A thermochemical study of thiol collector surface reactions on galena and chalcopyrite

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ABSTRACT

The mechanism whereby thiol collectors adsorb onto a mineral surface has been widely studied. Most of these studies examine the mineral surface at equilibrium state and, often, well above monolayer coverage. However, the formation of species at the mineral surface is a complex process that is both kinetically and thermodynamically controlled. In a typical industrial application, the dosage of collector will be around monolayer level. This study uses isothermal titration microcalorimetry to measure the heat evolved during the reaction of sodium ethyl xanthate (SEX) and sodium isobutyl dithiocarbamate (SIBDTC) and their mixtures with galena and chalcopyrite. The sensitivity of the instrument allows heats of reaction of sub-monolayer quantities of thiol collector to be measured.

The study found that the nature of the reaction between a collector and a mineral surface was dependent on the type of mineral and the type of collector. Proposals are made for the reactions based on previously reported results and the evidence from this investigation. It was found that when collectors reacted with mixtures of galena and chalcopyrite, the magnitude of the reaction was lower compared to that measured for the pure minerals alone. This may be due to galvanic interactions between the minerals, resulting in a passivating effect on one or both of the minerals.

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1. Introduction

Microcalorimetry is an extremely sensitive surface science tool that measures the heat evolved when a chemical reaction takes place. It has experienced limited use in a mineral processing application despite widespread applications in pharmaceutical, soil and environmental and catalysis research (e.g., Buckton (1995), Rong et al., (2007), Spiewak and Dumesic (1998)).

Maier and Dobias (1997) and Maier et al. (1997) performed work using galena, chalcocite and sphalerite and various different collectors. The results reported did not indicate large differences in the thermochemical behaviour of the collectors with galena and chalcocite at sub-monolayer coverage, but sphalerite behaved differently. This may have been expected since it is well known that sphalerite requires an activator in order to promote collector adsorption. Above monolayer dosages on galena, a second reaction was reported to occur which they attributed to the formation of dixanthogen even though Finkelstein and Poling (1977) proposed that "there can no longer be any doubt that a lead xanthate is the only product that can be formed... when xanthate reacts with (galena)". In a critical review of the literature, Finkelstein and Poling (1977) reported that the oxidation of the thiol to the dithiolate depended on the rest potential of the surface under the particular conditions and it was concluded that it was not possible to form dixanthogen on a galena surface in the presence of dissolved oxygen. Chalcopyrite, on the other hand, was proposed to catalyse the formation of dixanthogen, with the latter being considered the dominant surface species.

Since sulphide minerals are electron conductors, when two sulphide minerals come into contact with one another there will be an electrochemical interaction with a flow of electrons from the less cathodic mineral to a more cathodic mineral. The higher the rest potential of the mineral, the more relatively cathodic is that mineral (Nava and Gonzalez, 2006). In the case of chalcopyrite and galena, chalcopyrite has a higher rest potential than galena and thus, galena will be oxidised i.e. be the electron donor (Rao, 2004). These electrons will reduce dissolved oxygen to hydroxide according to Eq. (1). The hydroxide may result in the formation of metal hydroxides on the mineral surfaces.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{1}$$

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It has also been found that the galvanic interaction affected the floatability of the "noble" mineral, chalcopyrite, significantly without having much effect on the floatability of the "active" mineral, galena (Yelloji Rao and Natarajan, 1989). In a study of the galvanic interactions between pyrite and pyrrhotite, Moslemi et al. (2012) found that pyrite, having the highest rest potential, acted as the cathode. They noted that the surfaces of cathodes were passivated by oxide or hydroxide compounds, which are inherently hydrophilic, while the oxidation of the anode, pyrrhotite, resulted in a hydrophobic surface.

Majima (1969) found that galena, sphalerite and covellite oxidised 8–20 times faster when pyrite (acting as the cathode) was present. Building on this study, it was subsequently found that the dissolution of metal ions increased for the anodic mineral and decreased for the cathodic mineral (Sui et al., 1995). These dissolved ions transferred between two minerals in contact, but the larger proportion of Fe remained on the parent mineral (pyrite or pyrrhotite) while 50% or more of the Zn (from sphalerite) and Pb (from galena) transferred to pyrite.

The technique used in the present investigation has been previously reported in a study of the reaction between galena and a variety of collectors and collector mixtures (McFadzean and O'Connor, 2014). This paper extends those findings with a view to comparing the differences in the thermochemical behaviour between different sulphide minerals, viz. chalcopyrite and galena, with different thiol collectors. The enthalpy spectra obtained for each titration are also deconvoluted in order to attempt to distinguish between the different reactions occurring between the mineral surface and the collector.

2. Methodology

2.1. Mineral preparation

Pure galena and chalcopyrite mineral samples were obtained from Ward's Natural Science Establishment, Rochester, NY. Each sample was received in chunks of particles of up to 150 mm diameter. The mineral was hammered and then pulverised using a Sieb mill (Ferguson Industrial Group) for 15 s at a time. The pulverised material was then passed through a 38 μm sieve and the undersize was used for the experiments. Samples were stored under nitrogen at −30 °C to minimize mineral oxidation and were thawed and dried in a desiccator under nitrogen for at least 24 h prior to use. BET analysis showed the surface area of the −38 μm galena sample to be 0.2023 m^2/g and the chalcopyrite sample to be 0.596 m^2/g.

The presence of various surface species with respect to different sample preparation methods and the reaction of xanthate with these surface species has been the subject of much previous research (Fornasiero et al., 1994; O'Dea et al., 2001; Dunn, 1997; Fairthorne et al., 1997; Clarke et al., 1995). Fornasiero et al. (1994) found that, under oxidising conditions, the dissolution of lead and sulphide ions, and their subsequent precipitation onto the galena surface resulted in surface species of lead oxides such as $Pb(OH)_2$, PbS_2O_3, $PbSO_4$ and $PbCO_3$. In addition, XPS measurements found that the amount of oxygen on the galena surface was approximately the same for galena that was ground dry in air, compared to galena ground in an inert, wet environment and then conditioned with air at pH9 for two hours. Interestingly, there was a higher atomic percent of oxygen for samples that were conditioned at pH9 with nitrogen for two hours than for both the samples exposed to air. These findings point to the fact that the galena surface could be expected to be relatively oxidised at the pH's used in this study whether they were ground dry or wet. O'Dea et al. (2001) found that oxidised galena surfaces had relatively low concentrations of adsorbed xanthate compared to freshly cleaved

surfaces. They found no precipitated colloidal PbX_2 and theorised that the oxidised surface prevented dissolution of the lead ions. With respect to chalcopyrite oxidation, the copper and iron ions in chalcopyrite have been found to oxidise at different rates (Buckley et al., 2014; Goh et al., 2006) with the iron oxidising faster than the copper. Thus, it was found that iron oxide species were more predominant in chalcopyrite than copper oxide species.

It has been conceded in this and previous work (McFadzean and O'Connor, 2014) that the sulphide surfaces are likely oxidised. However, the extent of oxidation and the impact on the flotation performance remains debatable. In an extension of this work, which is being prepared for publication, the galena and chalcopyrite minerals were floated in a microfloation cell, with collectorless recoveries for galena of 97% and chalcopyrite of 65%. This shows that both minerals still have excellent natural hydrophobicity. Previous work on samples prepared in a similar manner (McFadzean and O'Connor, 2014) found large concentrations of lead ions in solution ($[Pb]_{max}$ of 9.13×10^{-5} mol/m^2), which suggests that the surface was not so oxidised that it prevented the dissolution of the lead ions, as found in the study by O'Dea et al. (2001). It should be borne in mind that the microcalorimetry samples were sonicated prior to placement in the calorimeter, which has been shown to remove oxidation products from mineral sulphide surfaces (Clarke et al., 1995). In addition, consideration should be given to the fact that different mineral processing plants with different circuit configurations would exhibit a range of degrees of oxidation of the sulphide minerals. Introduction of HPGR (and other dry grinding techniques) has made it more important and relevant to know the effects of dry grinding on flotation.

2.2. Reagents

The collectors used in this study were supplied by Senmin (Pty) Ltd. Table 1 lists the names, abbreviations, molecular structures, molecular weights and purities of the collectors. In all cases the sodium form of the thiol was used. R in SIBDTC refers to isobutyl and R′ refers to hydrogen. SEX was received in powder form. During manufacture, SIBDTC was stabilised in a high pH solution, which accounts for the low purity as shown in Table 1. Reagents were freshly prepared for each experiment using deionised water adjusted to pH 9 using NaOH.

2.3. Microcalorimetry

A TAM III isothermal titration microcalorimeter manufactured by TA Instruments was used in heat flow mode. The instrument has a liquid bath which is temperature controlled to within 0.0001 °C. The instrument was calibrated against a known electrical power input. Three constants are generated by this calibration: (a) the gain factor, which is the relative deviation from a temperature-dependent calibration constant and (b) two time constants (τ_1 and τ_2) that correct for the differences in heat flow monitored by the heat detector and the rate of heat actually produced by the sample due to the heat capacity and heat exchange coefficient of the microcalorimeter. In addition to these calibrations a test reaction was run using a ligand-binding reaction of Ba^{2+} with 18-crown-6 (1, 4, 7, 10, 13, 26-hexaoxacyclooctadecane). The enthalpy of reaction "tentatively" ascribed to this reaction is $\Delta H = -31.42$ kJ/mol (Wadso and Goldberg, 2001). In the present study the values obtained for two titrations were −32.10 kJ/mol and −33.38 kJ/mol, which yields an average of (−32.74 ± 0.91) kJ/mol.

All reactions were performed isothermally at 25 °C. 0.2 ± 0.0005 g of mineral were weighed out, respectively, into the stainless steel sample and reference ampoules. 0.7 mL of pH9