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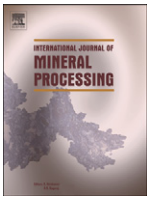

Interaction of cuprite with dialkyl dithiophosphates

Alan N. Buckley [a],*, Siew Wei Goh [a], William M. Skinner [b], Ronald Woods [c], Liang-Jen Fan [d]

[a] *School of Chemistry, The University of New South Wales, Sydney, NSW 2052, Australia*
[b] *Ian Wark Research Institute, ARC Special Research Centre for Particle and Material Interfaces, University of South Australia, Mawson Lakes, SA 5095, Australia*
[c] *School of Biomolecular and Physical Sciences, Griffith University, Nathan, Qld 4111, Australia*
[d] *National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan*

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ABSTRACT

The interaction of freshly abraded surfaces of cuprite, Cu_2O, with neutral or mildly alkaline aqueous solutions of diethyl or di-*n*-butyl dithiophosphate (DTP) has been investigated by means of conventional and synchrotron X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure spectroscopy. It was confirmed that DTP adsorbs readily on Cu atoms in the surface layer of the mineral treated with solutions of the collector at pH values near 7 and 9 in the presence of air, and renders the surface hydrophobic. When cuprite is treated with relatively high concentrations of DTP for sufficiently long periods, collector can also be adsorbed as CuDTP, but the coverage does not exceed a thin layer of CuDTP on the adsorbed DTP monolayer, unlike the situation with Cu metal or chalcocite where a thick multilayer can be formed.

1. Introduction

Cuprite, nominally Cu_2O, is one of the well-defined minerals found in the oxidised zones of copper sulfide deposits. Its behaviour as fine particles during the concentration by flotation of a mixed copper sulfide and oxide ore from near an oxidised zone is consequently of commercial importance. Therefore, in research designed to optimise the flotation of these minerals, the interaction of cuprite with thiol flotation collectors, such as ethyl xanthate (EX), diethyl or di-*n*-butyl dithiophosphate (EDTP or BDTP) and 2-mercaptobenzothiazole (MBT), is of considerable interest yet not thoroughly investigated.

In practice, most oxide copper minerals do not respond well to the thiol collectors normally used in copper sulfide flotation without prior sulfidisation with sodium or ammonium sulfide (Hanson and Fuerstenau, 1991; Lee et al., 1998). Typically, mixed copper sulfide and oxide ores are treated by flotation of the sulfide minerals before sulfidisation and subsequent flotation of the oxides (Kelsall, 1961). However, cuprite has been shown in laboratory experiments to be readily floatable with EX at pH 11 within the pulp potential range of −0.4 to 0.29 V (vs SHE) (Heyes and Trahar, 1979; Senior et al., 2006). Only low concentrations of EX were required, similar to those used for chalcocite (Cu_2S). At potentials higher than 0.29 V, flotation recovery of cuprite was found to be inhibited as it was for chalcocite (Cu_2S) and, for both minerals, this behaviour was assigned to oxidation of copper xanthate to CuO and dixanthogen. It was pointed out by Heyes and Trahar (1979) that, at pH 11, the cuprite surface would have been reduced to copper metal below −0.18 V. Copper metal is known to interact with xanthate at such potentials to form a chemisorbed xanthate monolayer (Woods, 1996), and this would explain the observed floatability of cuprite at low potentials and the apparent absence of a lower potential edge for flotation of this mineral. Curiously, at a pulp potential near zero, flotation recovery of cuprite with EX was low at pH values of ≤9 (Heyes and Trahar, 1979). Those authors concluded that their data were “insufficient to permit any useful conclusions to be drawn” regarding the influence of pH, but pointed out that “cuprite only floated at pH values above the zero point of charge” which they assumed to be near pH 9 on the basis of the work of Attia (1975). By contrast, it had been reported that whereas sulfides, cuprite and native copper all float with xanthates without sulfidisation, tenorite (CuO) floats only poorly (Rey, 1954), notwithstanding the fact that CuO is also a p-type semiconductor with a band gap smaller than that of Cu_2O (Ghijsen et al., 1988; Pierson et al., 2005).

Cuprous oxide is thermodynamically unstable relative to cupric oxide in the presence of oxygen and water, consequently a surface layer of a Cu^{II}–O species might be expected to form when a fresh cuprite surface is exposed to air under ambient conditions or in aqueous environments. Indeed, an investigation of mineral cuprite fracture surfaces by means of synchrotron X-ray photoelectron spectroscopy (SXPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy established that about a monolayer of cupric hydroxide was formed at the surface after exposure to air for 1 h (Harmer et al., 2009). Thus when cuprite particles are treated with a flotation collector, the initial interaction is expected to occur at a surface altered by oxidation and hydroxylation, and hence to also be of relevance to the flotation of Cu^{II} oxide minerals. Moreover, the way in which thiol collectors interact with cuprite is expected to have a strong bearing on the way in which those collectors interact with an oxidised copper sulfide mineral surface.

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* Corresponding author.
E-mail address: a.buckley@unsw.edu.au (A.N. Buckley).

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It is generally accepted that cuprite is normally copper-deficient to some extent (Shuey, 1975; Yoshimura et al., 1976; Ohyama et al., 1997), and it has been argued that the cation vacancies facilitate copper mobility (North and Pryor, 1970). Cuprite is a p-type semiconductor of band gap ~2 eV at ambient temperature (Weichman, 1960), and thus exhibits moderate electronic conductivity; reported values of ambient temperature resistivity for mineral cuprite have been 10^1–10^4 Ω m (Harvey, 1928; Shuey, 1975). Accordingly, it is possible that thiol collectors might chemisorb to the copper atoms in the outermost layer of the cuprite surface (which may be oxidised as noted above) in a manner analogous to the situation with chalcocite (Mielczarski and Minni, 1984; Richardson et al., 1984; Buckley and Woods, 1993) and copper metal. Furthermore, for DTP and copper metal or chalcocite, it has been established that at sufficiently high potentials and collector concentrations, multilayer copper dithiophosphate, CuDTP, can adsorb on top of the chemisorbed DTP monolayer (*e.g.*, Chander and Fuerstenau, 1975; Mielczarski and Minni, 1984; Buckley and Woods, 1993; Woods et al., 1993). Given the cation mobility and moderately high electronic conductivity of cuprite, if multilayer CuDTP were able to form as easily on that mineral as on chalcocite, then the presence of Cu oxides in oxidised sulfide ores could lead to higher than expected consumption of collector. Such ores often contain Cu^{II}–oxide minerals (*e.g.*, malachite), but there are chalcocite-rich ores in which cuprite is the principal oxide component.

In the research reported here, cuprite surfaces prepared by abrasion before and after treatment with DTP solutions at pH values of either 7 or 9 have been characterised by means of conventional XPS, SXPS and partial electron yield (PEY) NEXAFS spectroscopy to establish the extent of collector adsorption on the mineral surface. The emphasis was on relatively high DTP concentrations (10^{-2} or 10^{-3} mol dm^{-3}) and extended interaction times to establish whether multilayer adsorption occurred, but short interaction times were included to assess the rate of initial adsorption. No attempt was made to establish the precise conditions that would result in full monolayer coverage without any multilayer formation. Abraded rather than fracture surfaces were considered more representative of those for cuprite particles in a flotation pulp. The most common cleavage plane for cuprite is (111) therefore the outermost layer of a surface prepared by fracture would consist predominantly of O atoms, but a layer of incompletely-coordinated Cu atoms would be very close to the surface in a plane slightly below the plane containing the outermost O atoms. It is expected that other crystal planes such as {001} would also be exposed at the surface of cuprite that had been crushed during comminution. Some analogous DTP adsorption experiments on Cu metal were undertaken as a reference system for the formation of multilayer CuDTP. The abraded mineral and metal surfaces were sufficiently smooth to reveal hydrophobicity on emersion of the specimens from DTP solutions by the obvious non-wettability of the surface after, but not before, treatment with collector solution. This is one of the several advantages of using single piece mineral specimens in such research.

2. Experimental details

2.1. Cuprite mineral and DTP solutions

The cuprite used in the investigation was a massive, crystalline specimen from the Red Dome Mine, Chillagoe, Queensland, Australia. Bulk analysis of the mineral by ICP-MS confirmed the high purity of the sample investigated; no minor element was present at a concentration greater than 0.6 mg kg^{-1} and only a few had a concentration above 0.1 mg kg^{-1}.

The DTP used in the SXPS and X-ray absorption studies was potassium di-*n*-butyl DTP (BDTP), whereas that used in the conventional XPS measurements was potassium or ammonium diethyl DTP (EDTP). Establishing a pH of 9 was effected by dissolving the DTP in 0.05 mol dm^{-3} sodium tetraborate solution. No residual borate at surfaces treated with DTP at pH 9 and subsequently rinsed with water was detected by XPS. Because the possible formation of Cu thiolate multilayers was under investigation, treatment times were from 1 to 90 min in DTP solutions of concentration up to 10^{-2} mol dm^{-3}.

2.2. Spectroscopic measurements

The SXPS and NEXAFS spectroscopic measurements were carried out in the Australian Synchrotron Research Program (ASRP) soft X-ray spectroscopy end-station while connected to beam-line 24A at the NSRRC in Hsinchu or 14ID at the Australian Synchrotron (AS). BL24A is a bending magnet, wide range beam-line incorporating a grating monochromator. The synchrotron was operated in continuous top-up mode at a stored current of 300 mA. BL14ID is also a wide range, grating monochromator beam-line, but it has an elliptically polarising undulator source. The AS was operated in decay mode at a maximum stored current of 200 mA. The ASRP end-station, constructed by OmniVac and PreVac, is equipped with a SPECS Phoibos 150 electron energy analyser and an OmniVac UHV-compatible partial yield detector based on a multichannel plate behind retarding grids. Electron analyser pass energies of 10 or 20 eV and an electron take-off angle of ~54° were used for narrow range spectra. The pressure during surface characterisation was $<3\times10^{-10}$ torr. Conventional monochromatised Al K_α XPS measurements were carried out on a VG ESCALAB 220-iXL spectrometer with an analyser pass energy of 20 eV for narrow range spectra. An electron take-off angle of either 20° or 90° was used, the former value to enhance surface sensitivity and the latter to maximise the contribution from the mineral substrate underlying the adsorbed collector. Binding energies determined in this work are reported relative to a Cu $2p_{3/2}$ value of 932.6 eV for Cu metal, and binding energies from published studies have been quoted relative to a hydrocarbon C 1*s* binding energy of 285 eV. Only nominal photon energies (±0.4 eV) are usually delivered by synchrotron beam-lines, and the true photon energy for each spectrum should be established by a supporting measurement. The Cu $L_{2,3}$-edge NEXAFS spectra were determined together with the absorption current monitored concomitantly by a Cu metal mesh in the beam-line. During operation of the NEXAFS detector, negative grid potentials of 0.75 and 1.5 kV were used for Cu $L_{2,3}$-edge PEY and TFY spectra, respectively. The indirect determination of X-ray absorption by means of PEY provides NEXAFS spectra that are as surface sensitive as allowed by the kinetic energies of the Auger electrons corresponding to the absorption edge concerned. Thus the PEY mode surface sensitivity associated with Cu $L_{2,3}$-edge NEXAFS spectroscopy is that corresponding to the Cu LMM Auger electrons which have a maximum kinetic energy of ~920 eV.

2.3. Fitting of core photoelectron spectra

The CasaXPS (Version 2.3.5) software was used to fit photoelectron spectra. In almost all cases the background in narrow range spectra was linear. In agreement with the conclusion of Hesse et al. (2007), a Gaussian–Lorentzian sum SGL(p) with Lorentzian character ‘p’ of about 20 typically gave better fits on the low binding energy side than the more usual product, GL(p), used to approximate the Voigt profile.

3. Results

3.1. Spectroscopic data sought to establish collector coverage on cuprite

The presence of DTP adsorbed at the surface of cuprite would be revealed in conventional XPS by S 2*p*, P 2*p*, O 1*s* and C 1*s* photoelectron peaks if each was at the expected binding energy and relative intensity, but differentiating monolayer and multilayer coverage would not be straightforward. Previous XPS investigations