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Bench-scale flotation of chrysocolla with n-octanohydroxamate

G.A. Hope [a,*], A. Numprasanthai [a], A.N. Buckley [b], G.K. Parker [a], G. Sheldon [c]

[a] Queensland Micro- and Nanotechnology Centre, Griffith University, Nathan, QLD 4111, Australia
[b] School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia
[c] AMML, West Gosford, NSW 2250, Australia

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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 n-octanohydroxamate with chrysocolla and malachite surfaces. The flotation response of a single mineral chrysocolla–quartz sand sample and mixed chrysocolla–malachite–quartz sand sample using n-octanohydroxamate collector has been investigated. Recoveries of 95% were achieved in bench-scale flotation testing, with the best Cu grades achieved at pH > 9. Long conditioning times adversely affected flotation performance. Moderate recovery of impurity minerals in the mineral and sand was also observed.

1. Introduction

Chrysocolla forms a large potential copper resource that has not been concentrated due to difficulties associated with floating ores containing this mineral. The flotation of this oxide copper mineral is an area of considerable interest to miners and processors where acid leaching is not economic, but disparities 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 with n-octanohydroxamate, largely based on the results obtained from Hallimond tube experiments with some contact angle data (Aplan and Fuerstenau, 1984; Barbaro et al., 1997; Fuerstenau et al., 2000; Fuerstenau and Pradip, 1984; Herrera-Urbina et al., 2010; Peterson et al., 1965). Unfortunately, these laboratory studies have not been translated into practice. The nature of the chrysocolla structure, porosity and properties have been discussed by Parker et al. (2012).

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 μm 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. The same bench-scale flotation cell has been used previously 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 bench-scale flotation testing of a chrysocolla–sand mixture as a function of copper content, pH, collector and frother concentrations, conditioning time, NaSH addition or ammonium hydroxide addition. The nature of the collector–mineral interaction is discussed and the role of the solution potential measured at a platinum electrode is considered.

2. Experimental methods

2.1. Chemicals and materials

The chrysocolla sample ($Cu_{2-x}Al_x(OH)_4H_{2-x}Si_2O_5{\cdot}nH_2O$, with $x < 1$, typical ww%; Si, 15.2; Cu, 34.4; Al, 1.4; Ca, 0.5; Mg, 0.2 (RRUFF, 2011)) used in the flotation studies originated from Clifton, Arizona. The colour varied from dark blue green to bluish green with some isolated brown impurity visible to the eye. Natural malachite and azurite samples were obtained from the Democratic Republic of Congo and Canada. The flotation collectors, potassium hydrogen n-octanohydroxamate (AM28), $(C_8H_{17}O_2N)_2$ (H,K) and the commercial variant, AM2 (~25% $C_8H_{17}O_2N$ and 25% $C_{10}H_{21}O_2N$ (H,K), ~50% water and a minor amount of potassium n-octanoate) were provided by Axis House. Frothers, either methyl isobutyl carbinol (MIBC) or IF50 (from Chemicals and Mining Services Pty Ltd.), were used for the 2.5 L stirred flotation cell experiments. The pH was raised when required with ~1 M NaOH solution. Selected tests were also run with the addition of potassium or ammonium hydroxide. Sodium hydrosulfide hydrate (NaSH), (ACROS Organics) was used to investigate sulfidisation/hydroxamate synergies during flotation plant testing. Flotation in the 2.5 L stirred cell was undertaken using tap water and compressed air.

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* Corresponding author. Tel.: +61 7 373 57550; fax: +61 7 373 57773.
E-mail address: g.hope@griffith.edu.au (G.A. Hope).

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A 5 kg sealed stainless steel laboratory rod mill manufactured by ESSA Australia, model RM 250 × 300, with 10 stainless steel rods was used to grind minerals, ore and sand samples. Chrysocolla was dry ground to approximately 100 μm particle size, while malachite ore and the quartz sand samples were wet ground to the same approximate particle size. Particle sizes were measured with a Mastersizer X from Malvern. Sand samples were dried prior to mixing with 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.

2.2. Analytical techniques

2.2.1. Vibrational spectroscopy

Raman spectra were acquired with a Renishaw System InVia spectrometer. The excitation wavelength was 632.8 nm from a HeNe laser. Raman spectra were calibrated using the 520 cm^{-1} silicon band. Spectral manipulations such as baseline adjustment, smoothing and normalisation were performed by using Renishaw WiRE 3.2 software. Fourier transform infrared (FTIR) 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^{-1} with 0.5 cm^{-1} 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.

2.2.2. Electroanalytical techniques

pH and E_H were recorded in flotation testing and also in titrations to investigate the interaction of the flotation reagent with the sample. E_H measurements during titrations were undertaken at a Pt wire (*vs.* a Ag/AgCl reference electrode) and monitored using a Pine WaveNow USB potentiostat interfaced with a PC running Pine Aftermath software V1.2.4361. All E_H values are reported against a Ag/AgCl (3.0 M KCl) reference electrode.

2.2.3. 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 h then fine ground for XRF measurement using Thermo Scientific analysis software.

2.2.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectra were collected from particulate mineral concentrate specimens embedded in freshly exposed indium foil surfaces. 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 Kα 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 5×10^{-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 1*s* photoelectrons. The possibility of beam damage by the flood gun 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.

2.2.5. Scanning electron microscopy

An FEI Quanta 200 Environmental 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 μm and 3 μm diamond paste laps followed by sonication for 10 min in de-ionised 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.

2.2.6. Atomic absorption spectroscopy

An atomic absorption spectrometer (AAS) Varian spectrAA-10 with a Cu/Fe cathode lamp was used to measure the Cu and Fe content of the Canadian malachite ore and concentrates. Samples were prepared by digesting the samples in aqua regia, followed by fuming to dryness, then adding excess hydrochloric acid and diluting with DDI water as required.

2.3. Flotation experiments

Flotation experiments were conducted using a 2.5 L stirred flotation cell. The target flotation charge of 84 g or 42 g of chrysocolla, mixed with ∼1 kg of sand, was slurried with 1 L of water and transferred to the flotation cell. The slurry was stirred at 660 rpm for 2 min. The solids content in the cell was then adjusted to 33% by addition of approximately 1 L of water and stirred at 500 rpm for 2 min. The pH was adjusted to the desired value with ∼1 M NaOH or ∼1 M HCl 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 min. 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.

3. Results and discussion

The surface topography of the ground chrysocolla and sand samples was investigated using SEM, prior to flotation. Images of the ground chrysocolla sample are presented in Fig. 1. The particles exhibited rough surfaces and edges with numerous surface protrusions.

The particle roughness appeared to be independent of the particle size, with 100 μm particles having similar surface roughness to the <20 μm particles. EDX analysis of a chrysocolla particle gave the following composition as ww%: O; 39.95, Cu; 38.23, Si; 20.51, Al; 0.58, Fe; 0.84, Ca; 0.28. EDX analysis of an iron-rich particle observed in the chrysocolla matrix gave a stoichiometry of Fe_3O_4. Treatment of the ground chrysocolla sample 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.

The sand was non-porous with liberated iron oxide particles that exhibited magnetism. The actual particle size distribution achieved by grinding was determined using the Mastersizer software and is presented in Fig. 3. The sand particle size distribution was considerably narrower than that of the chrysocolla: whereas