Reactions at Base Metal Sulfide Surfaces

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Base metals such as Cu, Pb, Ni and Zn are produced from sulfide ores. Individual metal sulfides are separated from each other and from unwanted minerals in complex ores by means of froth flotation, a process that depends on the relative hydrophobicity, and hence surface chemical composition, of the mineral particles. Typically, hydrophobicity is imparted to one or more of the sulfides in an ore by the selective adsorption of a sub-monolayer coverage of a thiol surfactant or 'collector'. Therefore the surface states formed at sulfide mineral fracture surfaces, the chemical composition of the surface layer altered by exposure to air, and the interaction with aqueous solutions of thiol collectors, are all important and have been studied intensively for many years. In such studies, surface characterisation has been effected largely by cyclic voltammetry and conventional XPS, but in recent years static SIMS, synchrotron XPS (SXPS) and to a lesser extent NEXAFS spectroscopy have been applied. Nevertheless, the interaction of collectors with sulfide minerals is still not fully understood.

In the work reported here, NEXAFS spectroscopy and SXPS have been used to complement XPS and SIMS data to investigate the interaction of the thiol collector 2-mercaptobenzothiazole (MBT) on abraded chalcocite (Cu2S) and galena (PbS) fracture surfaces. There have been previous NEXAFS studies of the interaction of MBT with very flat surfaces such as CdS wafers, but one objective of the present investigation was to determine whether abraded yet relatively smooth surfaces could be used instead. While some metal sulfides such as PbS cleave to produce crystal planes, others such as Cu2S fracture to leave surfaces that are too rough to allow angle-resolved NEXAFS information to be obtained.

It was found that conventional XPS was able to detect chemisorption of MBT on Cu2S and PbS from the S 2p component for the endocyclic S in MBT, but precise exocyclic S 2p binding energies could not be obtained because of the proximity of the S 2p contribution from the underlying mineral. XPS was also able to detect the onset of metal thiolate (multilayer) formation via the relevant metal X-ray excited Auger electron (Cu LMM) or core level photoelectron (Pb 4f) spectrum. Metal thiolate stoichiometry could be determined from a thick multilayer. Surface-optimised SXPS was able to provide precise chemisorbed MBT S 2p binding energies. Previously reported 2p3/2 binding energies for the exocyclic S in chemisorbed MBT have varied within a energy near 164 eV for the endocyclic S. The value for the exocyclic S on Cu2S was found to be 162.5 eV, and the value for PbS confirmed as 162.0 eV. Although in principle variable photon energy SXPS data are superior to variable electron take-off angle measurements wide range from 162.0 eV for a PbS substrate to 162.9 eV for CdS, compared with an essentially constant binding for deducing adsorbate orientation on irregular surfaces, obtaining this information for Cu2S was not straightforward because of the complex S 2p spectrum prior to MBT adsorption. Abrasion of the surface had given rise to an additional S 2p component which indicated that the surface had become S-rich.

NEXAFS spectra at the N and C K-edges were different for different photon beam angles of incidence for monolayer coverage on both Cu2S (Fig. 1) and PbS. The significantly different intensity of the π^* absorption peaks relative to the σ^* absorption for monolayer MBT on Cu2S revealed that adsorbate orientation can be determined even for an abraded (albeit relatively smooth) surface rather than a single atomic plane. For a largely complete monolayer on Cu2S, the MBT was found to be upright but tilted, whereas no preferred alignment was discernible for the corresponding multilayer. Cu L2,3-edge NEXAFS spectra are able to detect much lower surface concentrations of Cu(II) than Cu 2p photoelectron spectra, and some Cu(II) and hence Cu(MBT)2 was detected in MBT multilayers on Cu2S.

Static SIMS data provided strong evidence for the interaction of both N and exocyclic S with metal atoms in the substrate surface layer for Cu2S. Together with the NEXAFS data, the secondary ion spectra also revealed that the predominantly metal monothiolate multilayer on Cu2S included some metal dithiolate. For adsorption of MBT on CdS, a density functional theory investigation had shown that chemisorption should occur via both the N and exocyclic S atoms to adjacent Cd atoms in the CdS surface. However, no evidence was obtained in the present work to suggest that interaction of the MBT was with adjacent metal atoms in the Cu2S or PbS surface.

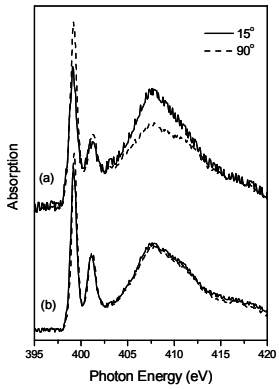

Figure 1. N K-edge spectra determined with X-ray beam incident at 90o or 15o for (a) monolayer and (b) multilayer MBT adsorbed on Cu2S.