



Investigating the interaction of thiol collectors and collector mixtures with sulphide minerals using thermochemistry and microflotation



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ABSTRACT

In order to recover minerals by flotation, the sub-processes of collector adsorption onto the valuable minerals followed by bubble-particle attachment should occur efficiently. This paper investigates both of these sub-processes for various thiol collectors and their mixtures onto base metal sulfide minerals. The aim of the work was to investigate whether there is a correlation between the strength of the collector interaction with the mineral and the subsequent bubble-particle attachment. The collector-mineral interaction was measured experimentally using an isothermal titration calorimeter in order to determine the molar enthalpy of adsorption for each collector-mineral system. The bubble-particle attachment was measured using a microflotation device which essentially determines the hydrophobicity of the mineral. Sodium ethyl xanthate (SEX) and sodium diethyl dithiocarbamate (diethyl-DTC) and mixtures thereof were used as collectors with either single minerals or binary mixtures of pyrite and chalcopyrite, respectively. The adsorption enthalpies of the collectors were interpreted with reference to the chemical structure of the collector molecule and showed that the greater the positive inductive effect of the collector, which may be qualitatively related to their pK_a values, the greater their affinity for the mineral surface. When mixtures of collectors were used there was clear evidence of synergistic effects in enhanced enthalpies of interaction between collectors and the mineral surface and in increased microflotation recoveries. When mixtures of pyrite and chalcopyrite were used the flotation recovery and enthalpy of adsorption of SEX onto the individual pyrite particles in the mixture also increased substantially compared to the case of pyrite alone. Mechanisms are proposed to interpret these observations.

1. Introduction

In order to recover sulfide and platinum group minerals by flotation, the sub-processes of collector adsorption onto the valuable minerals followed by bubble-particle attachment should occur efficiently. As is well known, collectors react with mineral surfaces rendering them hydrophobic and resulting in the formation of stable particle-bubble agglomerates. However, it has been found that mixtures of collectors show better flotation performance than the single component collectors at the same dosage (e.g. Bradshaw and O'Connor, 1994; Mankaza et al., 2008; McFadzean et al., 2012). Various reasons have been offered for these improvements. Plaskin and Zaitseva (1960) postulated that more even surface coverage was achieved by collector mixtures due to “collector-specific” sites. Bagci et al. (2007) proposed a similar theory of strong and weak sites to account for improvements seen when using mixtures of xanthate and dithiophosphate. In a report on the synergistic interactions involving xanthates and dithiocarbamates Lotter and Bradshaw (2010) have suggested that DTC catalyses the formation

of dioxanthogen from xanthate. Since dioxanthogen is more hydrophobic than xanthate, this would result in enhanced flotation performance.

In attempting to explain the reasons for the enhanced flotation caused by the use of mixtures of collectors it is proposed in the present investigation that it is of critical importance that the dosage of the respective collectors be at sub-monolayer levels. This ensures that the mineral-collector interactions at the surface are not limited by the unavailability of surface sites. In studies reported in the literature the dosages were generally much greater than that required for pseudo-monolayer coverage and hence the system may be dominated by multilayer coverage of either collector. One of the most useful methods to investigate the interaction between the mineral surface and an adsorbing collector is to determine the enthalpy of adsorption by using microcalorimetry.

Most such calorimetric studies have focused on isolated sulfide minerals (e.g. Chen et al., 2013; Maier et al., 1997; McFadzean and O'Connor, 2014; Partyka et al., 1987). However, real sulphide ores processed in a flotation plant exist as an association of sulfide minerals.

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It is generally accepted that when two different sulfide minerals are brought into contact, a galvanic interaction is established with electrons flowing from the anodic to the cathodic mineral (Rao and Finch, 1988). This galvanic interaction has been shown to have a significant effect on collector adsorption and floatability of the pure minerals (Rao and Finch, 1988; Smart, 1991; Ekmekçi and Demirel, 1997; Mielczarski and Mielczarski, 2003; Peng et al., 2003; Owusu et al., 2014). It follows that the results obtained for single mineral systems have limited value in developing an understanding of the behaviour of real ores.

In the present study, microcalorimetry has been used to characterise the sub-process of collector adsorption by measuring the enthalpies of adsorption when pure collectors or collector mixtures interact with sulfide minerals. Chalcopyrite and pyrite were chosen as typical sulphide minerals. Microflotation was used to determine the floatability of the particles by measuring their recoveries in a microflotation system with a view to relating these recoveries to the enthalpies of adsorption when the minerals were contacted with sodium ethyl xanthate and diethyl-DTC. The combined effects of mixtures of the two collectors and the interaction of the collectors with mixed mineral systems on the enthalpy of adsorption and recovery were also investigated.

2. Experimental

2.1. Materials and reagents

Chalcopyrite and pyrite samples of up to 150 mm diameter were obtained from Ward's Natural Science Establishment NY. These were hammered and then pulverised for 15 s in a laboratory disk mill (Siebtechnik) to 100% passing 106 µm. The decision to dry-mill the mineral samples would have implications for the surface properties. It is known that wet-milling can influence the pulp potential through interactions between the milling media and the mineral. In addition, surface oxidation may be promoted in an aqueous medium (Wei and Sandenbergh (2007)). Thus, dry milling maintains the mineral surface in as unaltered fashion as possible before the addition of water and reagents. The material was then dry sieved into two fractions, viz. –38 µm for microcalorimetry experiments and 38–106 µm for microflotation tests. The material was split using a rotary splitter into 10 samples. All the samples were immediately stored under nitrogen at –30 °C to minimise oxidation of the samples. X-ray diffraction (XRD) was used to determine the mineralogical composition of the sulphide minerals and the results are shown in Table 1. XRD analysis showed that chalcopyrite and pyrite were relatively pure.

Thiol collectors used in this study were sodium ethyl xanthate (SEX) and diethyl-DTC. The samples were supplied by Senmin (Pty) Limited. SEX was supplied in pure powder form while diethyl-DTC was supplied in solution form at basic pH to stabilise the sample. Gas chromatography showed that there were no impurities present in the liquid diethyl-DTC.

All collector dosages were calculated based on active content and the total molar dosage was maintained constant at ~50% pseudo monolayer coverage (2.88×10^{-6} mol/m² of the available mineral

Table 1
X-ray diffraction results for chalcopyrite and pyrite.

Sample	Expected mineral	XRD results		Chemical formula
		Mineral	Composition (%)	
1	Chalcopyrite	Chalcopyrite	82.0	CuFeS ₂
		Pyrite	2.4	FeS ₂
		Bornite	7.8	Cu ₅ FeS ₄
		Quartz	7.8	SiO ₂
2	Pyrite	Pyrite	94.9	FeS ₂
		Chalcopyrite	1.5	CuFeS ₂
		Quartz	3.6	SiO ₂

Table 2
Surface area of the –38 µm and the +38–106 µm size fractions of all minerals.

Mineral	BET surface area (–38 µm) (m ² /g)	BET surface area (+38–106 µm) (m ² /g)
Chalcopyrite	0.6678	0.3795
Pyrite	0.6213	0.3946

surface area). The Brunauer–Emmett–Teller (BET) method was used to determine the surface areas of the mineral samples, both the –38 µm and the 38–106 µm size fractions. The BET surface areas of chalcopyrite and pyrite samples are shown in Table 2. Collector dosages were calculated based on the BET surface area of the mineral and assuming the cross-sectional area of the thiol head group to be 28.8 Å (Grano et al., 1997).

2.2. Microcalorimetry

A TAM III isothermal titration microcalorimeter manufactured by TA instruments was used in the heat flow mode to measure enthalpies of adsorption at 25 °C. Details of the equipment, calibration tests and equipment reproducibility are described in detail elsewhere (McFadzean and O'Connor, 2014; Taguta et al., 2017). Sodium hydroxide was used as a pH modifier to maintain pH at 9.2 to mimic typical conditions used in processing basic base mineral sulphide (BMS). A detailed experimental procedure for the microcalorimetric experiments has been described previously (Taguta et al., 2017). The heat of interaction between the mineral and the collector was obtained by subtracting the heat of blank experiment (heat of dilution of the collector into a solution with no mineral present) from the measured total heat of interaction. The heat of the mineral-collector interaction was calculated by integrating the area under the heat flow (W) vs time (s) plot which is the raw data output from the microcalorimeter. The heats of interaction were normalised by dividing by the number of moles dosed to obtain molar enthalpy of adsorption. Adsorption tests showed that the entire amount of collector adsorbs onto the mineral surface at the low, sub-monolayer dosages reported in this paper. Results from these tests are given in supplementary material.

2.3. Microflotation

A microflotation rig was used to infer the relative hydrophobicities of different mineral surfaces using recovery as an indicator. The experimental procedure for the microflotation tests have been described previously (Taguta et al., 2017). 3 g of the mineral was fed to the microflotation cell, the air flow rate was maintained at 10 ml/min and the pH was 9.2. Collector dosage was maintained at ~50% monolayer coverage (2.88×10^{-6} mol/m² of the available mineral surface area) and conditioning time was 6 min. Four concentrates were collected at intervals of 2, 4, 6 and 8 min. Microflotation experiments were done in duplicate and the averages are reported in this work. The microflotation cell and the microflotation procedure gave reproducible results as evidenced by the low standard deviations, around 1.5%. Flotation was also investigated in the absence of a collector to establish a baseline against which to compare the effect of the collector.

For both microcalorimetry and microflotation, pre-mixed SEX:diethyl-DTC collector mixtures with, respectively, 90:10 and 70:30 mol ratios, were used. Chalcopyrite-pyrite mineral mixtures were prepared such that each mineral contributed equal surface area to the total available surface area. This translated to a wt.% feed ratio of chalcopyrite: pyrite of 51:49.

2.3.1. Flotation data analysis

When mixtures of chalcopyrite and pyrite were used, microwave digestion followed by atomic absorption spectroscopy was used to

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