Minerals Engineering 36–38 (2012) 81–90

Contents lists available at SciVerse ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

The interaction of the flotation reagent, *n*-octanohydroxamate, with sulfide minerals

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ARTICLE INFO

Article history:
Available online 4 April 2012

Keywords:
Mineral processing
Flotation collectors
Sulfide ores

ABSTRACT

We have utilized electrochemistry, vibrational spectroscopy and X-ray photoelectron spectroscopy to investigate the interaction of KH *n*-octanohydroxamate with the sulfide minerals chalcocite, pyrite, chalcopyrite, covellite and bornite. Each of these techniques showed that a multilayer of cupric hydroxamate formed on chalcocite, bornite and chalcopyrite conditioned in the hydroxamate collector, and visual inspection revealed that this multilayer had rendered the mineral hydrophobic. Hydroxamate adsorbed to Fe atoms, co-adsorbed hydroxamic acid and some ferric hydroxamate were also observed on the ternary sulfides. Only limited adsorption of collector was observed on pyrite fracture surfaces, unlike abraded surfaces which were rendered hydrophobic by significant adsorption. These results have implications in the use of hydroxamates for the flotation of mixed sulfide–oxide and transitional ores, including the possible collection of gangue minerals in the concentrate.

1. Introduction

Declining orebody quality means that low-grade and complex ores are increasingly being considered for recovery of their valuable metals. Such ores, including low-grade oxide ores, transitional ores and tarnished former tailings or waste rock will need further beneficiation to make them amenable to smelting or hydrometallurgical processing. Flotation with controlled potential sulfidization is one approach that is used, but chemical control can be difficult and costly. Hydroxamates were proposed by Pöpperle (1940) as collectors for both sulfide and oxide ores, but subsequent studies have yielded equivocal results for the hydroxamate flotation of sulfide minerals. Another approach would be to use mixed oxide–sulfide collector systems (Lee et al., 2009). It is, therefore, important to characterize the interaction of sulfide mineral surfaces with hydroxamate collectors.

The interaction of *n*-octanohydroxamate with some sulfide minerals has been reported. Notably, pyrite was floated along with chrysocolla, the target mineral, with hydroxamate collector (Fuerstenau et al., 1967), although another study showed minimal recovery of pyrite with hydroxamate between pH 5 and 10.5 (Ackerman et al., 1999). Electrochemical studies (Hanson and Fuerstenau, 1987, 1991) have demonstrated the feasibility for *n*-octanohydroxamate to be a collector for chalcocite and oxidized copper ores, but Fuerstenau et al. (2000) reported that the copper sulfide minerals chalcopyrite and covellite were not rendered hydrophobic by hydroxamate. Elsewhere 'oxidized' chalcopyrite has been reported to float with hydroxamate (Das and Pradip, 1987), with moderate recoveries reported for chalcopyrite, covellite and bornite compared to high recovery (94%) for chalcocite at pH 8.5 (Ackerman et al., 1999). Under the same conditions the recovery of malachite was only 60%, suggesting the collector concentration used was probably too low.

In order to elucidate possible reasons for the conflicting findings of previous studies, there is a need to investigate the surface interactions between sulfide minerals and *n*-octanohydroxamate at concentrations comparable to those used in practice. This is of significance to the potential application of hydroxamate collectors, either alone or in conjunction with thiol collectors, for at least partly oxidized sulfide ores. To this end we have investigated the interaction of hydroxamate with air-exposed sulfide mineral surfaces at conditioning times relevant to flotation, applying cyclic voltammetry, X-ray photoelectron spectroscopy (XPS) and surface-enhanced Raman scattering (SERS) spectroscopy. We also report characterization of product multilayers via Raman spectroscopy. This information should be of assistance not only in collector selection, but also in flow-sheet optimization when hydroxamate collectors are employed.

2. Experimental

2.1. Minerals and reagents

Electrolyte and reagent solutions were made with Analytical Reagent (AR)-grade chemicals and doubly de-ionized (DDI) water. Potassium hydrogen *n*-octanohydroxamate was supplied by Axis House, a company which markets this compound within its AM2

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http://dx.doi.org/10.1016/j.mineng.2012.02.017

flotation collector formulation. The potassium compound of *n*-octanohydroxamate has been shown to be the acid salt (Hope et al., 2010a), although previous authors refer to the compound they investigated as potassium *n*-octanohydroxamate. The potassium acid salt was recrystallised from methanol and dried in air. The *n*-octanohydroxamic acid was precipitated by treating a solution of the potassium salt dissolved in hot methanol with sulfuric acid, chilling and adding DDI water: the precipitate was filtered and washed with DDI water and dried in air. The sample was then recrystallised from ethyl acetate and dried in air before investigation. Copper *n*-octanohydroxamate was synthesised using a two-phase technique; copper acetate was dissolved in water and the hydroxamic acid was dissolved in diethyl ether. The hydroxamic acid phase was carefully added to the aqueous phase held in a test tube and the tube sealed. The solid copper salt formed at the interface between the aqueous and organic phases. The resultant solid was collected by filtration, washed with 0.1 M KOH to remove residual hydroxamic acid, rinsed with DDI water and dried in air. Ferric *n*-octanohydroxamate was synthesised by dissolving ferric chloride in water and mixing with *n*-octanohydroxamic acid dissolved in ethanol: potassium carbonate was added to the ethanol/water mixture until a precipitate formed. The precipitate was recrystallised from ethanol:water (1:1).

The mineral specimens investigated were bornite from the Central African Copperbelt, chalcopyrite from Messina, Transvaal, pyrite from China and Spain, and, chalcocite and covellite from Butte, Montana. The minerals were conditioned with hydroxamate solutions after fracture or after abrading with 600 or 1200 grit SiC paper and rinsing/ultrasonicating with DDI water. Unless otherwise stated, specimens were treated with a freshly-prepared, nominally saturated aqueous solution (~0.02 M) of pure potassium hydrogen *n*-octanohydroxamate at its unadjusted pH (~9.5) in air at ambient temperature. This pH was selected as it is near the middle of the range used in practice for this collector with oxide copper ores (Hughes et al., 2007; Lee et al., 2009). The relatively high concentration was used on the basis that in practice, up to 1200 g/t of hydroxamate collector is utilized (Lee et al., 2009).

2.2. Raman spectroscopy

Raman studies were conducted on a Renishaw System 100 or InVia Raman spectrometer. The System 100 and InVia spectrometers used 632.8 nm red excitation from a HeNe laser or 514.5 nm irradiation from a Ar ion laser. The scattered light was detected with Peltier-cooled CCD detectors with spectral resolution ~2 cm^{-1}. In the case of the System 100, the laser and scattered radiation were focused through the spectrometer objective, an ultra long working distance 20× Olympus Plan Fl lens (NA = 0.4), while on the InVia spectrometer the laser and scattered light were usually focused through a 50× Leica N Plan lens (NA = 0.75). Raman spectra were calibrated using the 520 cm^{-1} silicon band. Spectral manipulations such as baseline adjustment, smoothing and normalization were performed either with the Renishaw WiRE 3.2 software or with GRAMS32AI software (Galactic Industries, Salem, NH, USA).

2.3. Voltammetry

Sulfide mineral electrodes were prepared for electrochemical experiments by attaching copper wire to the mineral specimens with silver-loaded epoxy, encasing the copper wire in Teflon shrink tubing and covering the join with epoxy resin. Potential control of the conventional three electrode cell (sulfide mineral working electrode, Ag/AgCl reference electrode and Pt counter electrode) was maintained with a Pine Wavenow USB potentiostat interfaced with a PC running Pine Aftermath software V1.2.4361. Electrolytes were not sparged prior to voltammetric scanning. All potentials are reported against the Ag/AgCl (3.0 M KCl) reference electrode.

2.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectra were collected from a surface of single piece mineral specimens of size approximately 5 mm × 5 mm × 1 mm. There are numerous advantages to be gained by the characterization of such surfaces in flotation-related research (Buckley, 2010), most importantly the facility of rinsing any weakly adsorbed collector from the surface, and the ability to determine by visual examination whether that surface had been rendered hydrophobic by interaction with the collector. Each fracture surface, or surface abraded until relatively smooth to the unaided eye, was rinsed with water after conditioning in collector solution and before characterization by XPS at ambient temperature.

XPS data were obtained on an ESCALAB 250Xi spectrometer using monochromatised Al K_α 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. In most cases, photoelectron spectra were obtained initially without the use of a flood gun, in which case the outermost strata of any adsorbed multilayer would be expected to experience some charge-shifting, and subsequently under the influence of flood gun electrons when the semi-conducting sulfide mineral substrate would remain largely unaffected, but adsorbed layers would be shifted to lower binding energy to an extent that would depend on the effectiveness of their electrical contact with the substrate. In those cases, binding energies were referenced to 285.0 eV for the hydrocarbon C 1*s* photoelectrons. Whenever the flood gun was used, the possibility of beam damage by the low energy electrons was monitored. However, in all cases, spectra were obtained as quickly as possible, at the expense of signal-to-noise, in order to minimize any damage arising from the secondary electrons associated with the X-ray photoemission.

3. Results

3.1. Electrochemical studies

We have reported voltammograms from a bornite electrode in hydroxamate solutions (Fig. 1a) previously (Parker et al., 2012). As *n*-octanohydroxamate concentrations exceeded 1 mM the Cu^{II} oxide reduction process at ~−0.1 V is decreased as cupric *n*-octanohydroxamate had been produced in the preceding forward-going scan. There are also some changes to the iron removal and re-insertion potentials to the sulfide lattice (Parker et al., 2012).

Cyclic voltammograms from a chalcocite electrode in tetraborate (Fig. 1b) were consistent with previously published voltammograms in the absence of the collector. Anodic current commenced flowing at ~−0.1 V, with the anodic process resulting in the formation of intermediate non-stoichiometric copper sulfide phases (Hanson and Fuerstenau, 1987; Parker et al., 2003) and cupric hydroxide. This reaction is reversed in the negative-going scan. The addition of hydroxamate affects the redox behavior of chalcocite by decreasing the peak anodic current and shifting the onset of anodic current to more negative values, which has been reported previously (Hanson and Fuerstenau, 1987). At sufficiently high concentrations the oxidation and reduction of the sulfide phases becomes inhibited, indicating multilayer formation of cupric *n*-octanohydroxamate.