. The pH was re-adjusted after the reagent addition to ensure that flotation occurred at the target pH during the conditioning period that was normally set at 2 minutes. Flotation was commenced by introducing a compressed air flow of 7 L/min. Several concentrate collections were undertaken sequentially to emulate plant operation, a flotation time of 2 minutes was selected for the first concentration, followed by 3 minutes for each of the second, third and fourth concentration steps.

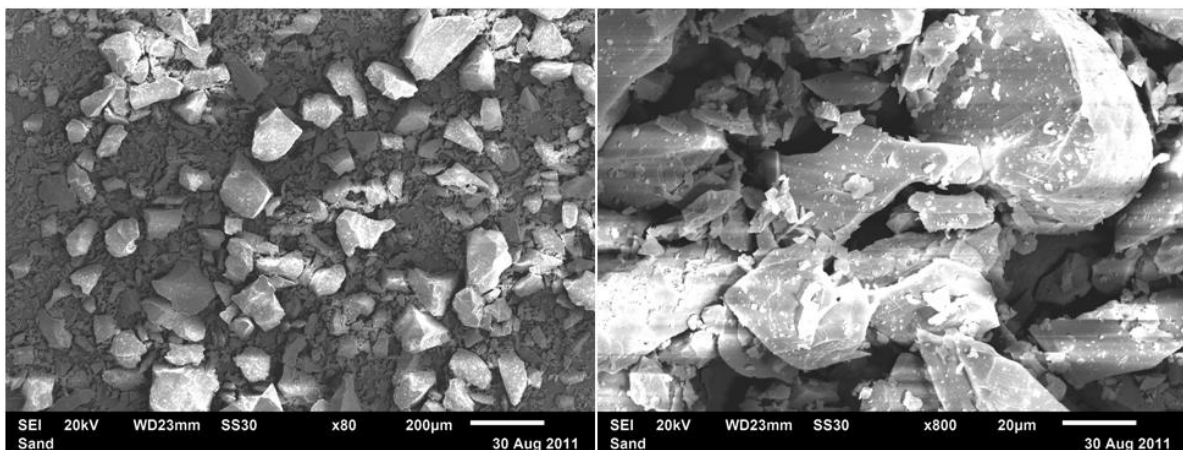
## **RESULTS AND DISCUSSION**

The surface topography of the ground chrysocolla and sand materials was investigated using SEM prior to flotation. Fig. 1 presents representative images of the ground chrysocolla sample. The particles exhibited rough surfaces and edges with numerous surface protrusions.



**Fig. 1.** Scanning electron micrographs of ground chrysocolla

The particle roughness appeared to be independent of the particle size, with 100µm particles having similar surface roughness to the < 20 µm particles shown in Fig.1 . EDX analysis of a chrysocolla particle gave the following composition as % w/w: O; 36.13, Cu; 40.21, Si; 22.63, Al; 0.46, Fe; 0.36, Ca; 0.2. EDX analysis of an iron rich particle observed in the chrysocolla matrix gave a stoichiometry of  $Fe_3O_4$  . Inspection of the ground chrysocolla with a permanent magnet enabled collection of magnetic iron oxide particles. In Fig. 2, the SEM images of the sand particles illustrate the sharp, compact, fractured structure that was exhibited by the ground sand.

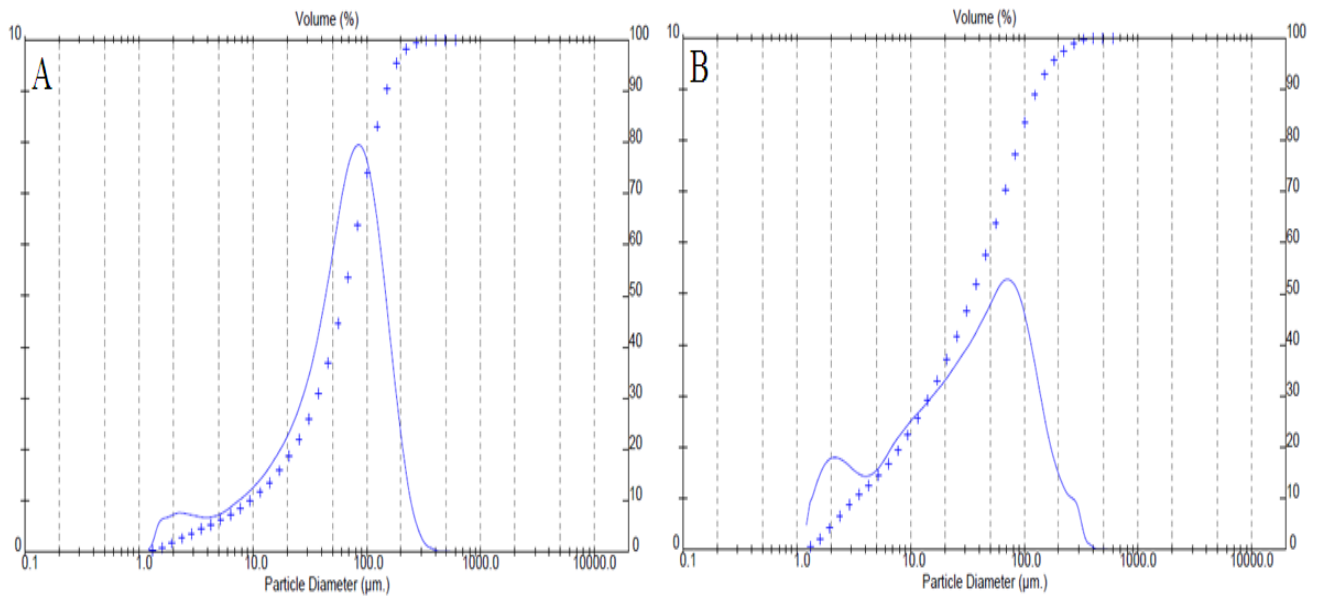


**Fig.2.** Scanning electron micrographs of sand after grinding



The sand was non porous with liberated iron oxide particles that exhibited magnetism and could be collected from the sample using a permanent magnet..

The actual particle size distribution achieved was analysed using the Mastersizer software. Fig. 3. presents size distribution graphs for the ground sand, (3A) and chrysocolla, (3B). The sand particle size distribution was considerably narrower than that of the chrysocolla: whereas 35% by volume of the chrysocolla particles were under 20  $\mu\text{m}$  in diameter only 18% by volume of the sand was in this particle size range. The volume passing 100  $\mu\text{m}$  was 77% for the sand and 83% for the chrysocolla.



**Fig. 3.** Particle size analysis of sand and the chrysocolla sample

The results of an XRF analysis for metals in the chrysocolla and sand samples are presented in Table 1.

<b>Chrysocolla (metal ww%)</b>		<b>Sand (ww%)</b>	
Cu	24.37	Fe	0.18
Fe	0.77	Cr	0.05
Zn	0.08	Ni	0.02
Mo	0.06	Cu	0.01
Pb	0.03		
Bi	0.01		
Nb	0.01		

**Table 1** XRF metals analysis of Clifton chrysocolla and Gosford sand samples.

The XRF analysis showed that the sand contained appreciable iron. The typical charge for the stirred flotation cell contained 40 g of chrysocolla and 1 kg of sand, the nominal composition of the charge was 0.98% Cu and 0.21% Fe, with 87% of the iron in the charge being contained in the sand fraction. The iron was present predominantly as magnetite from both sources.

### **Column Cell**

The feed for the column flotation test was an oxide copper ore from Canada (Lee et al., 2009). It had a total copper content of 3.5%, almost exclusively as malachite in a quartz / feldspar / biotite matrix. The particle sizing was 80% passing 150 µm. The cell was investigated for suitability as it was intermediate in size between the micro scale Hallimond tests, that have been widely used in the past, and the Denver type cell stirred testing regimes.

Atomic absorption spectroscopy was used for chemical analysis of products. Recoveries of

77.3% copper and 16.3% iron were obtained from the malachite ore in the column flotation test. The grades were 37.8% copper and 2.41% iron. Pure malachite contains 57.5% copper.


Bench testing by column flotation here performed poorly compared to the stirred cell flotation tests run in a previous investigation (Lee et al., 2009) and this line of investigation was not continued.

### **Batch flotation tests**

A series of batch tests were undertaken on a kg scale in the 2.5 L stirred flotation cell. An initial run investigated the flotation of a 1.7% Cu sand - chrysocolla mixture prepared by mixing 85.29 g of the dry-ground chrysocolla with 993 g of ground sand. Target pH for the test was 10, and the flotation collector was added in four steps to emulate a four stage flotation process with sequential collector dosage to the flotation cell train. The AM2 dose level was determined by the observed flotation response without consideration of the reagent consumption level. In Fig. 4 we present the flotation test data sheet recorded for this test with a total AM2 dose of 1.2 kg/t (tonne of ore) (equivalent to 700 g/t for each 1% of contained copper).

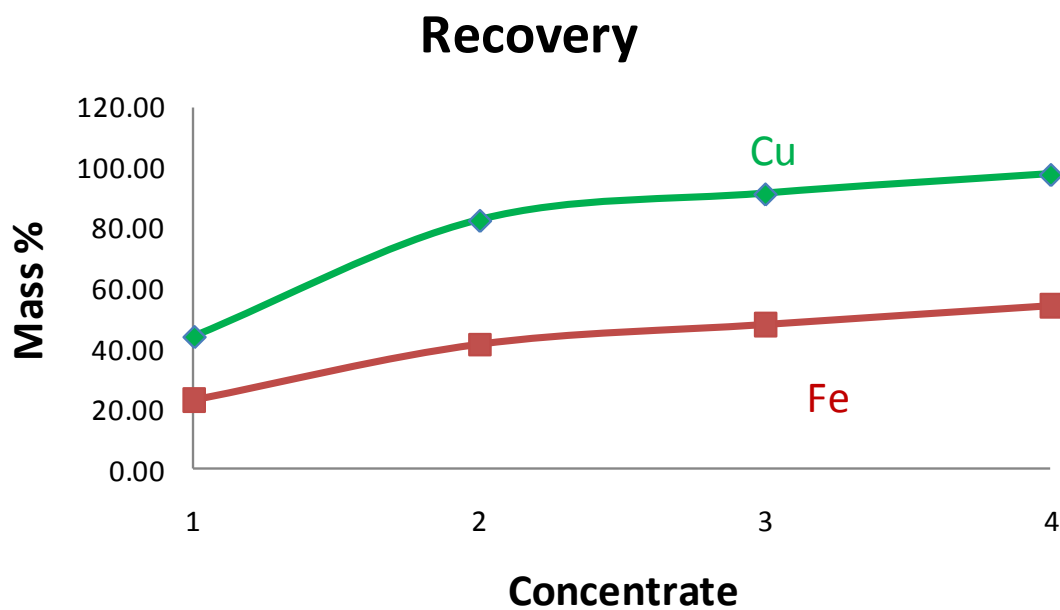
The flotation of the chrysocolla recovered 97.5% of the total copper in the four stage addition of AM2, with MIBC frother used for the first two stages and IF50 added as the frother in the final two stages. 54.2% of the total iron was also collected (1.4 g), the majority of this coming from the sand fraction. Assay of the copper gave the highest proportion of acid soluble copper in the first concentrate sample (97.4%), a proportion which decreased with the extent of collection, the final concentrate sample having 92.1% acid soluble copper. These results indicated that the fastest floating copper minerals contain the highest acid soluble copper content. The overall AM2 consumption in this test was 1.2 kg per tonne of ore. In a commercial plant environment, it is unlikely that the fourth stage would be employed to

recover 5% of the acid soluble copper.

 <b>Flotation Test Data Sheet</b>												
<b>PROJECT NO.:</b> 0188			<b>GRINDING MILL #:</b>				<b>FLOAT CELL:</b> AMML					
<b>PROJECT :</b> AM2 (Chrysocolla)			<b>P80 (µm)</b> 100				<b>RGHR CELL (mL):</b> 2500.0					
<b>TEST NO.:</b> 1			<b>RODS</b>				<b>RGHR CELL rpm:</b> 500.0					
<b>SAMPLE:</b> Sand/chrysocolla			<b>SOLIDS (g):</b> 1077.8				<b>CLNR CELL (mL):</b>					
<b>DATE:</b> 22/06/2011			<b>GRIND % SOLIDS:</b>				<b>CLNR CELL rpm:</b>					
<b>OPERATOR:</b> GS			<b>MINUTES</b>									
<b>OBJECTIVE :</b> AM2 prepared as 2% in 1% KOH. Ground sand + dry chrysocolla added to cell as dry solids (P80 sand ~120µm). Target pH ~ 10 85.29g chrysocolla added							<b>SLURRY/FLOTATION CONDITIONS</b>					
<b>REAGENTS (g/t) :</b>		AM2 g/t	KOH g/t	MIBC g/t	IF50 g/t			AIR (L/min)	pH	Eh mV	COND (min)	FLOAT (min)
Grind												
Attrition		660 rpm with 1000ml of water, adjust to 30% solids							5.7	300	2	
Cond			100						6.9	260	2	
Cond		800		10					9.7	-30	2	
Con 1				10								2
Cond		200							9.9	-34	2	
Con 2				25								3
Cond		100			10				9.8	-40	2	
Con 3												3
Cond		100.0			25				10.0	-44	2	
Con 4												3
<b>PRODUCTS</b>		<b>Wt ASSAYS (%)</b>					<b>DISTRIBUTION (%)</b>					
		g	%	Cu	Acid Sol Cu	Fe			Cu	Acid Sol Cu	Fe	
Con 1		34.5	3.20	23.4	22.8	2.26			43.8	46.5	22.9	
Con 2		38.1	3.54	18.6	16.8	1.66			38.5	37.8	18.5	
Con 3		15.0	1.39	10.8	9.45	1.50			8.77	8.35	6.58	
Con 4		14.5	1.35	8.16	5.94	1.47			6.43	5.09	6.26	
Tail		975.7	90.5	0.05	0.04	0.16			2.54	2.30	45.8	
Calculated Head		1077.8	100.0	1.71	1.57	0.32			100.0	100.0	100.0	
<b>CUMULATIVE PRODUCTS</b>		<b>Wt</b>		<b>CUMULATIVE ASSAYS (%)</b>			<b>CUMULATIVE DISTRIBUTION (%)</b>					
		g	%	Cu	Acid Sol Cu	Fe			Cu	Acid Sol Cu	Fe	
Con 1		34.5	3.20	23.4	22.8	2.26			43.8	46.5	22.9	
Con 1-2		72.6	6.74	20.9	19.7	1.95			82.3	84.3	41.4	
Con 1-3		87.6	8.13	19.2	17.9	1.87			91.0	92.6	48.0	
Con 1-4		102.1	9.47	17.6	16.2	1.81			97.5	97.7	54.2	

**Fig. 4.** Flotation test data result sheet for the chrysocolla / sand test with sequential AM2 addition.

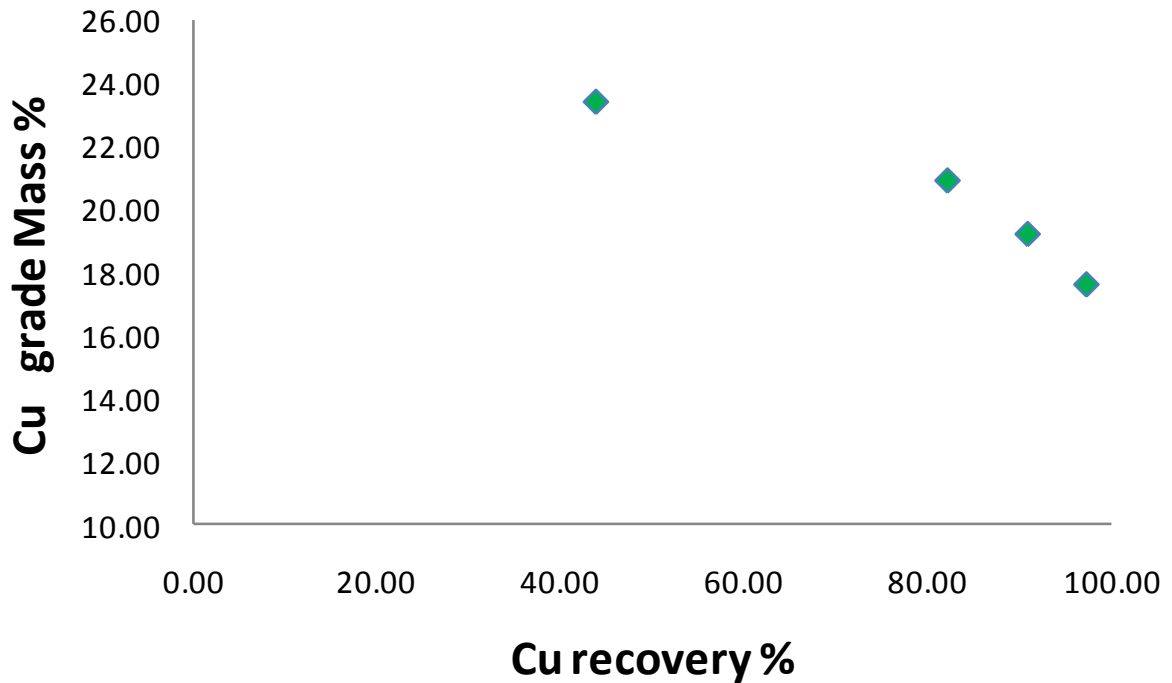
In Fig. 5 we present a graph of the recovery of the contained copper and iron that was achieved for the 4 concentrate collection steps undertaken in the flotation test. The chrysocolla was recovered efficiently and 82.3% of the mineral had been collected after the second addition. The iron (mainly from the sand) was also collected, with 41.4% recovered at the same stage.



**Fig. 5.** Percentage recovery of total copper and iron for the 4 stage AM 2 flotation

The sand - chrysocolla charge is a combination which was chosen to minimise the collector interaction with gangue materials and for demonstration of the chrysocolla collection effectiveness. The grade of the concentrate achieved in this case was indicative of the carry-over of silica in the flotation process. Fig. 6 shows a graph of the copper grade achieved for each of the collection steps. The maximum grade achievable would be the mass % of copper in the ground Clifton chrysocolla sample, 24.37%. It is apparent that the first concentrate sample collected was almost pure chrysocolla, with sand being an increasing proportion of

the collected material as the process lowered the chrysocolla content of the flotation cell charge.



**Fig. 6.** Variation in copper grade with recovery for the 4 stage AM 2 flotation.

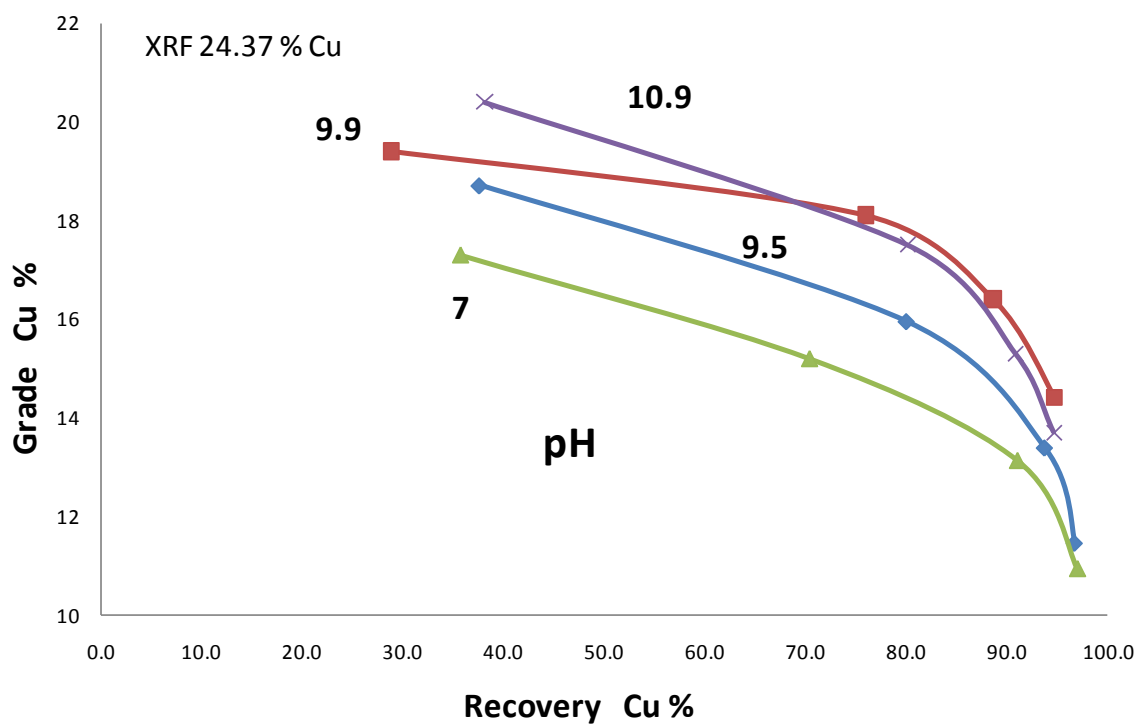
There have been a number of reports of the pH dependence of flotation concerned with n-octanohydroxamate and oxide copper ores. These have employed contact angle measurements (Herrera-Urbina et al., 2010) , Hallimond flotation cells (Fuerstenau and Pradip, 1984) and Denver cells (Lee et al., 2009; Lee et al., 1998).

Experiments were undertaken to assess the recovered copper grade dependence on the pH used for the flotation of the chrysocolla. The test conditions determined for these measurements were similar conditioning and collection times as presented in Fig. 1 but with a lower initial chrysocolla content and scaled collector addition levels. A four step sequential addition of AM2 as a 2% solution in 1% KOH was employed: 400 g/t with 20 g/t IF50 for the first step, followed by 100 g/t AM2 + 20 g/t IF50, then 2 further collections at 50 g/t AM2

+ 20 g/t IF50.

We present the grades obtained in this series of flotation experiments as a function of the pH of the first flotation step, for chrysocolla – sand charges initially containing 0.85% Cu in Fig. 7.

The data is indicative of poorer flotation performance observed for hydroxamate at pH below 9.5 under the conditions used for these experiments. The recovery is presented as the contained copper content of the blended sand-chrysocolla charge.

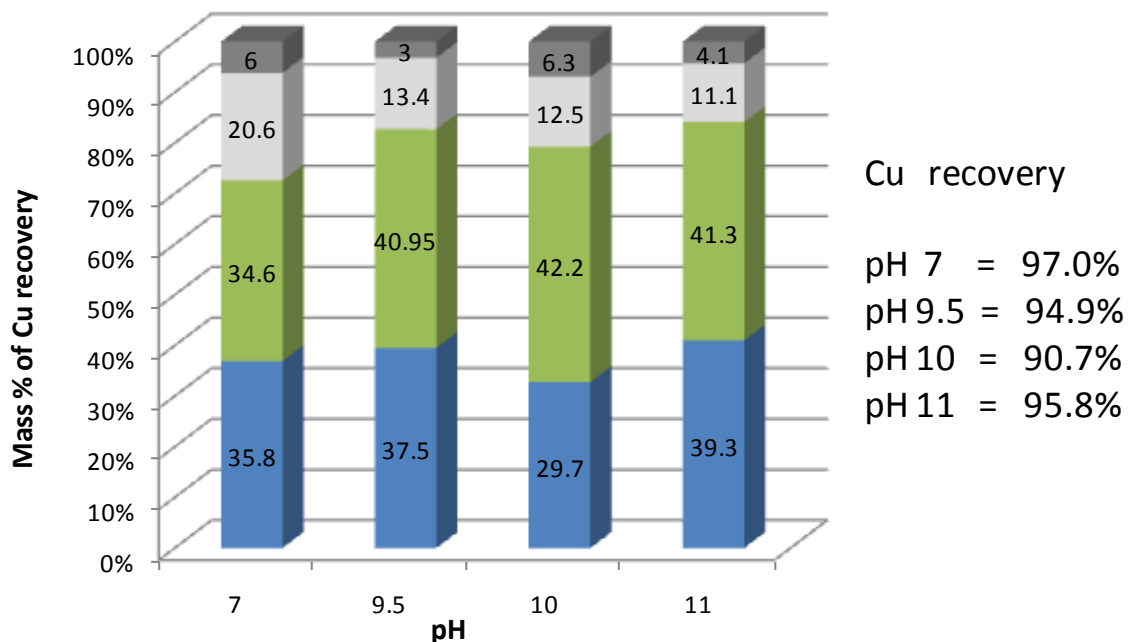


**Fig. 7.** pH dependence of Cu grade as a function of Cu recovery for sequential AM2 addition at 600 g/t.

The grade response exhibited by the data presented as Fig. 7 is of noticeably lower copper content than that observed for the 1.2 kg/t data obtained from a 1.71% copper head grade.

While the data indicates that (predominantly) more sand is collected under the lower AM2 / copper content conditions, this can be attributed (in part) to the fact that at a starting grade of 0.85% Cu, the grade recovery curve presented as Fig. 7 covers only the lower half of the chrysocolla / sand copper content range that is covered by the data that is presented as Fig. 6.

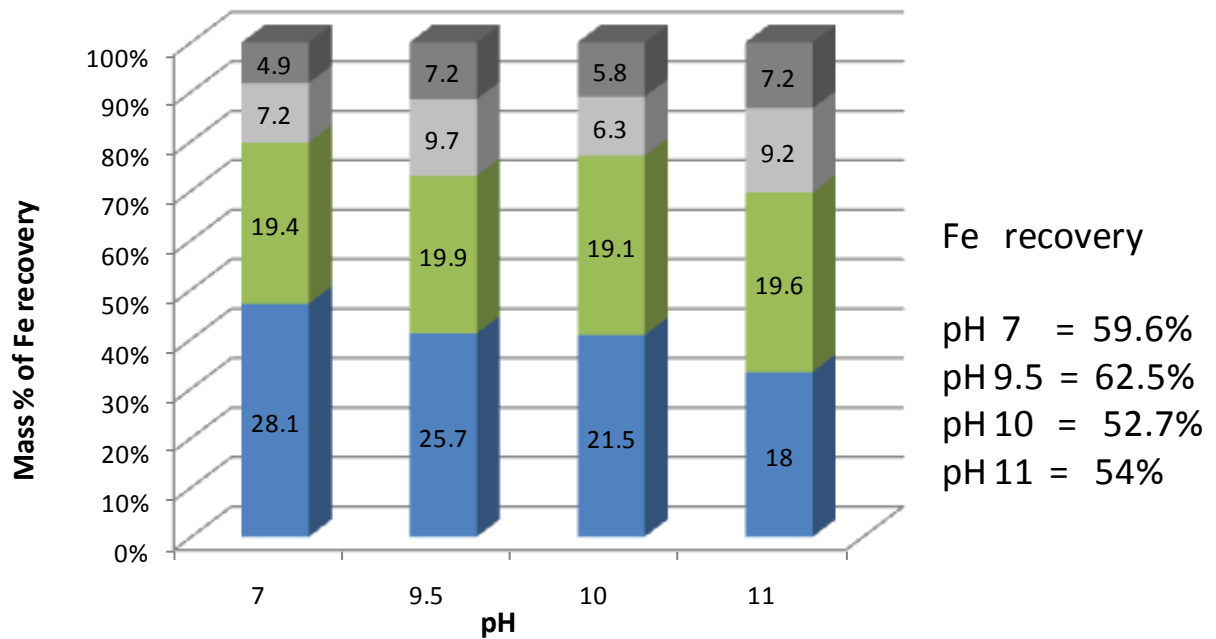
The recovery of the contained iron exhibited a greater pH dependence than that observed for the chrysocolla in sequential AM2 addition experiments. In Figs 8 and 9, column charts are presented that illustrate the distribution of the collected metals between the four collection steps for four pH levels. The relative contributions of the collection steps are apparent, and it can be seen that the contained iron floats to a greater extent than the copper in the latter flotation steps. The columns represent the total mass recovery as fractions of the 100% collected, whereas the numbers are the percentage recovery of the contained metal in the feed.



**Fig. 8.** Copper recovery at selected flotation pH showing the 4 concentrate collections.



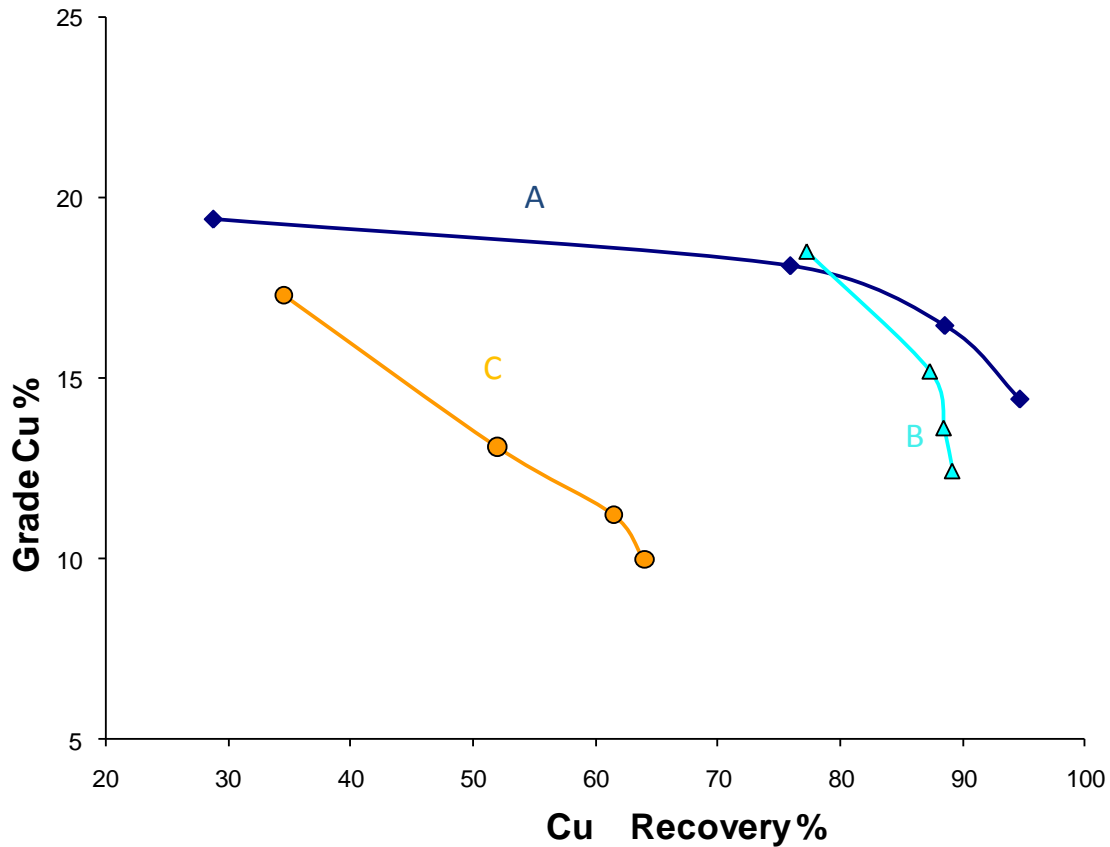
At all pH values tested, the majority of the chrysocolla was collected in the first two flotation steps.



**Fig. 9.** Iron recovery at selected flotation pH showing the 4 concentrate collections.

Less than two thirds of total iron was recovered from the sand – chrysocolla charge, the recovery was most rapid at lower pH and was more even across the 4 collections compared to the measured copper recovery.

The sequential addition of flotation reagent in bench scale testing was an attempt to emulate the role of flotation banks in the plant. In many plants available for oxide ore flotation, it is not convenient to have multiple collector dosing points. This impacts on the flotation process where grade and recovery can be affected by time and dose dependent reagent losses. The grade – recovery data for sequential AM2 + IF50 addition, single dose AM2 + sequential IF50 addition and for the single dose AM2, stirred for 30 minutes prior to flotation + sequential IF50 addition are presented in Fig. 10.



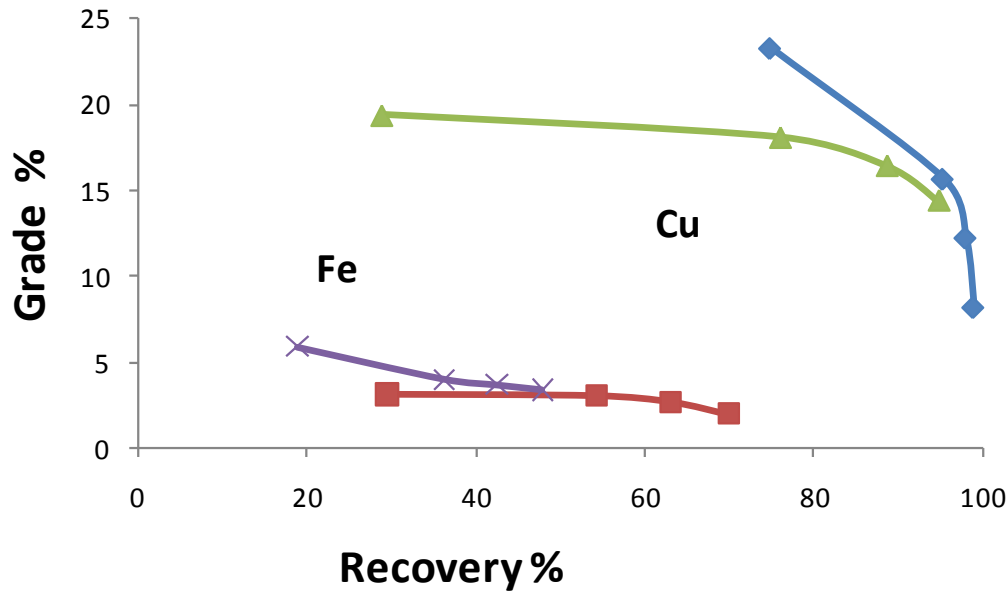
**Fig. 10.** Curve A is sequential AM2 addition, B is for a single dose at the start of the flotation experiment and C is dosed with AM2 and stirred for 30 minutes prior to commencement, pH 10.

The AM2 single dose addition was undertaken to investigate whether the flotation response observed for the sequential addition was sufficient to utilise a single point collector addition. The recovery rate of copper for the AM2 single dose addition is compared to that of a similar total dose AM2 4 stage addition in this figure. The collection protocol for the single dose experiment was the same as for the 4 stage addition, except that all the AM2 was added in the initial float, the subsequent flotation steps only added a dose of IF50. The initial collection yielded 77.2% of the copper at a grade of 18.5%. The total recovery result for AM2 single dose addition indicated 91.3% of copper was recovered and a 55.5% iron recovery, values that were slightly lower than the recovery rate of the AM2 stage addition of 95.3% and 52.7%

for copper and iron respectively. Fig. 10 also presents data on the loss of AM2 with residence time in the flotation pulp. In Fig. 10 curve C, an extended conditioning time prior to chrysocolla flotation of 30 minutes for the single dose regime of AM2 and the same collection protocol clearly demonstrated that the a flotation performance for the AM2 was substantially reduced when the time between collector addition and concentrate collection was extended. The copper recovery was reduced to 70.8% from the 95.3% obtained for the 2 minute single AM2 dose system, and iron recovery fell from 55.5% to 47.6%. Herrera - Urbina et al. have observed lower copper recovery when conditioning time was extended during Hallimond tube experiments at pH values lower than those used here (Herrera-Urbina et al., 2010). They attributed their low recovery to significant dissolution of copper from their chrysocolla. Dissolution of copper would lead to formation of copper hydroxamate and removal of the collector from solution, but any large free hydrophobic copper hydroxamate particles dislodged from the chrysocolla surface by sand abrasion would report to the concentrate, small copper hydroxamate particles may not be collected. A lower grade also may be attributable to collection of copper hydroxamate coated or iron hydroxamate coated silica. Copper could be lost from the system through silica particles that were only partially covered by abraded copper hydroxamate, the larger particles may not be sufficiently hydrophobic to be floated, these report to the tailings and the metal recovery decreases.

The dependence of the flotation process on the nature of the copper mineral was investigated by utilizing chrysocolla and malachite/azurite components to prepare a sand / chrysocolla / malachite-azurite charge with a combined copper content of 1% by mass. The grade vs recovery measured from this sample could then be directly compared to the chrysocolla / sand samples. In Fig. 11 we present the recovery grade curves obtained from the mixed

silicate/carbonate sample and a chrysocolla sand sample of the same copper head grade treated under the sequential addition flotation conditions observed at pH 10.



**Fig. 11.** Grade vs recovery for chrysocolla (Cu ▲, Fe X) and chrysocolla + malachite/azurite (Cu ◆, Fe ■) samples pH 10.

The sample comprised of the mixture of chrysocolla and malachite/azurite minerals exhibited a faster, higher grade copper flotation and a lower grade recovery for the iron than that of the chrysocolla sand mixture. The grade for the chrysocolla is 36% Cu, and, for our sample, the maximum grade from XRF analysis was 24.37%. Assuming 56% as a maximum grade for the copper carbonates, we would have a grade near 56% if only carbonate material floated initially or 24% if only the silicate floated. It is apparent the copper minerals are being floated simultaneously, and it is possible that the faster (and higher) recovery rate is determined by the greater theoretical grade in the composite copper sample tested.

Ammonia solution was tested for pH adjustment, and at the concentration required for maintaining a pH of 9.5 was found to have no measurable effect on the grade or recovery for

the copper or the iron contained in the chrysocolla charge.

### **XPS studies of concentrate samples**

Two samples of the first collection of concentrate from sequential addition experiments were investigated. These were from a 0.8% Cu content chrysocolla + sand sample floated at pH 6.5 (mass recovery data first section of column labelled 7 in Fig. 8 and Fig. 9), and from the chrysocolla + malachite + azurite sand charge floated at pH 10 (grade vs recovery data presented as Fig. 10).

The concentrate was dried on a paper filter using heat lamps then transferred to a glass dish and held in an oven at 60° C for 12 h. The sample for XPS study was taken after the mass of dried concentrate had been determined. The concentrate samples were transported in zip-lock plastic bags. Especially because of the absence of special handling of the concentrate samples, it might be expected that the residual collector concentration on the particles would be lower than while the particles were in the flotation froth.

The samples were sub-sampled for XPS characterisation and a small quantity mounted on double-sided adhesive tape with only very gentle pressure applied to the particles to assist their adhesion, but to minimise further damage to any adsorbate on the surface of the particles. Spectra were obtained from a single 500 µm area of each specimen. Because of the poor electrical conductivity of the oxide Cu minerals, the use of an electron flood-gun is necessary for XPS analysis with monochromatic X-rays to compensate for specimen charging as a result of photoemission. The low energy electrons (175 µA, ~4 eV) from the flood-gun can potentially stimulate desorption and reduction of Cu<sup>II</sup> to Cu<sup>I</sup>, therefore N 1s and Cu 2p spectra were determined as soon as possible after the flood gun had stabilised, and a second

N 1s spectrum was determined at the end of the spectral suite to assess the extent of any beam damage. All spectra were obtained as rapidly as possible, at the expense of signal-to-noise, to minimise beam damage.

In minimising peak broadening from a non-uniform potential within the specimen surface layer, the low energy electrons ‘over-compensate’ for charging and the measured photoelectron binding energies are typically 4 eV lower than their correct values. The measured binding energies are corrected by assuming that they will all be affected by the same energy, and adjusting them so that the hydrocarbon C 1s binding energy is 285.0 eV. For chrysocolla, the Cu  $2p_{3/2}$  and Si  $2p_{3/2}$  binding energies are available as a check on the validity of the correction procedure.

### **Sample collected at pH 6.5, 400 g/t AM2 and 20 g/t IF50**

Surprisingly, the surface C concentration (~15 at%) was relatively low, suggesting not only that extraneous post-collection contamination of the concentrate might not have been a serious problem, but also that residual adsorbed hydroxamate might also be low. However, the surface Cu concentration was only ~5.5 at% whereas that of Si was ~22 at%, raising the possibility that sampling and/or sub-sampling might not have been representative. About 1 at% Fe was also present, but the Ca concentration (~0.2 at%) and Al concentration (~1.7 at%) were consistent with the Cu concentration. The XRF analysis of the ground chrysocolla sample (Table 1) gave a Cu concentration of 24.4 wt %, whereas a model chrysocolla sample would be expected to be close to 36% Cu by weight, or near 6.7 at% including all atoms (H inclusive). Relative to the Cu content, the surface N concentration (~0.7 at%) was unexpectedly high.

The N 1s spectrum, determined at the outset, comprised a major component at 400.0 eV accounting for 80% of the intensity, with the remaining 20% near 402 eV. In the spectrum determined at the end, the 400.0 eV component accounted for 85% of the intensity, with the other 15% at ~401.7 eV. Minor (~7%) desorption of N in the intervening period was evident, and essentially all of that loss was N with the higher 1s binding energy, implying that this component was more likely to have arisen from protonated hydroxamate N in co-adsorbed hydroxamic acid than from metal hydroxamate. The retention of some co-adsorbed hydroxamic acid would not be unreasonable given the relatively low pH of flotation test T9. The principal N 1s component at 400.0 eV is consistent with the presence of Cu hydroxamate.

Potassium was quite evident (0.25 at%) at the surface of the particles, and it is possible that the source of at least some of that K could have been the KH(hydroxamate)<sub>2</sub> collector. It should be noted that when single-piece mineral specimens are rinsed with water following conditioning in potassium hydroxamate solution, residual K is usually not present.

Approximately 7% of the C 1s intensity (equivalent to ~1 at% at the surface) would have arisen from carbonate, most probably from malachite in the predominantly chrysocolla ore. The Cu 2p spectrum was largely characteristic of that observed for chrysocolla, including the obvious, but unresolved component near 933.4 eV. That low binding energy component can be assigned to Cu<sup>I</sup> that has been reduced from Cu<sup>II</sup> by secondary electrons, in association with water loss from the chrysocolla structure to the UHV of the spectrometer, rather than Cu<sup>I</sup> oxide in the unaltered chrysocolla (Parker et al., 2011). However, the Cu 2p final state satellite structure was consistent with the presence of Cu hydroxamate at the surface of the chrysocolla and/or the presence of some malachite in the concentrate.

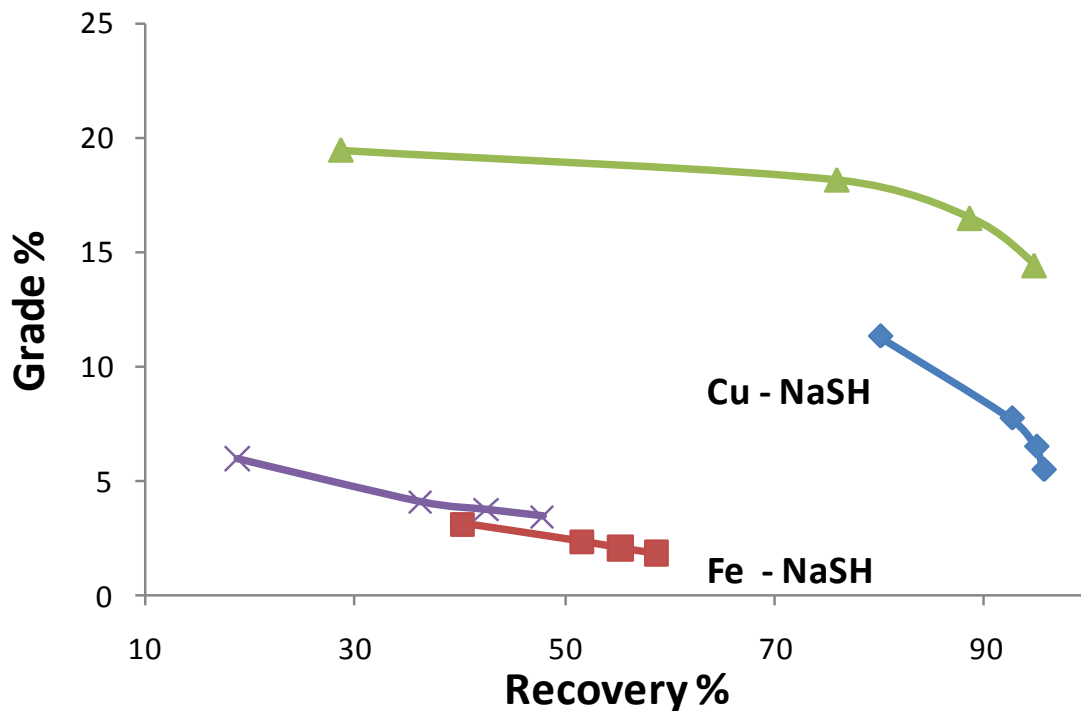
**Sample collected at pH 10, mixed oxide copper sand flotation, 400 g/t AM2 and 20 g/t IF50.**

The elemental composition estimated by XPS of this stage 1 concentrate was comparable with that for the chrysocolla + sand sample. Minor differences included slightly lower concentrations for Cu, Al and Fe, and slightly higher values for Ca and K. For this concentrate, the N 1s spectrum consisted essentially of one component at 400.0 eV. The absence of any co-adsorbed hydroxamic acid can be rationalised because the flotation had been carried out at pH 10. The Cu 2p spectrum was largely similar to that for chrysocolla, including the Cu<sup>I</sup> component near 933.4 eV, with a superimposed contribution from Cu hydroxamate and/or malachite and azurite. The carbonate peak in the C 1s spectrum was more intense, as expected given the presence of the basic Cu carbonates in the ore floated.

**Sulfiding conditions**

A combination of NaSH and AM2 was also tested in the stirred flotation cell in order to investigate the flotation response of chrysocolla in the presence of sulfiding chemicals. A single dose of 200 g/t of NaSH was added to the flotation cell before adding the first dose of AM2 in a four stage sequential flotation test.





**Fig. 12.** Effect of added NaSH to the grade and recovery of chrysocolla concentrate pH 10, sequential addition of AM2.

The combination of NaSH and AM2 addition produced a 96.6% copper recovery and 62.1% iron recovery compared to the AM2 only addition yield of 95.3% Cu and 52.7% Fe. The major effect of added NaSH was a substantial decrease in the concentrate grade (for both Cu and Fe) and a significant increase in the total iron recovery of the collected concentrate.

### **pH - Eh measurements**

The stirred bench scale flotation cell was monitored for pH and the potential measured at a platinum electrode (Pt vs saturated calomel electrode, commonly but incorrectly referred to as Eh) during experiments undertaken collecting the chrysocolla concentrate. The Pt electrode potential was observed to exhibit a non-linear change near pH 9 in these experiments. The sand \ chrysocolla (\ magnetite) system being investigated was not expected to deviate from a linear potential pH dependence (59.1 mV / pH unit) determined by the

reduction of oxygen on the Pt surface of the monitoring electrode.

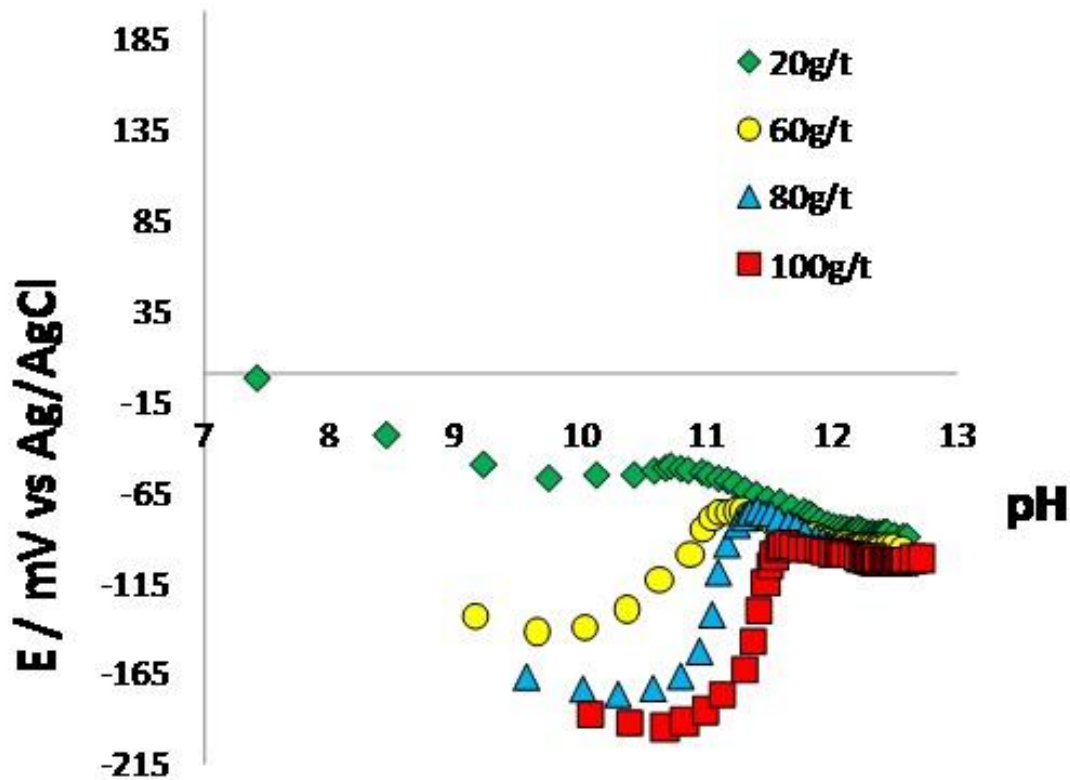


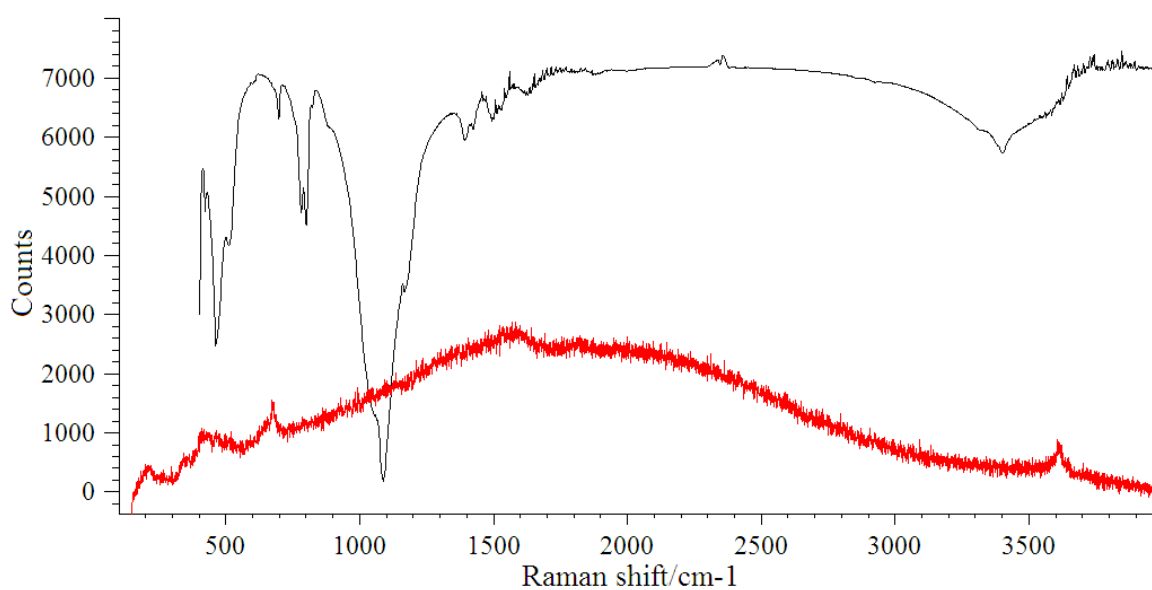
Fig. 13. Pt rest potential vs pH at various levels of AM2 in chrysocolla sand slurry titrated with 0.178 M KOH.

The nature of this deviation was investigated through monitoring Pt electrode potential changes during titration of chrysocolla/sand/hydroxamate slurry with KOH. The non linear potential pH dependence was observed to be dependent on the dose rate of AM2. In Fig. 13 we present the Pt electrode potential vs pH dependences observed from a dose of 20 g/t to 100g/t for a 30% w/w slurry of 0.8% copper as chrysocolla in sand.

It is possible that we are observing an interaction between iron and the n-octanohydroxamate at the Pt electrode, and that this is responsible for observed pH dependence deviation of the rest potential of the Pt electrode from the Nernstian slope expected for the  $O_2/H_2O$  couple (59.1 mV).

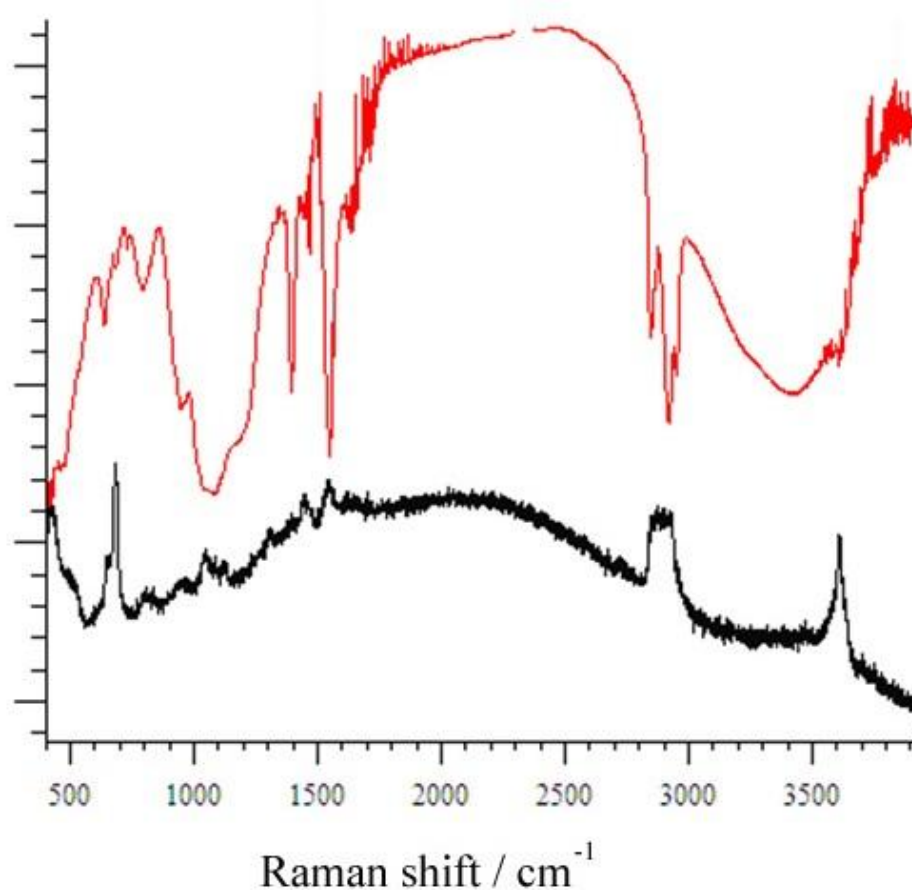
### Vibrational spectroscopy

Raman and FT-IR spectroscopy can be used to identify the hydroxamate species present in or on the chrysocolla particles, provided the quantity present is sufficient. In Fig. 14 we present the Raman spectrum from one particle and FT-IR spectra obtained from the ground chrysocolla sample.



**Fig. 14** spectra from ground chrysocolla in KBr (FT-IR) (top) and a single particle (Raman). The spectral features observed are described in Parker et al. (2011). Inspection of the concentrate samples after drying and weighing for the determination of grades and recoveries revealed that there was insufficient hydroxamate concentration present on the sample to yield spectra with reliable data. However, samples investigated for Eh pH studies did give good quality spectral data. In Fig. 15 we present the FT-IR and Raman spectra obtained from

ground chrysocolla exposed to 1,200 g/t AM2 for 2 h in a non stirred solution at pH 10, followed by washing with DDI water and air dried. These spectra demonstrate that the AM2 has formed copper hydroxamate with the chrysocolla sample. There is no hydroxamic acid, potassium hydrogen hydroxamate or iron hydroxamate observable in the sample by these vibrational spectroscopy techniques, a result that shows that the pores of the chrysocolla do not adsorb substantial quantities of hydroxamate that is not copper hydroxamate. The signal to noise and intensity of the vibrational spectra obtained was consistent with the formation of bulk copper hydroxamate. Vibrational spectroscopy is not surface sensitive, and could be sampling hydroxamate up to a micron below the surface of the sample.



**Fig. 15** spectra from ground chrysocolla in KBr (FT-IR) (top) and a single particle (Raman), after exposure to AM2 at pH 10.

## CONCLUSIONS

The bench scale flotation of Clifton chrysocolla / sand mixtures with AM2 hydroxamate collector using IF50 frother has yielded copper recoveries of over 97% and copper grades that varied from close to the value measured for the bulk chrysocolla in the first flotation collection, to grades closer to half that value after a fourth collection. Copper recovery was only partially improved by the sequential additions of collector compared to a single dose while the grade achieved was slightly lower. Increased residence time of the collector in the pulp prior to flotation substantially degraded the recovery and lowered the grades collected. Magnetite was present as a gangue mineral in both the Clifton chrysocolla and Gosford sand used in the flotation experiments. The iron was collected at recoveries of up to 70%, at grades of less than 7% . The theoretical grade of pure magnetite is 72.4%, so the flotation of magnetite, does not achieve the relative grade levels observed for the chrysocolla.

XPS investigation of the first chrysocolla concentrate fraction collected at pH 6.5 gave a reduced copper concentration (~ 5.5 at%) at the surface of a particulate specimen compared to the value measured from abraded surface of a sample prior to processing (~ 14 at%). The measured surface composition of copper for the collected concentrate would be reduced due to any overlaying hydroxamate species, but the high Si concentration would indicate that the surface might have been leached of copper. The area sampled (0.5 mm) during XPS analysis also could have contained silica gangue material. The surface nitrogen 1s spectrum was consistent with copper hydroxamate contributing 85% of the signal with 15% attributable to hydroxamic acid. The value for the N 1s concentration was high when the surface copper composition was considered.

Investigation of a mixed carbonate / silicate / sand sample yielded higher grades and a faster

Cu recovery which would be expected from the higher initial copper grade attributable to the azurite and malachite. The XPS investigation found that for this sample collected at pH 10, the hydroxamate was present on the surface in a form consistent with copper n-octanohydroxamate, though significant levels of potassium were detected. Carbon (from carbonate) and associated copper were observed from the XPS data.

Vibrational spectra obtained from chrysocolla particles exhibited formation of copper hydroxamate following exposure to AM2 under flotation conditions, but no hydroxamic acid or AM2 like hydroxamate species were observed.

## **ACKNOWLEDGEMENTS**

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