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THE THERMOCHEMICAL BEHAVIOUR OF THIOL COLLECTORS AND COLLECTOR MIXTURES WITH SULPHIDE MINERALS

By

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2015

A thesis submitted to the University of Cape Town as fulfilment of the requirement for the degree of **Master of Science in Chemical Engineering**

CENTRE FOR MINERALS RESEARCH

SYNOPSIS

Thiol collectors continue to dominate the base metal sulphide (BMS) and platinum group mineral (PGM) flotation industry. The behaviour of thiol collectors and collector mixtures with sulphide mineral surfaces has been extensively studied using different techniques such as XPS, ToF-SIMS, UV-VIS, etc. However, most of these techniques require a collector dosage above monolayer coverage, take place under equilibrium conditions and may not simulate flotation conditions. Moreover, most of the studies focus on isolated minerals yet exploitable ores exist as an association of sulphide minerals. The use of thiol collector mixtures in the base metal sulphides (BMS) and platinum group mineral (PGM) flotation industries has been reported to offer several performance benefits by many researchers. However, the mechanism whereby these collector mixtures adsorb onto a specific mineral surface is still not clearly understood.

This study used isothermal titration microcalorimetry to monitor sub-monolayer reactions by continuously measuring the heats of adsorption as the reactions between thiol collector (and collector mixtures) and sulphide minerals (and mixed minerals) proceed in real time. The enthalpy of adsorption does not only characterise the intensity of adsorption between a collector and mineral surface but also gives insight into the reaction mechanism, whether physisorption (less negative than -40 kJ/mol) or chemisorption (more negative than -40 kJ/mol). Microflotation was also used to determine the hydrophobicity imparted onto the mineral particles as a result of the mineral-collector interactions. Sulphide minerals investigated were chalcopyrite, pyrite, pyrrhotite and galena. Thiol collectors investigated were xanthates of varying chain length (SEX, SIBX, PNBX and PAX) as well as dithiocarbamates (diethyl-DTC and n-butyl DTC) and diethyl-DTP.

The current study seeks to gain knowledge of which collector interacts best with which mineral and an understanding of the mechanism behind the reactions. This study also seeks to investigate the performance and adsorption mechanisms when single minerals are interacted with thiol collectors singly and also in a mixture. A better understanding of how to design collector mixtures is to be gained. Furthermore this study seeks to understand the effect of mineral-mineral interactions on thiol collector adsorption and on the floatability of the pure minerals.

The enthalpy of adsorption was found to increase with increasing collector chain length of xanthates on chalcopyrite. The same observation was made when pyrite, pyrrhotite and

galena were interacted and floated with SEX and PAX. The microflotation recoveries were found to increase with increasing collector chain length for chalcopyrite, pyrite, galena and pyrrhotite. It was observed that there is a positive correlation between the enthalpy of adsorption and hydrophobicity for xanthates of different chain length on sulphide minerals. It was concluded that increasing alkyl chain length promotes both collector-mineral interaction, as well as the resultant hydrophobicity of the mineral.

The effect of the branching of the hydrocarbon chain length on the enthalpy of adsorption was dependent on the ligand type. For the xanthates, PNBX produced a higher enthalpy of adsorption than SIBX on the chalcopyrite surface. However, n-butyl DTC and diethyl-DTC produced similar enthalpy of adsorption on the chalcopyrite. From microflotation tests, the linear collectors outperformed their branched counterparts for collectors with equivalent alkyl chain length.

The enthalpy of adsorption of diethyl-DTC was always greater than diethyl-DTP for chalcopyrite, pyrite, galena and pyrrhotite. In fact, diethyl-DTP showed barely any interaction with all the sulphide minerals, since extremely low enthalpies of adsorption, viz. around 4-6 kJ/mol were obtained. Diethyl-DTP showed unexpectedly high recoveries for galena, chalcopyrite and pyrrhotite despite low enthalpies of adsorption. Since the microflotation experiments excluded the froth phase, it was speculated that the diethyl-DTP stabilised the bubble-particle agglomerates, translating to higher recoveries. Diethyl-DTC and diethyl-DTP produced equal recoveries for each of the minerals studied, except for pyrrhotite. These results indicate that there is no correlation between the enthalpy of adsorption and hydrophobicity for collectors with the same alkyl chain length but different ligand type. The results further indicate that the alkyl chain length generally is the decisive parameter in imparting hydrophobicity in flotation.

It can be concluded that generally there is no correlation between the enthalpy of adsorption and hydrophobicity. The magnitude of the collector-mineral interactions do not necessarily translate to hydrophobicity. The enthalpy of adsorption cannot be used to predict the recovery of sulphide minerals. This was substantiated by the fact that diethyl-DTP hardly reacted with all the sulphide minerals, and yet produced unexpectedly high chalcopyrite and galena recoveries. Furthermore, PAX and diethyl-DTC produced similar enthalpies of adsorption when contacted with pyrite but produced markedly different recoveries of the same mineral.

An interesting result was that pyrite did not respond to SEX and diethyl-DTC in a microflotation cell although microcalorimetry showed that there was interaction between pyrite and the two collectors. This suggested that, although reactions were occurring with a resultant heat associated with them, these reactions did not result in sufficient hydrophobicity for flotation to occur. This is an interesting observation and from an economic perspective would result in the consumption of reagent with no recovery benefit.

It is interesting to note that the enthalpies of adsorption for pyrrhotite with different thiol collectors were about half of those measured for chalcopyrite, galena and pyrite. This implies that the magnitude of the reaction between these collectors and pyrrhotite was relatively lower than on pyrite, galena and chalcopyrite. This behaviour was attributed to the purity of the pyrrhotite sample that was used. The purest sample available was composed of only about 60% pyrrhotite. The microflotation recoveries produced when pyrrhotite was interacted with thiol collectors were relatively lower, which were attributed to the same fact – the lower pyrrhotite purity.

The enthalpy of adsorption for SEX: diethyl-DTC collector mixtures with mole ratios of 90:10 and 70:30 were similar to those of pure diethyl-DTC on chalcopyrite. However, these enthalpies of adsorptions were higher than those of SEX on the same mineral. Thermochemical measurements showed that synergistically higher enthalpies of adsorption were produced when a small amount of diethyl-DTC was contacted with SEX in a mixture. Microflotation tests showed that the use of collector mixtures resulted in improved kinetics and recoveries than in the case of pure collectors. Overall, the results showed that when mixtures of collectors are used to float chalcopyrite, synergistic interactions take place which result in improved recoveries and rates. The optimum ratio of the collectors in the collector mixtures was 90:10 as there was neither an increase in enthalpy of adsorption or terminal recovery when the diethyl-DTC content was raised from 10 mole% to 30 mole% in the mixture. The SEX: diethyl-DTC collector mixture with a mole ratio 70:30 resulted in faster kinetics than its 90:10 counterpart in chalcopyrite flotation. The significance of these findings is that for a slow floating mineral, increasing DTC could improve its flotation rate for a fixed residence time.

It was postulated that dixanthogen was formed when SEX: diethyl-DTC collector mixtures were contacted with chalcopyrite. It is proposed that the reaction is catalysed by diethyl-DTC. Thermochemical measurements showed that collector mixtures produced unexpectedly higher enthalpies of adsorption. This was attributed to the initial adsorption of the DTC and xanthate and the subsequent oxidation of the xanthate to dixanthogen by the DTC-modified chalcopyrite surface. The mechanism of dixanthogen formation was reinforced by the increase in chalcopyrite recoveries produced by collector mixtures above those produced by single collectors.

When SEX was interacted with a mixture of chalcopyrite and pyrite, the heat of reaction was higher than that measured for the reaction of SEX with the pure mineral alone. However, with diethyl-DTC, the magnitude of reaction was equal to that of the DTC reaction with pyrite. SEX, diethyl-DTC and SEX: diethyl-DTC mixtures with mole ratios of 90:10 and 70:30 produced similar enthalpies of adsorption and microflotation recoveries when interacted with chalcopyrite-pyrite mixtures. It was thus concluded that the mechanism of interaction of the single collectors and collector mixtures with the mixed mineral was the same. Pyrite showed extremely poor flotation behaviour singly, but showed improved and significant flotation behaviour once it was mixed with chalcopyrite, using both single and collector mixtures. Chalcopyrite recoveries were also improved once it was mixed with pyrite. There was no evidence of synergistic interaction when collector mixtures were used to float mixed minerals. Both thermochemical measurements and microflotation tests showed that the behaviour of the pure minerals changes significantly once they are brought into contact in a mixture. It can be concluded that the changes in the thermochemical behaviour and floatability of minerals once they are contacted in a mixture are a result of the galvanic interactions between chalcopyrite and pyrite which is the driving force for the dimerisation of the collector ions and the indirect activation of pyrite by Cu^{2+} ions released from the dissolution of chalcopyrite through oxidation.

Plagiarism Declaration

I hereby declare that this thesis is my own work in design and execution and has not been submitted for any degree at any institution. I understand the meaning of plagiarism and all the work in this thesis is my own work, except for the material contained herein that has been duly acknowledged.

Signature: Signed by candidate Signature Removed

Jestos Taguta

Date: 4 September 2015

Acknowledgements

Firstly I would like to thank God Almighty for giving me the necessary strength to accomplish this work. His grace has been sufficient to sustain me throughout the course of this work.

Special thanks to Dr Belinda McFadzean who has been my mentor throughout the course of the project. Her technical expertise and invaluable support have been pivotal to the success of this work.

Special mention goes to Professor Cyril O'Connor who offered useful advice and direction as the work progressed. The contribution of his wealth of experience and vast amount of knowledge can never be over-emphasised.

Funding from the South African Minerals to Metals Research Institute (SAMMRI), the Department of Science, National Research Foundation (NRF) and the Centre for Minerals Research, University of Cape Town is greatly acknowledged.

I would like to extend my gratitude to my lovely wife and friend, Julieth and my brilliant sons: Tadiwanaishe and Simbarashe. I owe everything to you guys; indeed your support and motivation made this work a resounding success. God bless you!!

Table of Contents

List of Figures

List of tables

Nomenclature

ΔH is the enthalpy of adsorption

pKa is the negative logarithm of the acid dissociation constant

k is the first order flotation rate constant

SE is the standard deviation of the sampling distribution of the mean

R is the measured terminal recovery

R_f is the maximum possible recovery

t is the flotation time (min)

Greek letters

Θ is the contact angle induced between a mineral particle and the air bubble

μ is the micron (= 10^{-6} m)

Abbreviations

SEX	Sodium Ethyl Xanthate
SIBX	Sodium Isobutyl Xanthate
PNBX	Potassium n-Butyl Xanthate
PAX	Potassium Amyl Xanthate
SIPX	Sodium Isopropyl Xanthate
Diethyl-DTP	Sodium Diethyl Dithiophosphate
Diethyl-DTC	Sodium Diethyl Dithiocarbamate
DTPI	Dithiophosphonate
n-butyl DTC	n-Butyl Dithiocarbamate
FTIR	Fourier transform infra-red spectroscopy
XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy
UV-VIS	Ultraviolet-Visible Spectroscopy
ToF-SIMS	Time of Flight Secondary Ion Mass Spectroscopy
EDTA	Ethylenediaminetetraacetic acid
SIMS	Secondary Ion Mass Spectroscopy
UCT	University of Cape Town
PGMs	Platinum Group Minerals
BMS	Base Metal Sulphides
BET	Brunauer–Emmett–Teller (surnames of the authors of the gas adsorption surface area estimation technique).
X_2	Dixanthogen
X^-	Xanthate anion

MX_n	Metal xanthate
Ccp	Chalcopyrite
Py	Pyrite
Po	Pyrrhotite
Gn	Galena

CHAPTER 1: INTRODUCTION AND LITERATURE REVIEW

Introduction

Increasing human population and advancement in technology translate to a higher demand for metals and metal products. Most non-ferrous metals are processed from base metal sulphides (BMS). These non-ferrous metals find their use in many critical industries, for example transport, high technology devices, construction, electronics, metallurgy, energy generation and telecommunications. The metals refined from Platinum Group Minerals (PGMs) find their use in the jewellery, automotive industries and in the manufacture of catalysts and alloys.

Flotation is arguably one of the most important unit operations in the mineral beneficiation process. In excess of 2000 million tonnes of over 100 different mineral species are recovered annually through the process of flotation. Today, about 400 million tons of sulphide ore is treated annually by flotation processes worldwide (Fuerstenau 2005; Kohad and Mines 1998).

In view of the depleting rich ore bodies, mining houses are faced with challenges of processing more complex and low grade ores in order to abate the ever growing demand for BMS and PGMs. Inefficiencies in the associated mineral processing operations translate to significant loss of revenue and unnecessary waste of the world’s valuable and steadily declining mineral reserves. An understanding of the fundamental interactions between the sulphide minerals and collectors will help mitigate these losses through optimum and targeted reagent dosing.

Despite a century of innovation, the fundamental aspects of flotation are still being intensively researched. . This is because flotation is a complex process which involves various parameters that are inter-related.

1.1 Theory of the Flotation process

Flotation is a central unit operation in a mineral beneficiation chain. It is concerned with the concentration of a mineral whereby the valuable minerals are separated from gangue minerals based on the differences in the wettabilities of the particles in the flotation pulp. It is a complex process, involving the solid, liquid and gas phase and is a combination of chemical, physicochemical and physical phenomena. The flotation pulp comprises particles of various minerals with different wettabilities, usually resulting from treatment with a surfactant that alters the surface properties of the particles or minerals in the pulp. Upon the introduction of air, the rising air bubbles attach to the particles that are partially or incompletely wetted. Thus the particle-bubble aggregates rise to the surface and collect in the froth as concentrate. The particles that are completely wetted remain in the pulp. A typical flotation cell is shown in Figure 1.

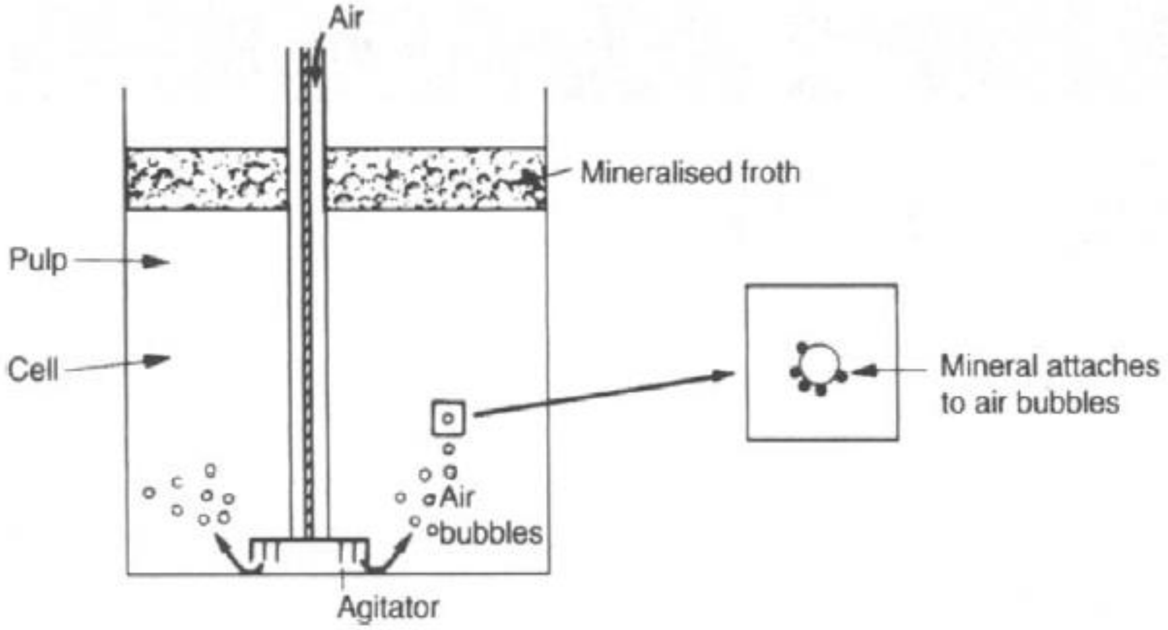


Figure 1: Schematic of the process of froth flotation (Wills and Napier-Munn 2006).

1.2 Factors affecting the flotation process

The froth flotation system is a complex system with many inter-related variables such as equipment, operation and chemistry variables. The variables are depicted diagrammatically in Figure 2. While it is acknowledged that many parameters influence the flotation process, this work focussed on the chemistry component, specifically collector chemistry highlighted in Figure 2.

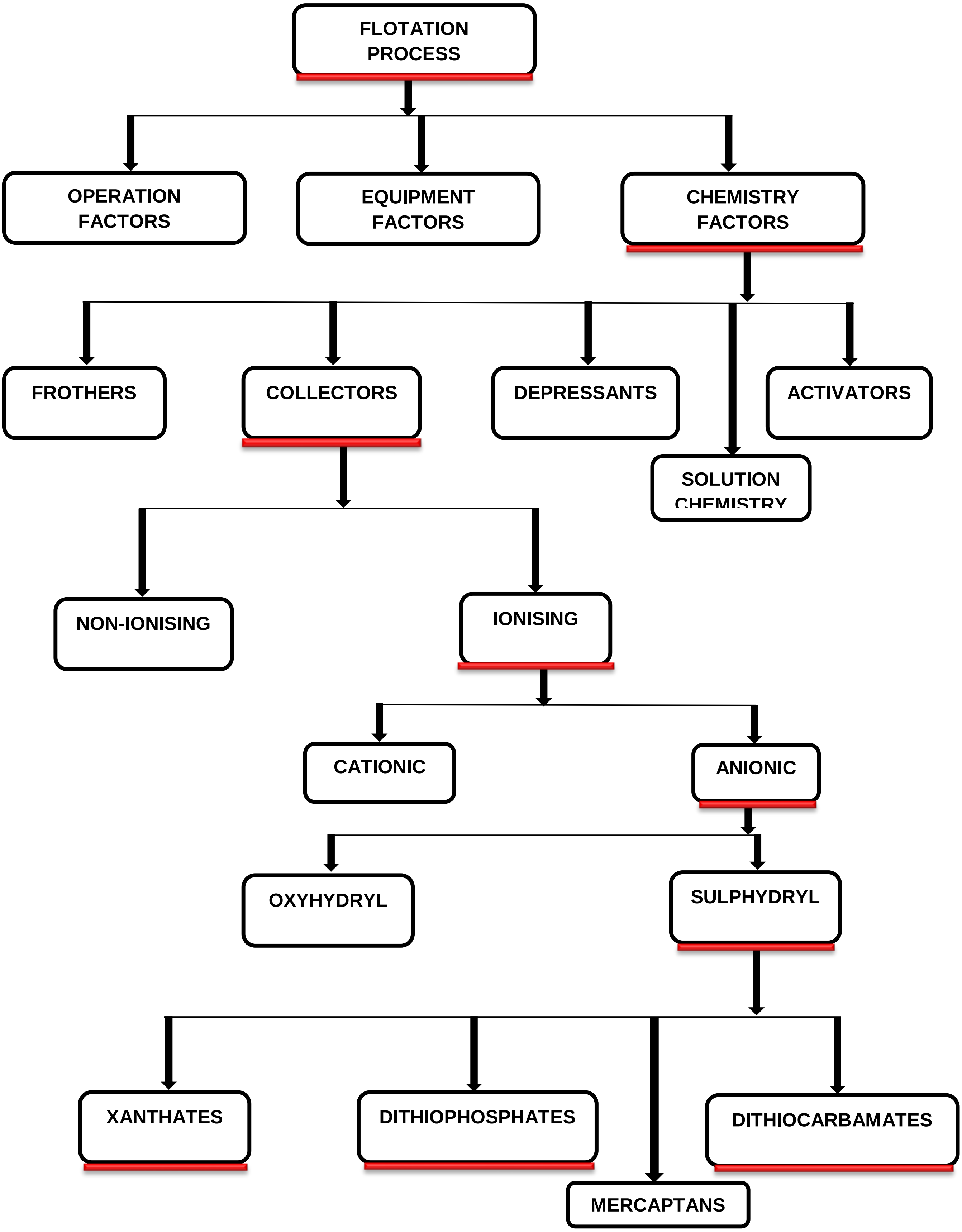


Figure 2: Variables affecting the flotation process and classification of flotation collectors

1.3 Sub processes of flotation

The overall froth flotation process is a combination of different sub-processes. Among them are:

1. Collector-mineral interactions;
2. Bubble particle interaction;
3. Particle recovery in the froth phase.

This investigation focussed on the first two sub-processes which take place in the pulp zone.

1.4 Mineral-collector interactions

This is one of the central sub-processes in flotation. Most minerals are naturally hydrophilic and do not have an affinity for air bubbles. For a bubble to attach to a mineral surface, a hydrophobic mineral surface is required. In mineral processing, the required hydrophobicity is usually achieved by addition of a surfactant called a collector. The sub-process of collector-mineral interaction is driven by the collector chemistry, mineral surface chemistry and the solution chemistry.

1.4.1 Collectors

A collector is a hetero-polar reagent that consists of the non-polar hydrocarbon chain which is hydrophobic and the polar head group which is hydrophilic. The polar head group reacts with the mineral surface while the non-polar hydrocarbon chain induces hydrophobicity onto the mineral surface by extending into the liquid phase in the flotation pulp. The reaction between thiol collectors and sulphide minerals takes place because the 3p electrons of sulphur atoms of thiol collectors and the d-electrons of metal ions of the sulphide minerals are located at the same energy level, hence the orbitals overlap easily (Raju and Forsling 1997). Collector adsorption onto a mineral surface is depicted diagrammatically in Figure 3.

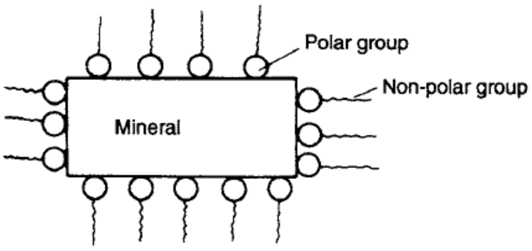
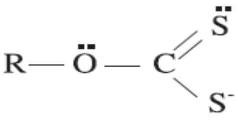
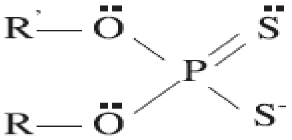
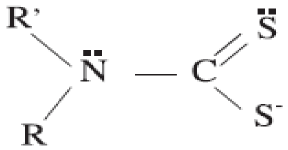


Figure 3: Schematic of collector adsorption on a mineral surface (Wills and Napier-Munn 2006)

Collectors significantly increase the contact angle thereby enhancing the bubble-particle interaction. As shown in Figure 2, there are different classes of collectors but this work focusses on sulfhydryl collectors, specifically the xanthates, the dithiocarbamates and the dithiophosphates since they find their use as the most common collectors in the BMS and PGM flotation industry. Xanthates are used in bulk sulphide mineral flotation because they are relatively cheaper and more powerful collectors, however they not selective (Chen et al. 2013; Wiese et al. 2005). The dithiophosphates and dithiocarbamates are usually used in selective flotation because of their improved selectivity (Chen et al. 2013; Wiese et al. 2005). The structures of the collectors used in this study are shown in Table 1.

Table 1: Generic structures of thiol collectors used in this work where R and R' represent the hydrocarbon chains of the thiol collectors.

Collector	Structure	Preparation
Xanthate		Prepared from an alcohol (R-OH), sodium or potassium hydroxide and carbon disulphide
Dithiophosphate		Synthesised from a single alcohol, or from two different alcohols, with sodium hydroxide and phosphorous disulphide.
Dithiocarbamate		Synthesised from an amine ($R-NH_2$) and carbon disulphide.

1.4.1.1 Collector Chemistry

Collector chemistry depends on the hydrocarbon chain length and the chemistry of the head group. It is also reported that the effectiveness of a collector is a function of both the hydrocarbon chain length and the polar group (Bradshaw et al. 2005).

The effect of the alkyl chain length on collector chemistry

The length of the carbon chain affects the hydrophobicity imparted to the mineral particle – the longer the hydrocarbon chain, the greater the hydrophobicity. In addition, the electron releasing or withdrawing behaviour of the organic group affects the electron densities around the donor atoms. In thiol collectors the electron densities on the sulphur atoms depend on the inductive effects in the molecules (Somasundaran and Nagaraj 1984). A longer hydrocarbon chain makes the collector more reactive due to a stronger positive inductive effect, which increases the electron density around the polar head group (McMurry 1996). Longer chain collectors are readily oxidised compared to shorter chain collectors (Kim et al, 2000; Lotter and Bradshaw, 2010). The nature of the alkyl chain length also affects the chemistry of the collector. For collectors with the same number of carbon atoms, the straight alkyl chain length has a stronger inductive effect towards the functional group as compared to the branched chain (McMurry 1996). This results in the increased electron density around the donor atoms, promoting the mineral collector interactions.

The effect of donor atoms in the collector head group

The differences in the electronegativity of the O, C, P or N atoms in the collector polar head groups affect the reactivities of the collectors (Somasundaran and Nagaraj 1984; McMurry 1996). According to Somasundaran and Nagaraj (1984), the electronegativities decrease in the following order:

O	N	S	P
3.5	3.07	2.44	2.06

Oxygen is the most electronegative in the above series. Thus, DTP is less reactive than the xanthate because of the two RO groups that are electron-withdrawing, thus reducing electron density around the donor sulphur atoms. The electron density on the sulphur atoms in xanthate is higher than in DTP due to the presence of only one RO group in xanthates. The N in the DTC is less electronegative than the O in either the xanthates or the DTP. Therefore, the electron releasing tendency of the R_2N in DTC increases the electron density around the donor S atoms, rendering DTC more reactive (Raju and Forsling 1997). Thus, the reactivity decreases in the following order: DTC > X > DTP (Somasundaran and Nagaraj 1984; Lotter and Bradshaw 2010).

The electron donating or withdrawing effects of the substituent groups in a collector molecule not only affects the electron density around the donor atom but also the pKa of the collector (Somasundaran and Nagaraj 1984). The pKa can also be used as a measure of the tendency of the donor atoms in the collector to donate electrons to metal ions. The collector acid-base equilibrium may be represented as:

$$HX \leftrightharpoons H^+ + X^- \qquad (1)$$

$$K_a \approx [H^+]\,[X^-] / [HX] \qquad (2)$$

where K_a is the dissociation constant

The greater the electron-releasing inductive effect, the greater is the electron density around the reactive head group. This implies a stronger HX bond, which results in less dissociation of the proton and a smaller K_a. The pKa is simply the negative logarithm of the K_a and, as such, the smaller the K_a, the larger the pK_a. Thus, collectors with a larger pK_a should have greater electron donating capacity and have stronger bonds with the mineral surface. The pKa of a variety of thiol collectors are shown in Table 2. It is evident from these values that the collector head group has a far greater effect on the electron donating capacity of the collector than the positively inductive effect of the carbon chain.

Table 2: pKa values of various thiol collectors used in this work

Reagent	pKa	Reference
Ethyl xanthate	2.20	Hayashi et al. (1984)
Propyl xanthate	2.22	Hayashi et al. (1984)
Butyl xanthate	2.23	Hayashi et al. (1984)
Diethyl-DTC	7.5	Raju and Forsling (1991)
Diethyl-DTP	~0	Rao (2004)

Collector strength vs selectivity

The strength of the collector has been conventionally defined as the ability of the collector to impart hydrophobicity. That is, the greater the hydrophobicity the stronger the collector. However, it might equally be argued that a strong collector should have a strong chemical bond with the mineral surface. As mentioned in Section 1.4.1.1, collectors with a larger pK_a should have greater electron donating capacity and have stronger bonds with the mineral surface. In light of Table 2, the strength of the collectors decrease in the following order: DTC > Xanthate > DTP. It is hypothesised that a strong collector should form a strong bond with the mineral surface translating to a higher recovery of the mineral.

A strong collector indiscriminately adsorbs onto all the mineral components in an ore resulting in a lower grade of the concentrate. Thus a stronger collector has poor selectivity. The order of selectivity decreases in the following order: DTP > Xanthate > DTC.

Stability of the hydrophobic species

The main collector species responsible for flotation are reported to be the metal-thiolates or the dithiolates. The stability of the hydrophobic species formed plays a key role in flotation in that the more stable the species, the higher the strength or efficiency of the collector (Marabini et al. 2007). The stability of the hydrophobic species depends on collector type and alkyl chain length.

The greater the stability of the metal complex formed, the lower the solubility of the complex because of the stable bond formed between the metal cation and the collector anion. It follows that the solubility of a salt is a measure of its stability. Thus an ideal collector is one that forms an insoluble complex with a metal cation

For the metal thiolate species, it is reported that an increase in collector chain length results in a decrease in the solubility of the metal thiolate formed (Kim et al. 2012). These authors report the variation of the solubilities of different metal xanthates with the hydrocarbon chain length and their findings are presented in Figure 4.

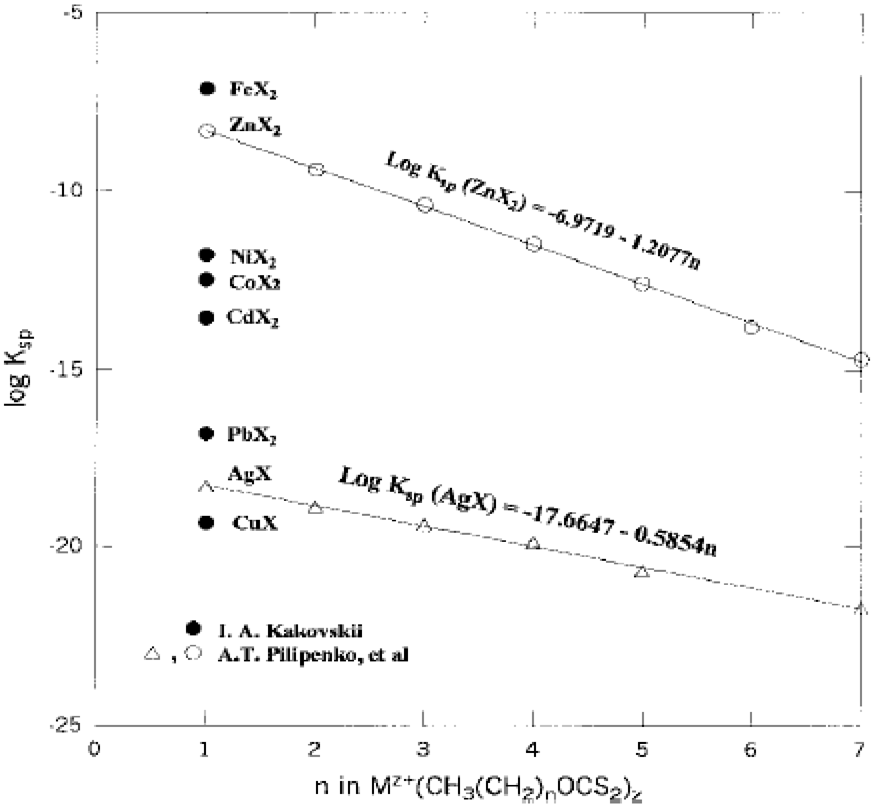


Figure 4: Solubility products (K_{sp}) of metal xanthates as a function of chain length (Kim et al. 2012)

It is clear from Figure 4 that the solubility of the metal xanthates decreases with increasing chain length of the xanthates. It is also seen that the solubility of the metal xanthates depends on the different types of metal ions bonded to the xanthate anions. The solubility of iron xanthate is seen to be much higher than lead and cuprous xanthate. Thus xanthate imparts less hydrophobicity to an iron mineral surface than lead and cuprous xanthate, which are more hydrophobic.

Hamilton and Woods (1979) established the solubility of various chain length dixanthogens and their findings are presented in Table 3.

Table 3: Solubility of short chain dixanthogen (Hamilton and Woods 1979)

Alkyl chain length	**Solubility of dimer (mol/dm^3)**
Methyl	1.16×10^{-4}
Ethyl	1.14×10^{-5}
n-Propyl	1.50×10^{-6}
n-Butyl	1.60×10^{-7}
n-Amyl	1.90×10^{-8}

It must be emphasised that an ideal collector is one that not only forms a strong bond with a mineral surface but also forms stable hydrophobic species which then forms stable particle-bubble agglomerates.

1.4.1.2 Collector adsorption mechanisms

Electrochemical model

It is generally accepted that the interaction between sulphide minerals and thiol collectors follow a mixed potential model (Alison et al. 1972; Finkelstein and Goold 1972; Rao 1982) where the sulphide minerals catalyse the anodic oxidation of thiol collector ions. It is also accepted that the cathodic reaction is the reduction of dissolved oxygen in the solution phase. Most sulphide minerals are by nature semi-conductors and hence allow electrons to be transferred from the collector ions to dissolved oxygen through them. Generally there are three types of hydrophobic species formed when sulphide minerals interact with thiol collectors namely the chemisorbed thiolate, the metal thiolate and dithiolate (Rao 1982; Sun et al. 2009).

Chemisorbed thiolate

This is formed when the collector ions react with metal ions in the lattice structure of the mineral (Rao 1982; Sun et al. 2009). The bonding takes place without disrupting the mineral lattice. This is usually restricted to a monolayer collector coverage.

Anodic: $X^- \rightarrow X\ (\text{adsorbed}) + e^-$ (3)

Cathodic: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (4)

Overall: $4X^- + 2H_2O + O_2 \rightarrow 4X$ (adsorbed) $+ 4OH^-$ (5)

Metal thiolate

This is formed through the electrochemical-dissolution mechanism (Lotter and Bradshaw 2010; Rao 1982; Sun et al. 2009). The mineral surface is first oxidised, and consequently releases metal cations into the bulk solution. The liberated metal cations then react with the collector ions forming metal complexes in the bulk phase which are then precipitated onto the mineral surface rendering it hydrophobic.

Anodic: $2X^- + MS \rightarrow MX_2 + S + 2e$ (6)

Cathodic: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (4)

Overall: $4X^- + 2MS + 2H_2O + O_2 \rightarrow 2MX_2 + 2S + 4OH^-$ (7)

Dithiolates

This is formed as a result of the catalytic oxidation of the collector ions at higher Eh (Lotter and Bradshaw 2010; Rao 1982; Sun et al. 2009). When the rest potential at the mineral-solution interface is higher than the reversible potential of X_2/X^- couple, the dithiolate is likely to be formed from a thermodynamic perspective.

Anodic: $2X^- \rightarrow X_2 + 2e$ (8)

Cathodic: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$ (4)

Overall: $4X^- + O_2 + 2H_2O \rightarrow 2X_2$ (dixanthogen) $+ 4OH^-$ (9)

The preferred hydrophobic entity in sulphide flotation is dixanthogen. The solubility of the hydrophobic species decreases in the following order: dixanthogen > metal thiolate > chemisorbed xanthate (Rao 1982). However, it is reported that dixanthogen is not necessarily required for flotation to occur, though its presence increases floatability (Finkelstein and Poling 1977). Even small islands of metal thiolate equivalent to 0.1 monolayer coverage was shown to cause significant flotation of galena (Prestidge and Ralston 1996)

1.4.2 Mineral surface chemistry

The mechanism of interaction between a sulphide mineral and thiol collectors depends on the reactivity of the mineral, which is determined by the nature of the mineral and its crystalline structure, specifically the sulphur–sulphur distances in the lattice structure (Persson 1994). It is reported that there is a strong correlation between the structure of the sulphide mineral and the thiol collector adsorption mechanism (Persson 1994). Persson stated that the sulphide minerals can be categorised into three main classes:

a) Disulphide ions, S_2^{2-} with S-S distance less than 3.1Aº, for example pyrite.
b) Sheets or clusters of sulphur atoms with S-S distances in the range 3.1Aº – 3.4A°, for example pyrrhotite.
c) Close-packed sulphide ions, S^{2-} with S-S distances longer than 3.7A°, for example galena and chalcopyrite.

Persson asserts that groups a) and b) form powerful oxidising agents, like $S_2O_7^{2-}$ and $S_2O_8^{2-}$ upon oxidation. These anions are strong enough to oxidise collector ions to corresponding dithiolates. Group c) forms metal thiolates as the hydrophobic species, since they form relatively weaker oxidising agents upon oxidation.

Table 4: Summary of the crystalline structure of sulphide minerals (Persson 1994)

Sulphide	**Chemical Formula**	**Crystalline Structure**	**Shortest S-S distance (A°)**
Galena	PbS	Cubic, has a rock-salt type structure with Pb^{2+} and S^{2-} ions in the place of Na and Cl^- ions respectively. Coordination number of 6.	4.194
Pyrite	FeS_2	Cubic structure made up of Fe^{2+} and S_2^{2-} ions with a modified rock-salt structure.Fe^{2+} ions are surrounded by 6 sulphur atoms in an octahedral fashion and each sulphur is surrounded by sulphur and 3 Fe^{2+} ions in a distorted tetrahedral configuration.	2.177
Chalcopyrite	$CuFeS_2$	Crystallises in a tetragonal structure where half of the cations are replaced by Cu and the other half by Fe. Cu(I), iron(III) and sulphide ions arranged in such a way that each Cu(I) and iron(III) is tetrahedrally surrounded by 4 sulphide ions and the sulphide ions are tetrahedrally surrounded by 2 Cu(I) and 2 iron(III) ions.	3.685
Pyrrhotite,	FeS_{1-x}	Complicated structure. The shortest S-S distance is 3.39A°	3.390

1.4.3 Interactions of thiol collectors with sulphide minerals

The interaction of sulphide minerals with thiol collectors has been widely studied using different surface science techniques, e.g. XPS, UV-VIS, ToF-SIMS and extraction and identification using infrared spectroscopy. Electrochemical methods, rest potential measurements and cyclic voltammetry, have also been used to identify the collector species on mineral surfaces. Despite more than a century of research, the mechanisms whereby sulphide minerals interact with thiol collectors are still widely researched.

The proposed mechanisms of interaction between the thiol collectors and sulphide minerals concerned with this work are discussed in the following paragraphs.

1.4.3.1 Galena

Woods and Gardener (1997) determined the contact angle between a nitrogen bubble and galena surface as a function of electrode potential and the amount of xanthate species formed from the galena-xanthate interactions was determined. They found that the galena surface was hydrophobic when interacted with ethyl and butyl xanthate, unlike when interacted with methyl xanthate. They attributed the hydrophobicity of the galena surface to the formation of a layer of chemisorbed xanthate. They also found that dixanthogen increased the contact angle compared to the metal xanthate. Valli and Persson (1994) suggested that small islands of lead xanthate were formed on the galena surface when xanthate ions reacted with aqueous lead ions which would have been produced from soluble oxidation products like lead carbonate or lead sulphate. Persson (1994) suggests that the lead xanthate was the only species formed. He argued that the rest potential of a galena electrode in aqueous xanthate solution is lower than that for the X^- / X_2 couple. Finkelstein and Goold (1972), using rest potential measurements and extraction and identification using infrared spectroscopy found that the lead thiolate was formed when galena was interacted with dithiocarbamate and dithiophosphate. Finkelstein and Poling (1977) agreed with these findings and expanded their study to show that the metal thiolate is the collector species formed when galena is interacted with xanthates, dithiophosphates and dithiocarbamates. This agrees well with Alison et al. (1972) who reported that lead xanthate is formed in the galena-xanthate system for xanthates of different chain length. These observations also agree with Persson's (1994) predictions discussed in Section 1.4.2 on the type of interaction that a galena surface is likely to undergo.

1.4.3.2 Pyrite

Most researchers report that xanthate forms a dimer when interacted with pyrite (Finkelstein and Goold 1972; Lo et al. 2005; Alison et al. 1972; Finkelstein and Poling 1977; Yoon and Basilio 1993; Valli and Persson 1994; Fuerstenau et al. 1968; Bradshaw et al. 1995; Leppinen et al. 1989). However some researchers report that a mixture of metal thiolate and dixanthogen are formed from the interaction of pyrite and xanthates. Nagaraj and Brinen (2001) using SIMS found that both dixanthogen and metal thiolates were formed when pyrite was interacted with xanthate. An iron complex and dixanthogen were found to coexist on pyrite for a monolayer coverage (Leppinen 1990). However, Fuerstenau et al. (1968) argues that chances of the formation of surface ferrous xanthate are low at moderate collector concentrations because of very high solubility of ferrous ethyl xanthate, and suggests that the collector ions are oxidised by ferric ions to dixanthogen in solution. The same mechanism for xanthate oxidation was reported by (Lo et al. 2005). Pyrite contains disulphide ions that are able to oxidise xanthates to corresponding dixanthogen (Valli and Persson 1994). It can be concluded that dixanthogen is the principal hydrophobic species on pyrite, however metal thiolates can also be formed depending on the collector concentration used.

Very little work has been conducted to investigate the adsorption mechanism of DTC and DTP on pyrite. Nagaraj and Brinen (2001) using SIMS found that both dimers and metal thiolates were formed when pyrite was interacted with DTC. They also found a metal thiolate alone being formed in the case of DTP. DTC has also been reported to form a corresponding dimer on pyrite (Finkelstein and Goold 1972; Finkelstein and Poling 1977). However, using thermochemical measurements Bradshaw et al. (1995) found that DTC formed a metal thiolate with a single step reaction unlike the xanthate that formed dixanthogen via a two-step reaction in which a metal thiolate is formed first and then oxidised to a corresponding dimer. They attributed the absence of further oxidation of the DTC thiolate to its low solubility compared to xanthate salts.

1.4.3.3 Chalcopyrite

Chalcopyrite was reported to react with xanthate, diethyl-DTP and diethyl-DTC forming metal thiolates using rest potential measurements and infrared spectroscopy (Finkelstein and Goold 1972). The same mechanism was supported by Finkelstein and Poling (1977) in a review paper. However, Alison et al. (1972) using spectrophotometric methods and rest potential measurements, reported that dixanthogen was the surface product when chalcopyrite was interacted with different xanthate homologues from methyl to hexyl chain length. The same conclusion that dixanthogen was the hydrophobic species on the chalcopyrite surface was made by Leppinen et al. (1989) and Yoon and Basilio (1993) at potentials close to the reversible potential of the xanthate/dixanthogen couple. They reported that the metal thiolate can form at higher Eh, at which the chalcopyrite surface is oxidised liberating Cu^{2+} ions into the bulk phase. Copper xanthate and dixanthogen were found to coexist on the chalcopyrite surface (Leppinen 1990). Valli and Persson (1994) using XPS and vibration spectroscopy found that the metal thiolate was the hydrophobic specie formed on chalcopyrite. Using the static bed adsorption method coupled with UV-VIS, Raju and Forsling (1997) found the metal thiolate as the hydrophobic species when chalcopyrite was interacted with SEX and diethyl-DTC. In light of the studies mentioned above, it can be concluded that when chalcopyrite is interacted with the xanthate, either a metal thiolate or dixanthogen is formed, depending on the Eh of the system. However, in the case of diethyl-DTC and diethyl-DTP only the metal thiolate is formed. This can be attributed to the fact that metal-DTC bonds are reported to be very strong and stable over a wide pH range and the complexes are reported to be highly insoluble (Lotter and Bradshaw 2010). DTP has been reported to be less readily oxidised than the xanthates and the DTC (Finkelstein and Goold 1972; N. Finkelstein and Poling 1977).

1.4.3.4 Pyrrhotite

Bozkurt and Xu (1998) using FTIR-ATR spectroscopy and rest potential measurements found dixanthogen as the main product when pyrrhotite was interacted with xanthate at pH 9.2. Dixanthogen was also found as the hydrophobic species on pyrrhotite using UV-VIS and rest potential measurements (Alison et al. 1972). Leppinen (1990), using FTIR-ATR and microflotation also found that dixanthogen was formed on the pyrrhotite surface. Valli and Persson (1994), using spectroscopy also reported that dixanthogen was formed when xanthate was interacted with pyrrhotite, however the amount of dixanthogen was less than that formed on the pyrite surface, all conditions being the same. They reasoned that S-S bond lengths in pyrrhotite are shorter than those in pyrite and hence pyrrhotite produced less oxidising agent. Using cyclic voltammetry and rest potential measurements, Khan et al. (2004) found that pyrrhotite developed a rest potential higher than the equilibrium potential for dixanthogen formation in oxygen-saturated solutions. Dixanthogen has been reported to form on the pyrrhotite surface at 200 mV/SHE (Miller et al. 2005). Thus many researchers agree that dixanthogen is the collector species formed on the pyrrhotite surface in the presence of xanthates. There is limited information on the interaction of DTP and DTC with pyrrhotite. Finkelstein and Goold (1972), using rest potential measurements and infrared spectroscopy did not identify any species for DTP and DTC.

1.5 Bubble-particle interactions

The sub-process of bubble-particle interaction is driven by the hydrophobicity of the mineral surface, particle size and density, hydrodynamics and bubble size. The objective of this study was to determine whether the interaction between the collector and mineral surface resulted in enhanced hydrophobicity. Hence the particle size and density, hydrodynamics and bubble size were held constant.

The interaction of the bubbles with the mineral particles is the back bone of the flotation process and determines the majority of the particles reporting in the concentrates. In order for a stable bubble-particle agglomerate to be formed, hydrophobic particle surfaces are required. This requires the addition of a collector that imparts hydrophobicity onto the mineral surface by changing the mineral surface chemistry. This would result in increased interaction between the particle and the bubble.

1.5.1 Hydrophobicity and contact angle

The flotation process takes advantage of the differences in the wettabilities of different minerals in order to effect separation. The wettability of a mineral particle is known as hydrophobicity (or hydrophilicity). Most minerals are naturally hydrophilic. Hydrophobicity is necessary to promote the bubble-particle interaction and consequently to have a stable particle-bubble agglomerate. As mentioned earlier, hydrophobicity of a mineral surface is achieved by addition of a surfactant called a collector. The collector alters the surface chemistry of a mineral particle and thus promotes particle-bubble interactions. A particle's hydrophobicity is a measure of the particle's affinity for air. That is, the higher the hydrophobicity, the greater the interaction between particle and air. The imparted hydrophobicity greatly influences the sub-process of particle-bubble interaction. The hydrophobic particles are carried into the froth phase by rising air bubbles when air is introduced. The hydrophilic particles remain in the pulp phase.

Hydrophobicity is conventionally determined using contact angle, which is the angle formed between the mineral surface and the bubble (Prestidge and Ralston 1996; Prestidge and Ralston 1996; Wark and Wark 1932; Bulatovic 2007). The higher the hydrophobicity, the higher the contact angle. However, the contact angle is limited in that it is measured in an equilibrium system, which does not occur in real flotation systems (Bulatovic 2007). Additionally the contact angle has been shown to be limited in describing real flotation systems (Bradshaw and O'Connor 1996). Flotation has been shown to happen at zero contact angle, and that different types of collectors with the same hydrocarbon chain length produced the same contact angle, independent of the mineral type (Wark and Wark 1932). This is despite the fact that different collector types show different flotation performance (Rao 2004).

The attachment of the air bubble to the mineral particle is determined by the interfacial energies between the solid, liquid and gas phases shown in Figure 5. At equilibrium, the contact angle, Θ in terms of the interfacial energies (forces) at the solid/water/air interface is given by the Young - Dupre Equation,

$$\Upsilon_{w/a}\cos\Theta = \Upsilon_{s/a} - \Upsilon_{s/w} \qquad (10)$$

where $\Upsilon_{w/a}$, $\Upsilon_{s/a}$, $\Upsilon_{s/w}$ are the surface energies of the water/air interface, solid/air interface and solid/water interface respectively. Θ is the contact angle between the mineral surface and the bubble.

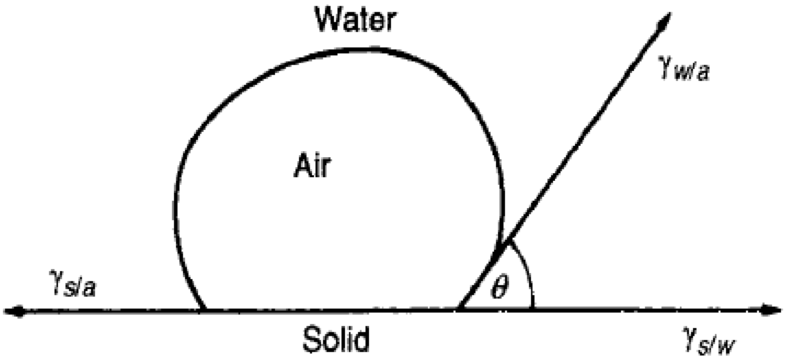


Figure 5: Contact angle between particle and air bubble in the liquid phase (Wills and Napier-munn 2006)

1.5.2 Effect of chain length on hydrophobicity, contact angle and recovery

The hydrophobicity of the mineral surface is a function of the length of the collector carbon chain. An increase in the hydrocarbon chain length of the collector was found to cause an increase in contact angle induced between the mineral surface and an air bubble (Wark and Wark 1932). The graph in Figure 6 shows the effect of the alkyl chain length on the contact angle induced by thiolates and dithiolates between the galena surface and the air bubble.

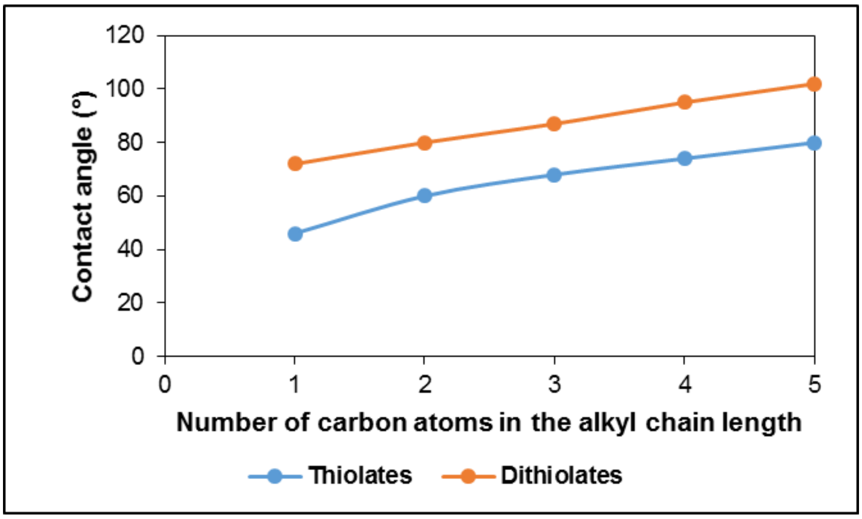


Figure 6: The effect of alkyl chain length on the contact angle induced by thiolates and dithiolates between galena surface and air bubble, adapted from (Rao 1982).

Consequently, the increase in alkyl chain length has been shown to increase the recovery of galena at a constant collector dosage as shown in Figure 7.

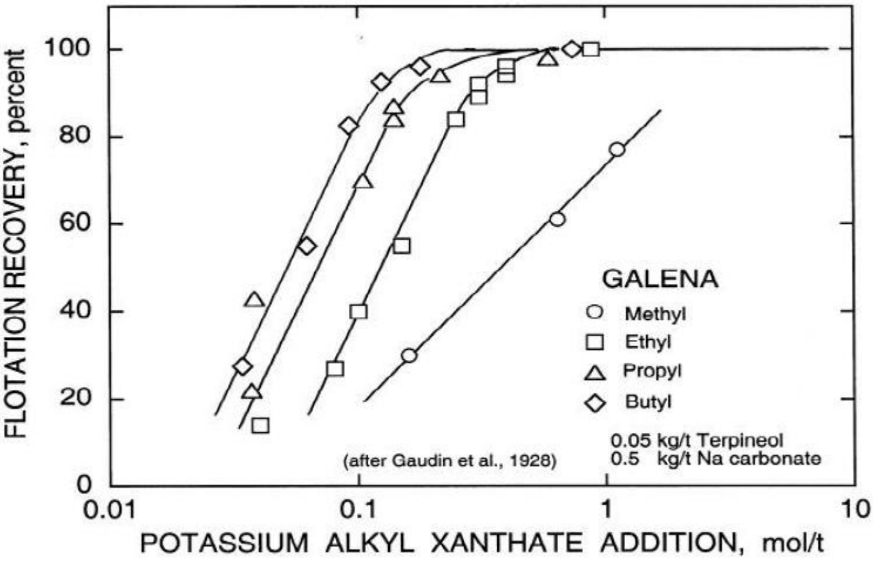


Figure 7: The effect of alkyl chain length on the contact angle induced by thiolates and dithiolates between galena surface and air bubble (Fuerstenau 2005).

Furthermore, an increase in chain length for the same type of collector has been shown to increase the recovery of other sulphide minerals such as chalcopyrite, pyrite and galena (Göktepe 2002; Ackerman et al. 1987; Fuerstenau 2005). Different collector types with the same hydrocarbon chain length were found to produce the same contact angles (Wark and Wark 1932).

Furthermore, the nature of the alkyl chain length also has an effect on the flotation performance of the thiol collectors. Ackerman et al. (1987) compared the flotation performance of straight chain versus branched chain collectors and they found that straight chain collectors outperformed their branched counter-parts in chalcopyrite, covellite and chalcocite flotation.

1.6 Solution Chemistry

Solution chemistry comprises of Eh, pH and ionic strength in the pulp phase. Pulp pH affects reagent stability and activity as well as species on the mineral surface (Wills and Napier-Munn, 2006). Thiol collectors are stable in alkaline conditions (Wills and Napier-Munn, 2006). The commonly used pH modifiers are lime and soda ash. This work was conducted at pH 9.2 to simulate conditions in typical PGM concentrators. The adsorption of collector ions onto the mineral surface depends on the pulp pH as there is competition between the hydroxyl ions and the collector ions. For any collector concentration, there is a pH beyond which the collector ions cannot adsorb onto the mineral surface and the mineral cannot float (Wills and Napier-

Munn, 2006). This pH value is called the critical pH. Each mineral has its own characteristic critical pH and the variation of critical pH with collector concentration is shown in Figure 8.

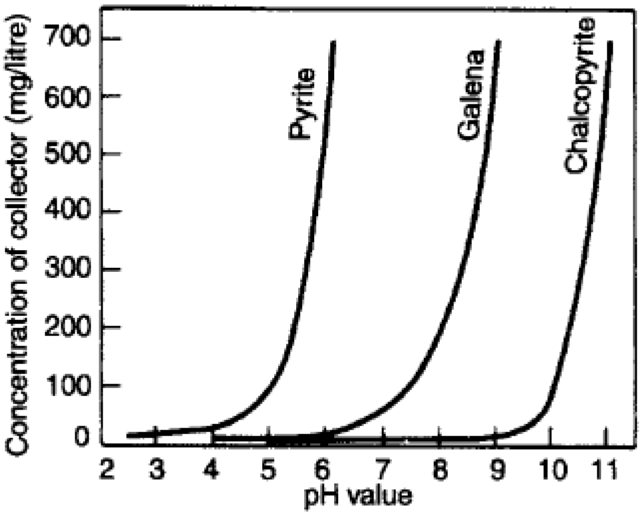


Figure 8: Variation of diethyl-DTP concentration and critical pH value (Wills and Napier-Munn, 2006).

Eh is dependent on pH and these two parameters have a significant influence on the flotation of sulphide minerals (Göktepe 2002). The potential difference of a mineral-solution interface has been reported to be closely related to the floatability of sulphide minerals (Göktepe 2002). At higher redox potentials, dixanthogen is formed. Xanthate readily forms dixanthogen but dithiophosphate has a lower chance of forming dithiophosphate (Fuerstenau, 1978b; Lotter and Bradshaw, 2010). However dixanthogen formation is pH dependent with more forming in acidic conditions than in alkaline conditions. The presence of ions in solution is known to have an effect on the floatability of sulphide minerals as these ions modify the chemistry of the system. Manono et al. (2012), using batch flotation found that the increase in ionic strength translated to an increase in water recovery implying that the ions in water were stabilising the froth phase. The increased ionic strength was reported to decrease the bubble size, reinforcing that the ionic strength has significant impact on froth stability (Manono et al. 2013).

1.7 Research studies using calorimetry in flotation research

Microcalorimetry has had limited application in flotation research though it has been extensively applied in many other fields such as the cement industry, the pharmaceutical industry, agricultural, soil and environmental science and catalysis (Pang et al. 2013; Gaisford and Buckton 2001; Zheng et al. 2007; Cai et al. 2001; Ball and Maechling 2009).

Very little work has been conducted to measure the enthalpies of adsorption when mineral surfaces react with thiol collectors. The galena-xanthate system has been the most widely studied using calorimetry (Arnaud et al. 1989; Maier et al. 1997; Chen et al. 2013; McFadzean and O'Connor 2014; Bradshaw et al. 1995). Some calorimetric work has also been conducted on pyrite (Bradshaw et al. 1995; Chen et al. 2013). However, different reaction mechanisms and collector affinities have been reported for both galena and pyrite.

Mellgren (1966) measured the enthalpies of the interaction between galena and xanthate collectors. It was observed that the enthalpy of adsorption of SEX onto the galena surface was equal to the enthalpy of reaction between lead ions (in the form of lead nitrate) and SEX (-95 kJ/mol). The authors used this as evidence to validate the ion exchange reaction mechanism between the galena surface and xanthate.

Partyka et al. (1987) investigated the adsorption of SEX on a galena surface at low surface coverages using calorimetry. They discovered that the enthalpy of adsorption decreased with successive addition of xanthate up to 70% of a theoretical monolayer, thereafter it remained constant and independent of surface coverage. They reported chemisorption through surface ions below a monolayer surface coverage. Above a monolayer surface coverage, they reported chemisorption through lead ions released into the bulk solution through dissolution of the galena surface.

Maier et al. (1997) conducted microcalorimetric experiments for three mineral-collector systems: 2-mercaptobenzoxazole (MBO)-chalcocite, 2-mercaptobenzothiazole (MBT)-galena and 2-aminothiophenol (ATP)-sphalerite. Their results of the interaction between galena with potassium amyl xanthate (PAX) and mercaptobenzothiazole (MBT) are shown in Figure 9. Their results for the galena-xanthate system are consistent with those of Partyka et al. (1987) at sub-monolayer coverages, with the exchange enthalpy decreasing from -78 kJ/mol to -46 kJ/mol in the sub-monolayer region. However, the enthalpy of adsorptions continued to progressively decrease up to the third monolayer. They reasoned that the second and third monolayers were a result of a liquid phase chemisorption reaction and subsequent precipitation of dissolved lead compounds in solution. Thereafter, the reaction enthalpy decreased to approximately -30 kJ/mol and this was attributed to the formation of dixanthogen on the galena surface.

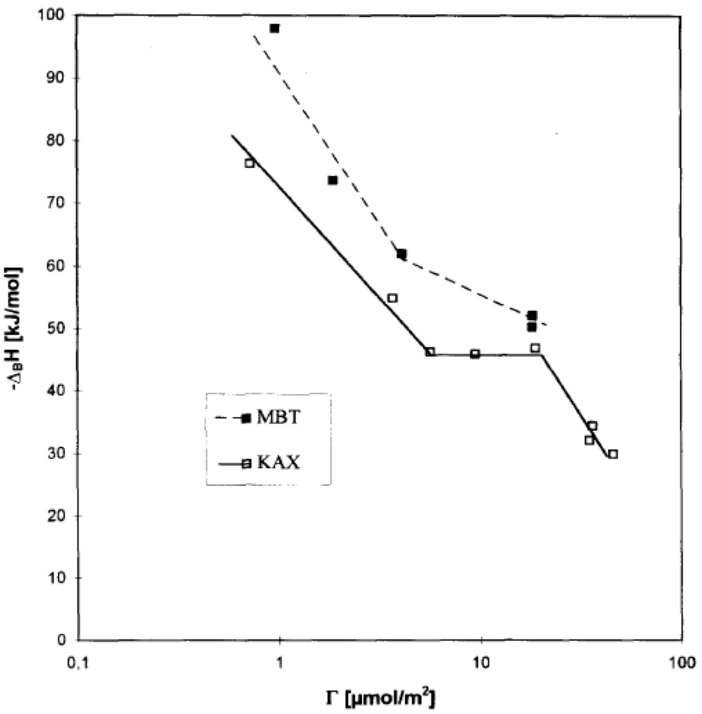


Figure 9: Variation of enthalpy of adsorption with collector coverage for interaction of galena with KAX (potassium amyl xanthate) and MBT (2-mercaptobenzothiazole) (Maier et al. 1997)

Bradshaw et al. (1995) used calorimetry to distinguish between the adsorption mechanisms occurring when xanthate, dithiocarbamates and mixtures thereof were interacted with pyrite. They observed a second, sequential reaction between pyrite and the xanthate suggesting that the metal thiolate formed via the ion exchange mechanism was further oxidized to the dixanthogen. However, there was only a single reaction for the dithiocarbamate.

This was the first thermochemical study to investigate the use of collector mixtures in flotation research. They also observed that the enthalpy of adsorption for the mixture of xanthate and DTC was greater than that for either collector alone (-90 kJ/mol), implying synergistic performance between the two collectors. However, no sub-monolayer information was obtained since a single increment of collector was used.

Chen et al. (2013) investigated the adsorption of different collectors on galena and pyrite surfaces using computer modelling and microcalorimetry. Using computer modelling, they found that all the collectors (xanthate, dithiocarbamates and dithiophosphate) interacted with both galena and pyrite via a one step or direct reaction. They also found that DTP's interaction with galena was stronger than that with pyrite using calorimetry. However, there is no sub-monolayer information and collector-mineral mechanisms were not elucidated. Their computational modelling was done in a vacuum and did not simulate real flotation conditions or even an aqueous environment Distilled water was used as medium during calorimetric experiments, implying the natural pH of the mineral, which is characteristic of the mineral. This means the microcalorimetric experiments for different minerals were carried out at different conditions of pH. Furthermore, blank experiments were not conducted and this could affect the results obtained. Corrections should be made for the measured heats of the collector with the aqueous medium.

McFadzean and O'Connor (2014) performed isothermal microcalorimetric titrations of various collectors with galena and their findings are shown in Figure 10. They discovered a second and sequential reaction for SEX and SIBX in sub monolayer coverages. The enthalpy of adsorption for SIBX was higher than that for SEX above monolayer coverage. Furthermore, the enthalpies of adsorption for dithiocarbamate were found to be very similar to those of xanthate. However, the dithiophosphate was found to have no interaction with galena at all.

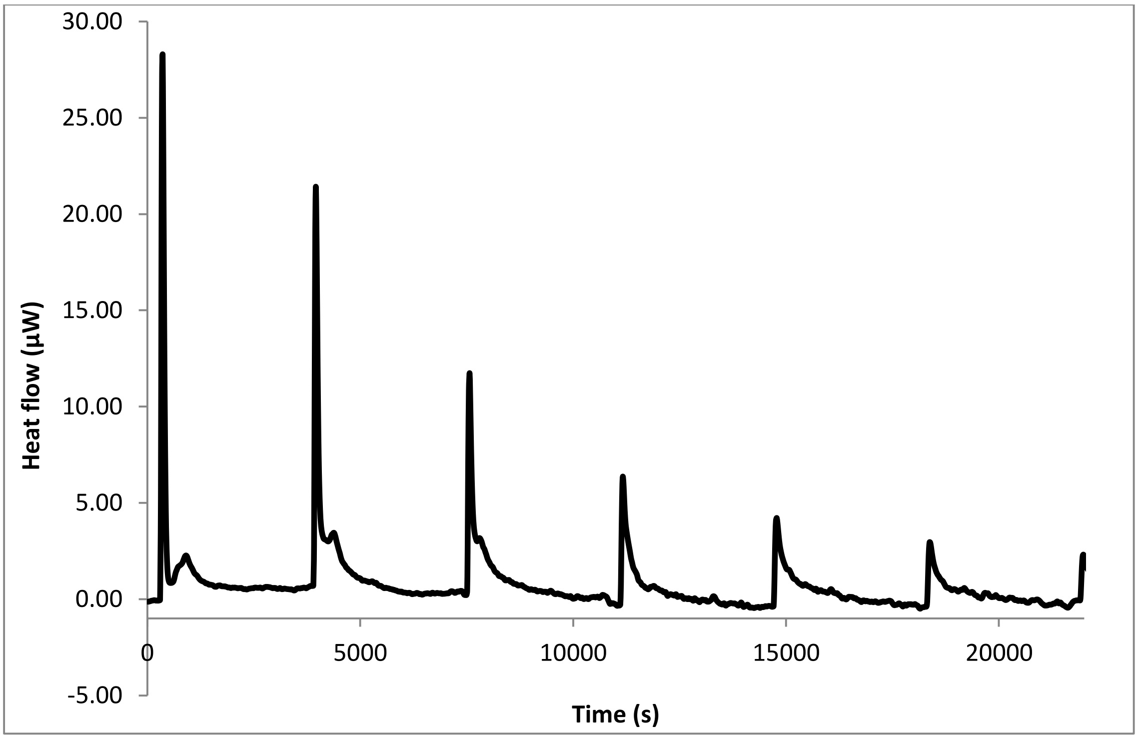


Figure 10: Heat flow curve for the galena-SEX system (McFadzean and O'Connor, 2014)

1.8 The use of collector mixtures

Thiol collector mixtures are finding increasing use in the base metal sulphide (BMS) and platinum group metal (PGM) flotation industry. Xanthates are normally used as the primary collector. However, they are not particularly selective (Chen et al. 2013; Wiese et al. 2005).

The dithiocarbamates and dithiophosphates are used in a mixture with the xanthates as they have better selectivity compared to the latter (Chen et al. 2013; Wiese et al. 2005). The use of collector mixtures has been reported to provide several performance benefits which include improved recoveries and grades, improved kinetics and improved recovery of coarse particles.

A collector mixture with a butyl xanthate: cyclohexyl dithiocarbamate ratio of 90:10 mole percent was shown to result in improved recoveries, grades and lower collector dosages for pyrite flotation at pH 4 (Bradshaw and O'Connor 1994). Similarly using batch flotation, improved recoveries and grades were reported in the flotation of a copper sulphide ore from Okiep using SEX: diethyl-DTC and SEX: diethyl-DTP collector mixtures with a mole ratio of 90:10 (Hangone et al. 2000). Makanza et al. (2008) also found that the use of collector mixtures in the flotation of auriferous pyrite resulted in improved gold and uranium recoveries. Improved kinetics and recovery was also observed by Mcfadzean et al. (2012) when galena was floated with collector mixtures in a microflotation cell. Thermochemical measurements conducted by Bradshaw et al. (1995) showed that a higher reaction enthalpy was obtained when a mixture of butyl xanthate and cyclohexyl dithiocarbamate was interacted with pyrite at pH 4 compared to either of the single constituent collectors. They concluded that there were synergistic interactions between the two collectors. However, in the case of DTP, McFadzean and O'Connor (2014) found that the enthalpy of reaction for SEX and diethyl-DTP mixtures with galena were simply additive, thus there was no evidence of synergism. This was in direct contrast to McFadzean et al. (2012) who reported synergism for the same collectors in a galena flotation system. Despite the reported performance benefits of using collector mixtures by different researchers, the mechanism whereby these collector mixtures synergistically improve flotation performance is still not clearly understood.

1.8.1 Mechanisms of synergistic flotation improvements using collector mixtures

A number of mechanisms are reported in literature for the synergistic interaction of collectors with sulphide minerals. Bradshaw et al. (1995) investigated the thermochemical behaviour of butyl xanthate and cyclo-hexyl dithiocarbamate and their mixtures on pyrite. They found that the interaction of collector mixtures produced a higher enthalpy of adsorption than in the case of pure thiols. Bradshaw et al. (1995), Bradshaw et al. (1998) and Bagci et al (2007) postulated that cyclohexyl dithiocarbamate preferentially adsorbed onto pyrite in the form of "anchors". They attributed this to the faster kinetics and a more stable complex associated with the dithiocarbamate. The xanthate would then adsorb onto the "anchors" in the form of dixanthogen.

Figure 11 illustrates the "anchor" mechanism for a mixture of sodium isopropyl xanthate (SIPX) and di-isobutyl dithiophosphonate (DTPI) in which the diethyl-DTP forms "anchors" upon which SIPX adsorbs in the form of dixanthogen.

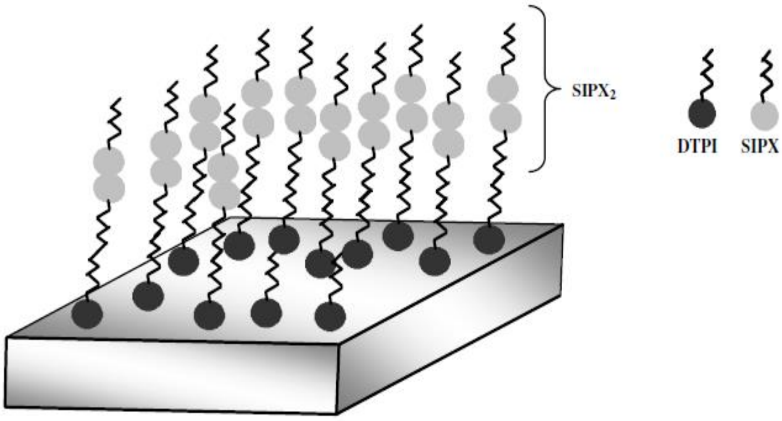


Figure 11: Schematic of the "anchor" mechanism for collector mixtures mechanism (Bagci et al. 2007).

Bagci et al. (2007) hypothesised that when collectors are dosed sequentially, with the weaker collector added first and the stronger collector added last, the weaker collector adsorbs on strong sites first, and the stronger collector adsorbs on the remaining weaker sites on the chalcopyrite surface resulting in a greater surface coverage. This mechanism lends its credibility to the fact that the sulphide mineral surface comprises of different energy sites. This same mechanism was reported by Bradshaw et al. (1998) in a review paper. Figure 12 illustrates this mechanism for a mixture of sodium isopropyl xanthate (SIPX) and di-isobutyl dithiophosphinate (DTPI) where DTPI adsorbs onto the strong sites while the SIPX adsorbs onto the remaining weak sites.

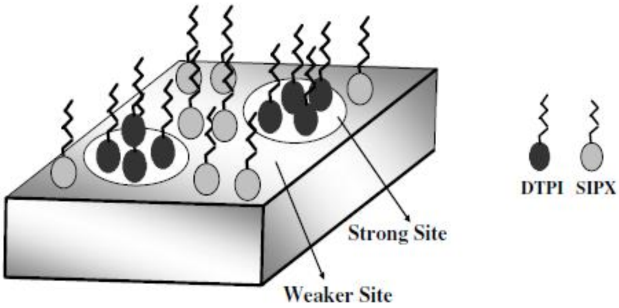


Figure 12: Strong sites – weak sites model of collector mixture interaction with sulphide minerals (Bagci et al. 2007)

Both hypotheses mentioned above are reported to result in improved adsorption for collector mixtures than single collectors.

1.9 Mineral-mineral interactions

While the interaction of thiol collectors with sulphide minerals has been widely researched, most of the studies focus on isolated sulphide minerals. However, real and exploitable ores exist as an association of sulphide minerals. It is generally accepted that sulphide minerals have different electrochemical reactivities, as evidenced by the differences in their rest potentials in distilled water (Rao and Finch 1988). When two different sulphide minerals are brought into contact, a galvanic cell is set up with electrons flowing from the anodic mineral to the cathodic one. This phenomenon is called galvanic interaction. It follows that the results obtained for single mineral systems fall short to describe the real situation since exploitable ore is complex, occurring as an association of sulphide minerals. These galvanic interactions have been shown to have a significant effect on collector adsorption and floatability of the pure minerals.

Many studies have investigated the effect of grinding media on the interaction between sulphide minerals (Peng and Grano 2010; Peng et al. 2003; Azizi et al. 2013; Huang et al. 2006; Huang and Grano 2005). Very few studies investigate the interactions between different sulphide minerals and the effect of these interactions on thiol collector adsorption and floatability of the pure minerals.

Rao and Finch (1988) used rest potential measurements to study galvanic interactions between sulphide minerals. Pyrite was found to have the highest rest potential in water and xanthate solution compared to chalcopyrite, galena and sphalerite. They found that the combination potentials of pyrite electrodes in contact with a second sulphide mineral were significantly lower than that of pyrite alone. Using adsorption experiments, they found that xanthate adsorption onto sphalerite was relatively lower than that on pyrite at pH 8.6, with approximately a monolayer adsorption on pyrite. However, the xanthate adsorption behaviour changed when sphalerite was mixed with pyrite, with approximately half a monolayer of xanthate being adsorbed under the same conditions. The flotation kinetics for a 50:50 weight percent galena-pyrite mixture were found to be lower than that of the pure minerals.

Smart (1991) studied the surface chemistry of base metal sulphides using surface sensitive techniques for both single and mixed minerals. For a 50:50 weight percent chalcopyrite-pyrite mixture, Scanning Auger microscopy analysis showed copper to be present both on the chalcopyrite and pyrite surfaces. It was further shown that copper can dissolve from the chalcopyrite surface, releasing copper (II) ions into the bulk solution. The copper (II) would then adsorb onto pyrite as copper (I) leading to the activation of the pyrite.

Ekmekci (1997) investigated the effect of galvanic interactions on the collectorless flotation of chalcopyrite and pyrite using cyclic voltammetry and microflotation. It was found that the galvanic interactions between the two minerals significantly affected the floatability of both minerals. Figure 13 shows galvanic interactions between chalcopyrite and pyrite whereby electrons are transferred from chalcopyrite to pyrite once they are in contact.

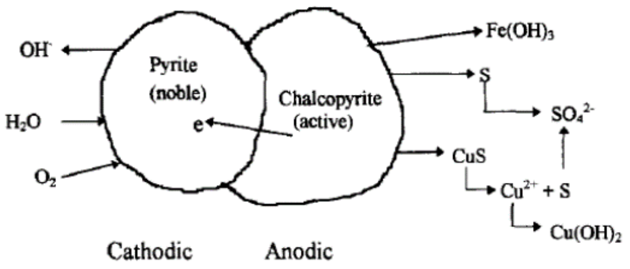


Figure 13: Proposed model of galvanic interaction between chalcopyrite and pyrite (Ekmekci 1997)

Mielczarski and Mielczarski (2003) studied the influence of galvanic effects on adsorption of xanthate on pyrite, galena, chalcopyrite and different mineral combinations using adsorption measurements and infrared spectroscopy. It was observed that galvanic interactions between two minerals in contact had a significant effect on collector adsorption on both minerals.

Microcalorimetry can be very useful in studying the effects of mineral-mineral interactions on collector adsorption, especially for the sub monolayer collector coverages.

1.10 Summary of Literature review and Gap Analysis

Literature reports different reaction mechanisms between thiol collectors on both galena and pyrite. Most of the studies focused on the galena-xanthate system. Detailed thermochemical investigations for pyrite, chalcopyrite and pyrrhotite are lacking. Very little sub monolayer information is available in literature, despite the fact that it is reported that SEX coverage as low as 10% of a monolayer produced a significantly high contact angle and flotation recovery of galena (Prestidge and Ralston 1996). Buckley and Woods (1997) also reported that a high galena and chalcocite recovery was produced by SEX coverages in the sub monolayer region with less than 0.2 coverage producing 50% recovery and half-monolayer coverage producing 90% recovery. There are also contradictions on the affinity of the collectors for the galena surface.

For the galena-xanthate system, Partyka et al. (1987) and Maier et al. (1997) reported the same mechanism in the sub monolayer region. They agree the mechanism is chemisorption through surface ions in the sub monolayer region. Both papers also report that the enthalpy of adsorptions significantly dropped with successive addition of xanthate in the sub monolayer region. However, they report different mechanisms above a monolayer coverage. While both papers reported chemisorption through the ion exchange mechanism above a monolayer, Maier et al. (1997) reported the physisorption of dixanthogen above the third monolayer. Similar to the findings by Maier et al. (1997), (McFadzean and O'Connor 2014) found that the second and third monolayers were due to the liquid phase reaction of Pb^{2+} and xanthate ions. Chen et al. (2013) reported that xanthates and galena react via a direct, one-step reaction while McFadzean and O'Connor (2014) discovered two sequential reactions up to a monolayer coverage. Bradshaw et al. (1995) observed a second and sequential reaction between pyrite and the xanthate suggesting that the metal thiolate formed via the ion exchange mechanism was further oxidized to the dixanthogen. However, Chen et al. (2013) reported a one-step direct reaction when pyrite was interacted with xanthates. It is interesting to note that both Bradshaw et al. (1995) and McFadzean and O'Connor (2014) observed a second and sequential reaction for pyrite and galena respectively. However, their interpretations were different. Bradshaw et al. (1995) attributed the second peak to the oxidation of the metal thiolate to a dimer, while McFadzean and O'Connor (2014) attributed it to the precipitation of the metal thiolate onto the galena surface. The difference in the mechanisms may be attributed to the differences in the mineral chemistry and the operating pH.

There are also some contradictions in the collector affinity for the galena surface. Chen et al. (2013) noted that the adsorption of dithiocarbamate on galena is the strongest due to the highest enthalpy of adsorption. On the contrary, McFadzean and O'Connor (2014) asserted that the enthalpy of adsorption for dithiocarbamate was similar to those of the xanthates. While Chen et al. (2013) showed that adsorption of dithiophosphate on galena surface is stronger than that on the pyrite surface, McFadzean and O'Connor (2014) found that dithiophosphate had no interaction at all with the galena surface. Both papers report that adsorption of dithiocarbamate on galena is stronger than that of DTP which was the weakest collector. However, it should be noted that the pH's of these systems were different in the two studies.

Furthermore, very few studies have related collector affinity for a mineral surface to the hydrophobicity imparted to the mineral particle by the same collector. The enthalpy of adsorption of interaction between a collector and a mineral is an indication of the collector's affinity for that mineral (Glembotskii 1981). Maier et al. (1997) investigated the relationship between collector affinity and collector strength for three mineral-collector systems: 2-mercaptobenzoxazole (MBO)-chalcocite, 2-mercaptobenzothiazole (MBT)-galena and 2-aminothiophenol (ATP)-sphalerite. They found that a higher collector affinity for a surface does not necessarily improve the collector's flotation properties. A number of studies investigated collector-mineral interactions and many studies investigate the effect of hydrophobicity on recovery, but few studies can be found that relate these two parameters. The length of the carbon chain will naturally relate one to the other. The longer the carbon chain, the greater the collector-mineral affinity and also the greater the hydrophobicity. However, studying collectors with different head groups but the same length carbon chain can give us information on the relationship between collector-mineral affinity and hydrophobicity.

The mechanism whereby synergy occurs when thiol collector mixtures interact with sulphide minerals remains unclear despite the reported performance benefits. Furthermore, most of the calorimetric investigations focussed on single minerals, yet most exploitable ores are found in association with other sulphide minerals.

1.11 Project Scope

The overall flotation process is divided into three sub-processes: mineral-collector interactions, particle-bubble interactions as well as particle recovery in the froth phase. This work will only focus on the first two sub-processes that take place in the pulp zone. The particle-bubble interaction is critical in flotation and the efficiency of this sub-process depends on the mineral-collector interactions.

The current study focusses on the fundamental interactions between sulphide minerals and thiol collectors. Therefore the study investigates only pure sulphide minerals and no attempt is made to investigate a real ore. The collectors used are limited to the xanthates, dithiocarbamates and dithiophosphates. Reactions between the sulphide minerals and the collectors are followed using isothermal titration microcalorimetry. Microflotation tests are also conducted to investigate whether mineral-collector interactions translate to any hydrophobicity.

Collector mixtures are further interacted with single minerals and mixed minerals with a view to investigate synergism and mechanism of interaction. The xanthates are used as primary collectors while the dithiocarbamates are used as co-collectors. Mixed mineral systems are prepared to simulate a real ore. These mineral mixtures are interacted with single thiol collectors.

1.12 Hypotheses

- Different single collectors will have different enthalpies of adsorption onto a pure mineral surface because of their different affinities for that surface.
- Each pure mineral will have a collector which has the greatest affinity for that particular mineral because each mineral surface will be unique.
- A mixture of two or more collectors added simultaneously to a mixture of minerals will have a higher enthalpy of adsorption than a single collector because each collector will adsorb preferentially onto the mineral for which it has the highest affinity.
- Different single collectors will produce different recoveries because of the differences in interactions between the collectors and the mineral surface(s).
- Different collector mixtures will produce increased recoveries than single constituent collectors because of improved surface coverages of the collector mixtures.
- Collectors with the same reactive head groups, but different carbon chain length will show a positive correlation between the enthalpy of adsorption and the mineral's floatability because the stronger the adsorption, the higher the hydrophobicity expected.

1.13 Key Questions

- Do differences in collector types have any effect on the magnitude of mineral-collector enthalpies of adsorption as well on the microflotation recoveries and accompanying kinetics?
- Is the thermochemical behaviour and flotation performance of mixtures of thiol collectors different from single collectors?
- Do mixtures of minerals respond to thiol collectors in the same way as single minerals?
- Do differences in alkyl chain length have any effects on the enthalpies of adsorption and microflotation recoveries and kinetics?
- Is there a relationship between enthalpy of adsorption and microflotation recovery?

1.14 Overall project objective

The overall objective was to better understand the interactions of sulphide minerals with thiol collectors. The proposed outcome is improved recovery and selectivity, optimising reagent consumption through targeted reagent dosing thereby reducing processing costs and loss of reagents to the waste streams in the process. A knowledge of which collector best interacts with which mineral is to be gained. Furthermore a better understanding of how to design collector mixtures is to be gained. These expected outcomes will help in improving the overall flotation recovery and grades by making the flotation process more efficient.

1.14.1 Project Objectives

To measure and compare the enthalpies and microflotation recoveries of the following reactions:

- Single thiol collectors added to single pure sulphide minerals
    - differences in reaction mechanism between different collectors and the same mineral; and different minerals and the same collector.
- Mixtures of thiol collectors added to single pure sulphide minerals
    - the collector mixture reaction mechanism.
- Single thiol collectors added to mixtures of pure sulphide minerals
    - affinity of a collector for a simulated ore.
- Mixtures of thiol collectors added to mixtures of pure sulphide minerals
    - affinity of a collector mixture for a simulated ore.

CHAPTER 2: EXPERIMENTAL PROGRAMME

Introduction

This chapter describes how the interactions between sulphide minerals and thiol collectors were investigated and followed using microcalorimetry. It goes further to describe how the hydrophobicity of the mineral surface was measured using microflotation. The major aim of this thesis was to investigate whether there was a correlation between the collector-mineral interactions and the hydrophobicity thus imparted to the mineral surface. Every microcalorimetric test conducted was therefore coupled with a microflotation test. The experimental program was designed to address the objectives of this study.

Figure 14 is a diagrammatical representation of the experimental procedure for the whole project. Each arrow represents microcalorimetric and microflotation tests. For collector mixtures, the molar fraction of the xanthates is given first. For example, a collector mixture with a mole ratio of 90:10 of SEX and diethyl-DTC comprises of 90 mole percent xanthate and 10 mole percent secondary collector.

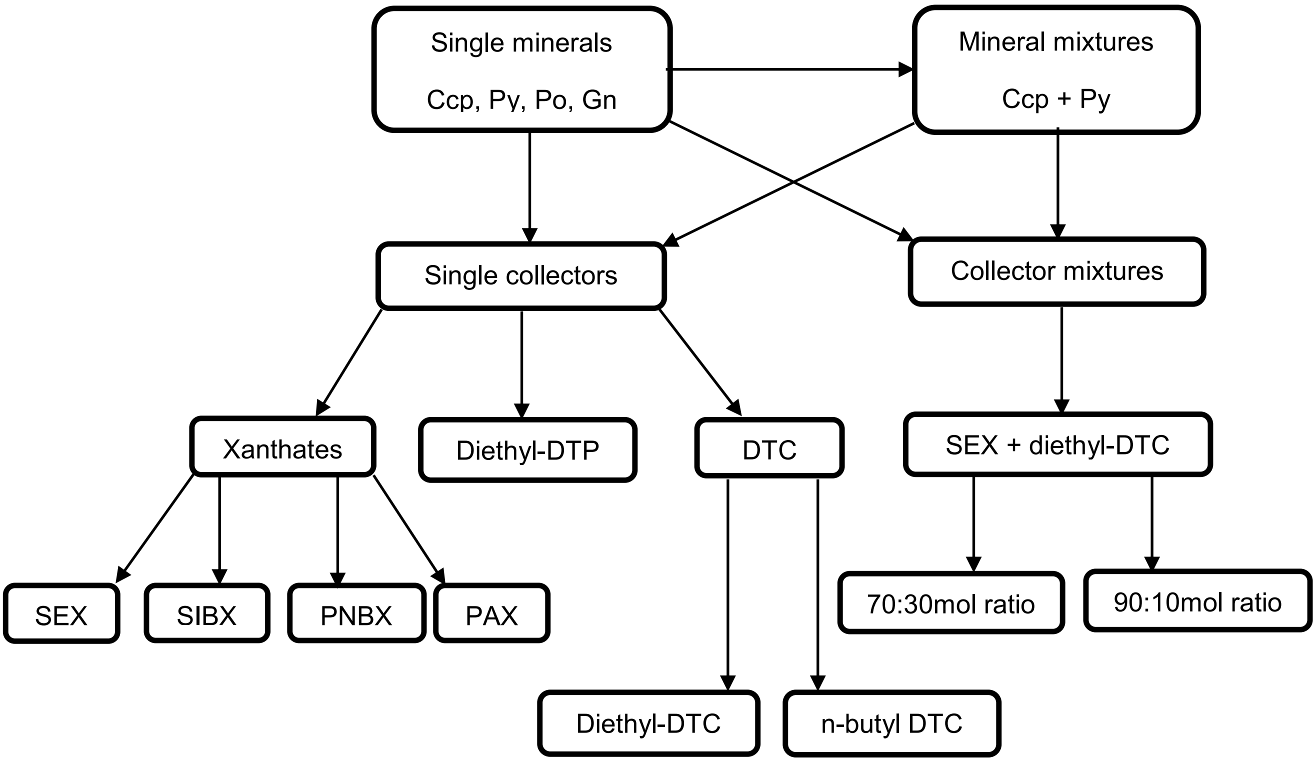


Figure 14: Flow diagram representing the experimental programme for the whole project.

The particle size range for microcalorimetric experiments was -38 μm while the size range for microflotation was from 38 μm to 106 μm. The -38μm size range was chosen for microcalorimetry since they are fine, providing a large surface area for reaction. The +38 μm

- -106 µm size range was chosen for microflotation since they are easily floatable with lower collector dosages and are less amenable to entrainment (Pearse et al, 2006). All the experiments were conducted at a constant pH of 9.2. For collector mixtures, SEX was used as the primary collector while diethyl-DTC was used as the secondary collector. For all collector ratios, the first number in the ratio represents SEX fraction. Collector ratios of 90:10 mole percent and 70:30 mole percent were investigated in this work. The objective was to investigate the effect of a secondary collector on the behaviour of the primary collector.

This chapter describes the mineral and reagent preparation as well as the microcalorimetric and microflotation procedures.

2.1 Overview of the test work

The test work was organised in the following order:

- Received mineral samples: chalcopyrite, pyrite, galena and pyrrhotite from Wards Natural Science Establishment, New York.
- Mineralogical analysis of the mineral sample using X-ray diffraction (XRD) using the Rietveld method. This was to investigate the composition of the sulphide minerals.
- Preliminary microcalorimetry tests to find a suitable pH modifier.
- Blank tests to determine the heats of dilution of the different collectors used in this study.
- Thermochemical measurements of the following interactions:
    a. Single minerals versus single collectors
    b. Single minerals versus mixtures of collectors
    c. Mixtures of minerals versus single collectors
    d. Mixtures of minerals versus mixtures of collectors
- Collectorless flotation of the pure sulphide minerals to establish a baseline upon which to compare the effects of mineral-collector interactions.
- Microflotation tests of the following systems
    a. Single minerals floated with single collectors
    b. Single minerals floated with mixtures of collectors
    c. Mixtures of minerals floated with single collectors
    d. Mixtures of minerals floated with mixtures of collectors

2.2 Mineral Preparation

Pure sulphide minerals of interest in this study are pyrite, galena, chalcopyrite and pyrrhotite. These were received from the Ward's Natural Science Establishment NY as chunks of up to 150 mm diameter. The chunks were hammered manually and then pulverised for 15 seconds in a laboratory disk mill (*Siebtechnik)* to 100% passing -106 µm. The material was then dry sieved into two fractions: - 38 µm for microcalorimetry and + 38 µm to -106 µm for microflotation. The material was split using a rotary splitter into 10 samples. All the samples were stored under nitrogen at - 30°C to minimise oxidation of the samples.

2.3 Mineralogical analysis of the sulphide minerals

X-ray diffraction (XRD) was used to determine the mineralogical compositions or phases of the sulphide minerals. Powder XRD spectra were obtained using a Bruker D8 Advance powder diffractometer with Vantec detector and fixed divergence and receiving slits with Co-Ka radiation. The phases were identified using Bruker Topas 4.1 software (Coelho, 2007) and the relative phase amounts (weight %) were estimated using the Rietveld method.

Pure sulphide minerals were desirable for this work as impurities would lead to complex interactions and interference with the targeted sulphide mineral-collector interactions. The mineralogical analysis is shown in Table 5.

Galena and pyrite were relatively pure, being 100% and 95% of the desired mineral type. In addition, 3.6% of the pyrite contaminant was quartz, an inert mineral. Pyrrhotite had the major amount of impurities, being only about 60% pure. The majority of the impurities came from non-sulfide minerals, thus minimising the risk of galvanic interactions. However, there was a substantial amount of floatable gangue in the form of talc, present. Since samples of greater purity could not be obtained, these impurities were borne in mind with respect to the results obtained.

Table 5: X-ray diffraction results for chalcopyrite, pyrite, galena and pyrrhotite.

Sample	Expected Mineral	XRD results		Chemical Formula
		Mineral	**Compositions (%)**	
1	Galena	Galena	100	PbS
2	Chalcopyrite	Chalcopyrite	82.0	$CuFeS_2$
		Pyrite	2.4	FeS_2
		Bornite	7.8	Cu_5FeS_4
		Quartz	7.8	SiO_2
3	Pyrrhotite	Pyrrhotite	59.5	$Fe_{1-x}S$
		Chalcopyrite	2.1	$CuFeS_2$
		Pentlandite	0.6	$(Fe,Ni)_9S_8$
		Talc	8.4	$Mg_3Si_4O_{10}(OH)_2$
		Calcite	4.3	$CaCO_3$
		Epidote	4.6	$Ca_2(Al,Fe)_2(SiO_4)_3(OH)$
		Enstatite	5.8	$Mg_2Si_2O_6$
		Hornblende	14.8	$Ca_2(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH)_2$,
4	Pyrite	Pyrite	94.9	FeS_2
		Chalcopyrite	1.5	$CuFeS_2$
		Quartz	3.6	SiO_2

2.4 Reagents

Thiol collectors used in this study were supplied by Senmin (Pty) Limited. Different xanthate homologues were supplied in powder form while diethyl-DTP and dithiocarbamates were supplied in solution form at basic pH to stabilise them. All the collectors used in this study are shown in Table 6. It must be emphasised that all collector dosages were calculated based on active content.

Table 6: List of collectors used in this work

Collector	Abbreviation	Molecular Mass (g/mol)	Purity, % (w/w)
Sodium Ethyl Xanthate	SEX	144	100
Sodium Isobutyl Xanthate	SIBX	171	100
Potassium n-Butyl Xanthate	PNBX	188	96.8
Potassium Amyl Xanthate	PAX	199	98.2
Sodium Diethyl Dithiophosphate	Diethyl-DTP	208	43.5
Sodium Diethyl Dithiocarbamate	Diethyl-DTC	171	24.6

2.5 Collector dosage calculations

The Brunauer–Emmett–Teller (BET) method was used to determine the surface areas of all the mineral samples, both the – 38 µm and the + 38–106 µm size fractions. The BET method is premised on the physical adsorption of gas molecules on a solid surface as a basis to approximate the specific surface area of a given material. The results are as shown in Table 7.

Collector dosages for both microcalorimetry and microflotation were calculated using the BET surface areas above and the cross Sectional area of the head-group of the collector molecule, 28.8A° (Grano et al. 1997). In these calculations, it was assumed that all the minerals were

100% pure for simplicity. It is assumed that the xanthate, dithiocarbamate and the dithiophosphate molecules have the same cross sectional area of the thiol head-group. It must be noted that the total molar dosage was maintained constant for the collector mixtures.

Table 7: Surface area of the -38 µm and the +38-106 µm size fractions of all minerals

Mineral	**BET surface area (m^2/g)**	
	-38µm	**-106µm / +38µm**
Chalcopyrite	0.6678	0.3795
Galena	0.3477	0.1142
Pyrite	0.6213	0.3946
Pyrrhotite	1.2673	0.5799

While it is acknowledged that both the pH and ionic strength affect mineral-collector interactions (Manono et al. 2012; Corin and Wiese 2014) these two parameters were outside the scope of this work and thus were maintained constant. Deionised water was used as the medium in all experiments since it contains no impurities. A pH of 9.2 was chosen as a typical basic BMS-processing pH.

2.6 Microcalorimetry

A microcalorimeter is a thermodynamic and kinetic tool that is used to accurately monitor the heat produced by exothermic reactions as they happen in real time, even at sub monolayer collector coverages. It is extremely sensitive, measuring heats in the microwatt range and it can detect small changes associated with both physical and chemical reactions (Wadso and Goldberg 2001).

Isothermal titration microcalorimetry

Isothermal titration calorimetry (ITC) is gaining popularity as a general, reliable and rapid surface science tool. All physical and chemical interactions are accompanied by energy changes and hence can be measured by microcalorimetry. The reactions in the microcalorimetry occur under isothermal conditions.

The ITC microcalorimeter consists of sample and reference cells which are equal in volume and are contained in an adiabatic jacket. The two cells are maintained at the same temperature using a feedback mechanism shown in Figure 15. During the titration, the control loop monitors the temperature differences between both the reference and sample cells. Power is supplied to both cells to maintain a constant temperature difference. If an exothermic reaction occurs, the control loop stops heating the sample cell until the temperature of the reference cell is equal to that of the sample cell. The equipment then records the rate of heat, $\frac{\mathrm{dq}}{\mathrm{dt}}$ supply to the sample cell over time until the reference and samples are at the same temperature. A schematic of the microcalorimetry system is shown in Figure 15.

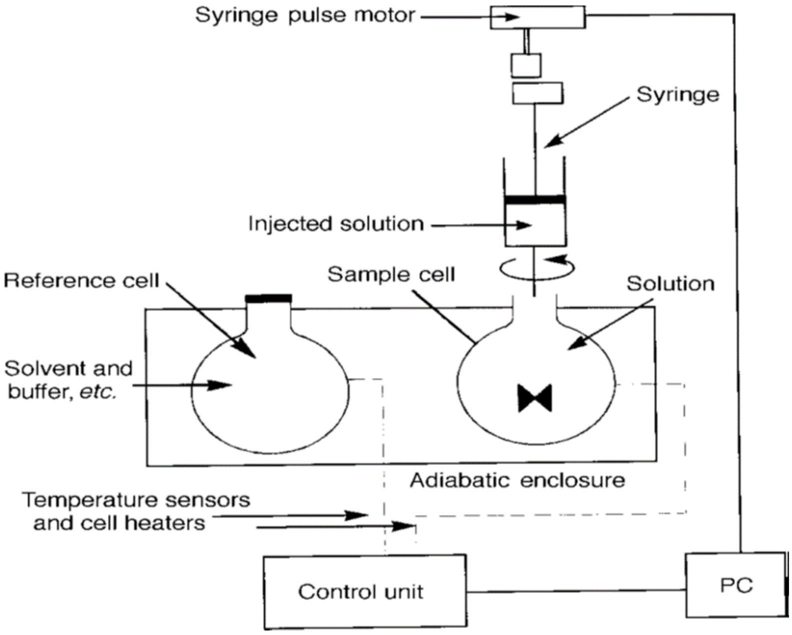


Figure 15: The microcalorimeter system, adapted from (Blandamer et al. 1998).

Measurement of reaction heats

The measured heat produced in a microcalorimeter is a sum total of three elements, namely:

1. Heat from the interaction between the substrate and the ligand, H_1
2. Heat of dilution of ligand when exposed to a larger volume in the reaction vessel, H_2
3. Mechanical effects of mixing, stirring and phase changes, H_3

In the majority of titration microcalorimetry experiments, the heat produced by processes like stirring, mixing and phase changes is negligible (Zogg et al. 2004; Wadso and Goldberg 2001). Thus H_3 is equal to zero. As a result, the enthalpy of reaction, ΔHr is given by:

$$\Delta H_r = H_1 + H_2 \tag{12}$$

For this reason, a blank experiment is performed in which the ligand is diluted into a solution with no substrate present. This establishes the value of H_2, which is subtracted from the total heat of interaction, ΔH_r, to give the heat of interaction between substrate and ligand, H_1.

TAM III Microcalorimeter

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. The instrument has a controlled temperature liquid bath that can be controlled with a temperature precision of 0.0001°C. The microcalorimeter is equipped with a titration ampoule accessory which comprises of a reaction vessel and gold impellor. The mineral slurries are loaded into the reference and sample cells and the titration assembly unit is loaded into the microcalorimeter. The titrant is injected using a micro-syringe driven by a motor. The TAM III calorimeter, titration ampoule accessory and the reaction vessel with impellor are shown in Figure 16.

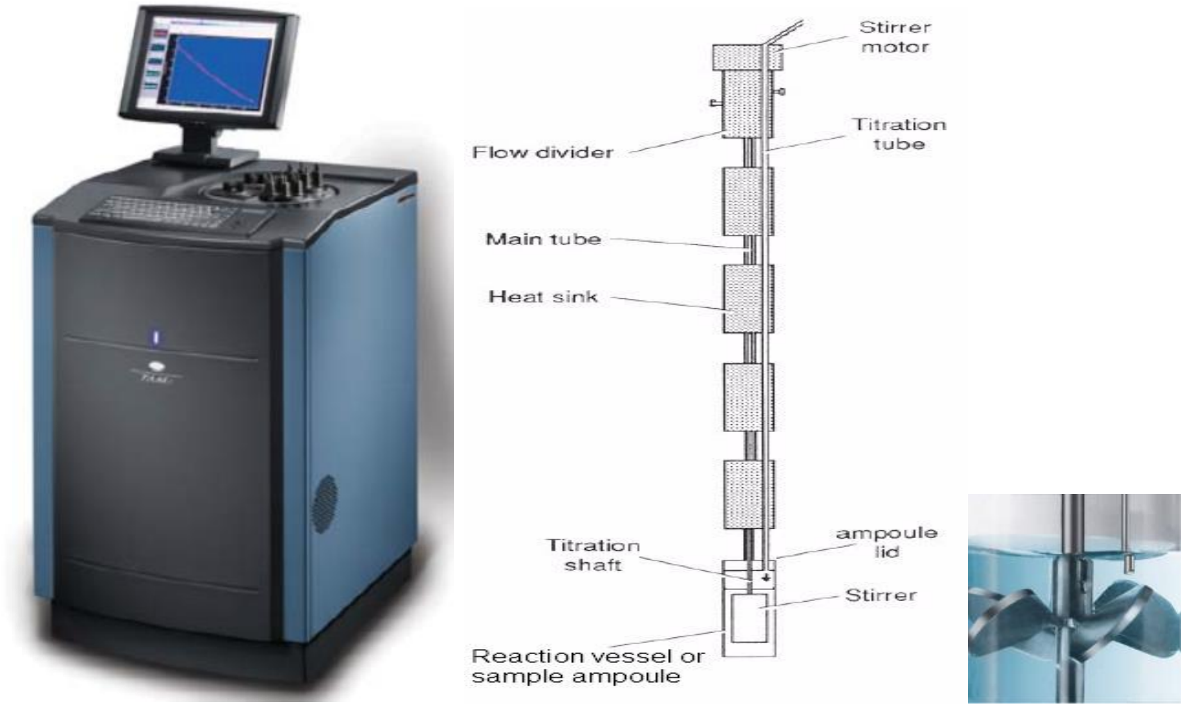


Figure 16: The photograph of the TAM III microcalorimeter, titration ampoule accessory and reaction vessel with impellor.

2.6.1 Microcalorimetry experimental procedure

Validation

Chemical validation was conducted on the equipment using the binding reaction between Ba^{2+} and the macrocyclic compound 18-crown-6. A heat of reaction of -31.42 kJ/mol is assigned to this reaction (Wadso and Goldberg 2001). This test reaction was performed twice and an average of ΔH of -32.46 ± 0.28 kJ/mol was obtained, which is within 3.2% of the assigned value and less than 1% relative standard deviation, which was considered adequate.

Calibration

The equipment was dynamically calibrated against a known power input. The calibration process gives three outputs:

1. The gain factor – the relative deviation from a temperature-dependent calibration constant;
2. Two time constants ($\tau 1$ and $\tau 2$) – The heat flow monitored by the heat detector and the actual heat rate produced by the sample are different because of the heat capacity and heat transfer from the sample to the surroundings. Time constants correct for these differences.

Experimental procedure

0.2 ± 0.0005 g of the mineral samples were weighed into the sample and reference ampoules. 0.7 mL of pH 9.2 water was added to each ampoule and sonicated for 30 seconds to disperse the slurry before being loaded into the microcalorimeter. The collector solution was loaded into the titration syringe and 2 µL, a volume equivalent to 0.25 monolayer, was injected every hour. 20 to 25 injections were performed, which are equivalent to 5 to 6 monolayers.

The output of the TAM III microcalorimeter is in the form of a power versus time curve which appears as peaks. The peaks are positive for exothermic reactions while they are negative for endothermic reactions. Each peak corresponds to the addition of an aliquot of titrant. The specific enthalpies of adsorption per injection were calculated by integrating the area under each peak and dividing it by the number of moles of collector contained in each injection.

The power versus time curves and the associated enthalpy as a function of collector surface coverage are shown in the Appendices Section. The enthalpy of adsorption corresponding to 50% pseudo-monolayer coverage is reported in this thesis. Half a monolayer was chosen because, above a monolayer , the collector ions are reported to adsorb as hemi-micelles in reverse orientation to form multilayers (Goh et al. 2008; Rao 2004; Bulatovic 2007) which is a very complicated situation beyond the scope of this study. 50% surface coverage was also chosen as the collector dosage for microflotation experiments to allow direct comparison between the calorimetric results with the microflotation results.

2.6.2 Blank experiments

The heats of dilution of the collectors used in this study were measured using the TAM III microcalorimeter. The source of the heat produced can be attributed to the dilution effects when the collector molecules are exposed to a larger volume in the reaction vessel. It is thus important to decouple the heats of dilution from the enthalpy of adsorption arising from the collector-mineral interaction. The results for the blank experiments for the various collectors are shown in Figure 17.

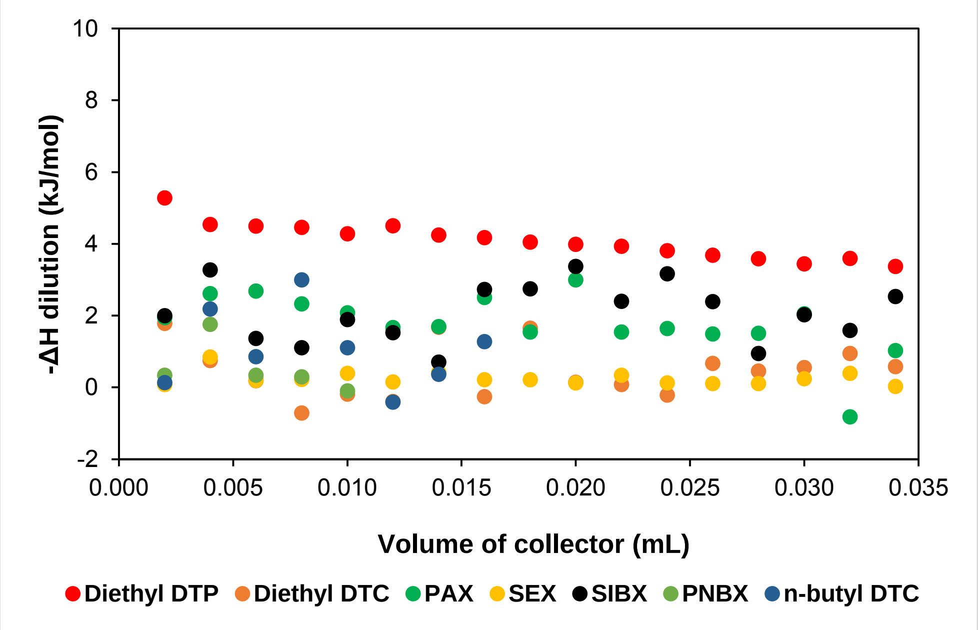


Figure 17: Heats of dilution for all the thiol collectors concerned in this work.

Figure 17 shows the variation of the dilution heats of the thiol collectors used in this study as a function of the volume of the collector added to the reaction vessel. It can be seen that the diethyl-DTP has the greatest heat of dilution. SIBX, n-butyl DTC and PAX had variable, but lower heats of dilution. The resolution of the peaks becomes difficult at low dilution heats. PNBX, SEX and diethyl-DTC had very small heats of dilution. It must be emphasised that all the enthalpies of adsorption reported in this work have been corrected for the dilution heats.

In most cases, apart from the case of DTP, the heat produced by the blank experiment was at least 10 to 20 times less than that of the interaction between the collector and the minerals.

2.6.3 Calculation of the enthalpy of adsorption corresponding to 50% monolayer coverage

The output of the TAM III microcalorimeter is a power vs time curve, which appears in the form of peaks. Each peak is produced by an injection of titrant. For the purpose of demonstration, the interaction of pyrrhotite with PAX was characterised using the TAM III microcalorimeter. The power vs time curve exported from the TAM III Assistant Software is shown in Figure 18 where each peak corresponds to a collector injection equivalent to 25% pseudo-monolayer coverage. Each injection was 2 μL containing 3.66 x 10^{-7} moles of PAX.

The area under each peak was integrated to calculate the specific enthalpy per injection, the area being equal to Watts x time which is Joules.

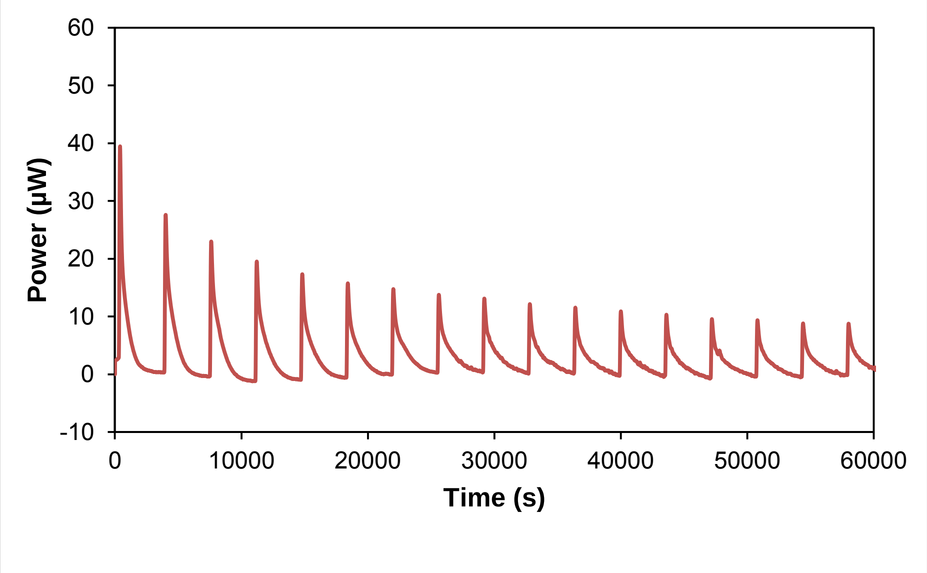


Figure 18: Power versus time curve for the pyrrhotite – PAX system at a pH of 9.2

However from Figure 17, PAX was shown to produce a small heat of dilution. This was subtracted from the integrated heats for every injection. The resulting enthalpy is the enthalpy of adsorption of the interaction between PAX and the pyrrhotite surface. To obtain a molar enthalpy of adsorption, the enthalpy in Joules is divided by the number of moles of collector that is added. A plot of the molar enthalpy of adsorption as a function of pseudo-monolayer coverages is shown in Figure 19.

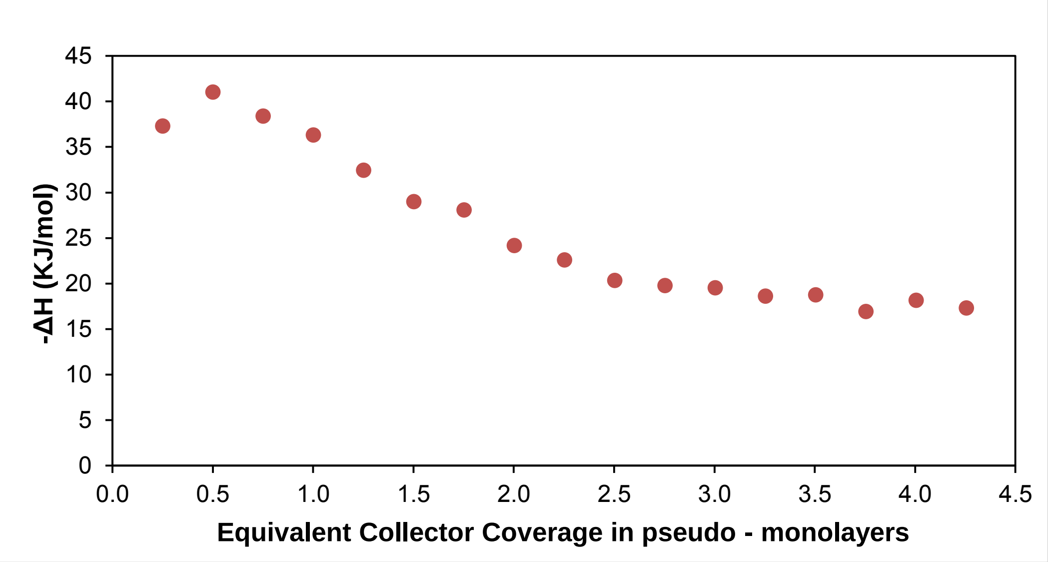


Figure 19: The enthalpy of adsorption as a function of fractional coverage for the pyrrhotite – PAX system at a pH of 9.2

As mentioned earlier, this thesis only focusses on the enthalpy of adsorption corresponding to 50% pseudo-monolayer coverage. This value is calculated using the area under the first and second peaks which were 13.9 mJ and 15.0 mJ in this case. As can be seen from the plots these equate to 0.5 pseudo-monolayer coverage. The two values were added to give a total of 28.9 mJ for the first two injections. This was normalised by dividing by the total number of moles corresponding to 50% monolayer coverage which was 7.32 x 10^{-7} moles. A value of -39.2 kJ/mol was obtained, which corresponded to 50% pseudo-monolayer coverage.

2.7 pH control

A suitable pH modifier was needed which would not affect the targeted mineral-collector interactions. Both a 0.05M sodium tetraborate buffer and NaOH were investigated as suitable pH modifiers.

The raw data for the interaction of both the NaOH and tetraborate buffer with distilled water is shown in Figure 20.

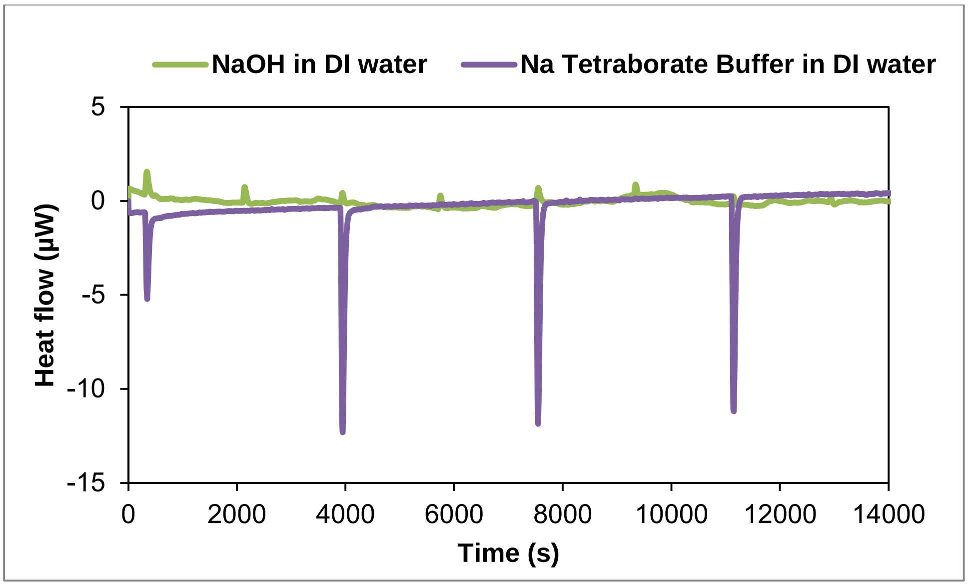


Figure 20: Raw data for the interaction of sodium tetraborate buffer and sodium hydroxide

The results in Figure 20 show that the sodium tetraborate buffer had a significant endothermic peak, resulting from its interaction with water. However, sodium hydroxide showed very little interaction with water. Thus, the tetraborate buffer would interfere with the collector-mineral interactions in that the measured heats would be the sum of the mineral-collector interactions, as well as the water-tetraborate buffer interactions. To verify this hypothesis, the effect of both sodium hydroxide and sodium tetraborate on the interaction of chalcopyrite with DTC was conducted. The raw data and the resulting integrated heats trend are shown in Figure 21 and Figure 22 respectively.

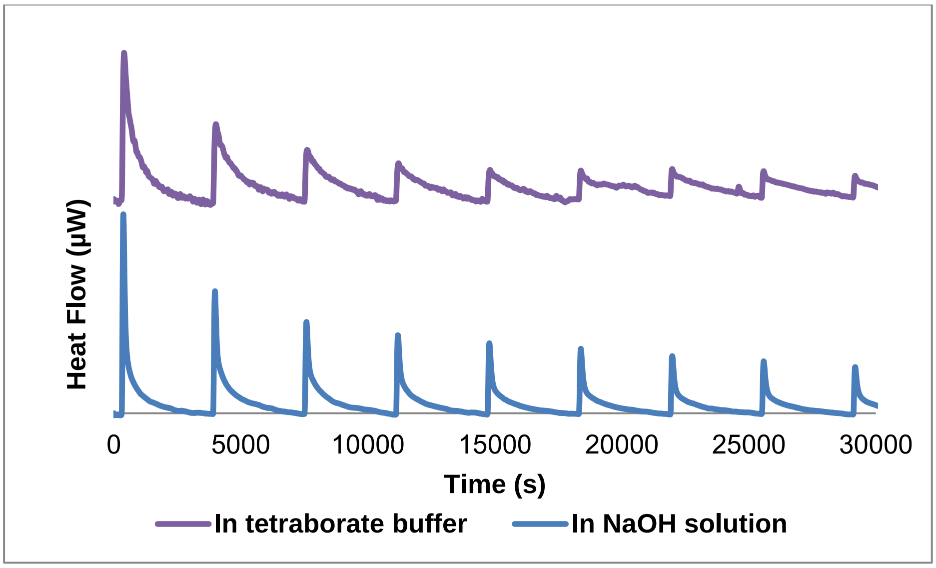


Figure 21: Raw data for the interaction of chalcopyrite and diethyl-DTC in the presence of sodium tetraborate buffer and sodium hydroxide, pH 9.2.

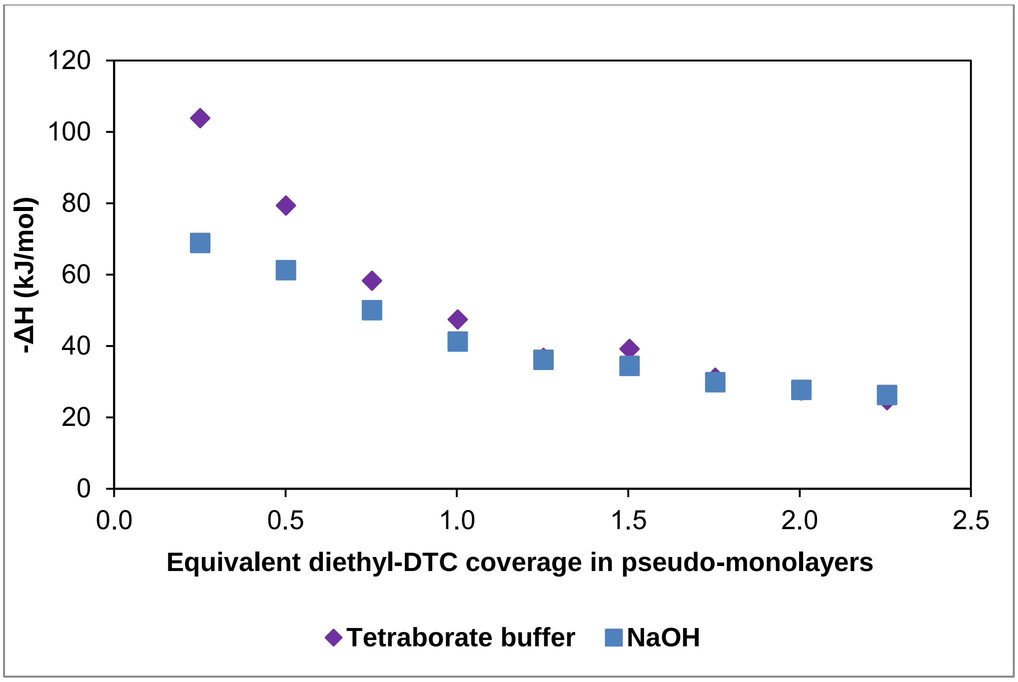


Figure 22: Thermograms for the interaction of chalcopyrite and diethyl-DTC in the presence of sodium tetraborate buffer and sodium hydroxide, pH 9.2

The results in Figure 21 show that the tetraborate buffer influenced the quality of the raw data obtained from the microcalorimeter. The heat evolution continued over a longer period than that for sodium hydroxide. This resulted in a larger enthalpy of adsorption in buffer solution than in sodium hydroxide as shown in Figure 22. The differences were more pronounced in the sub-monolayer region.

It could be concluded that the tetraborate buffer interfered with the mineral-collector interactions. The same results were reported by Wang (1996) who found that the tetraborate was not an inert buffer, but that it reacted strongly with the pyrite surface, promoting pyrite oxidation in the process. In light of these preliminary investigations, sodium hydroxide was chosen as the pH modifier throughout the investigations.

2.8 Microflotation

This is a technique used to measure the hydrophobicity arising from the mineral-collector interactions. Thus, it measures one of the sub-processes in mineral flotation: the particle-bubble interaction. The greater the hydrophobicity of the particle, the greater the recovery of bubble-particle aggregates. There is no froth present, which may reject particles above a certain optimum hydrophobicity. All other parameters such as bubble size, collector concentration and energy input being constant, the recovery from a microflotation experiment gives an indication of the hydrophobicity of the particle. Thus the microflotation technique is a hydrophobicity meter. The UCT microflotation rig is shown in Figure 23.

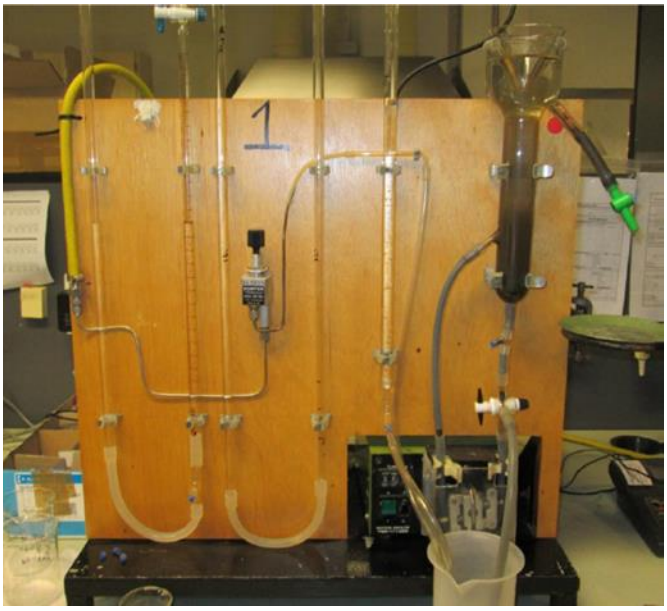


Figure 23: The UCT microflotation rig

A UCT microflotation rig was used to determine the flotation response and the floatability of the pure sulphide minerals by measuring the relative hydrophobicity of different mineral surfaces (Bradshaw and O'Connor 1996). A schematic of the microflotation cell is shown in the Figure 24.

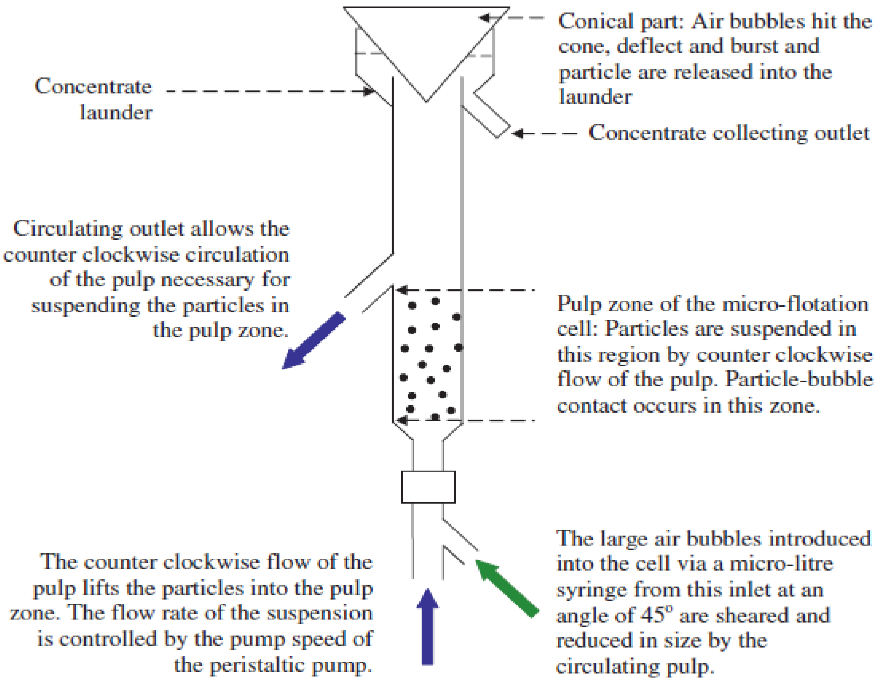


Figure 24: Schematic of the microflotation cell used in this study, adapted from Min and Nguyen (2013).

The microflotation cell consists of conical tapered cylindrical tube with a concentrate launder at the top. Synthetic air is introduced at the bottom of the cell through a needle, producing a single stream of bubbles in the cell. The bubbles produced collect hydrophobic particles in the pulp zone as they rise to the top of the cell. The particle-bubble aggregates are deflected by the cone at the top of the cell, dislodging mineral particles in the process. The mineral particles are then collected in the concentrate launder. The peristaltic pump keeps the particles in suspension.

2.8.1 Procedure for microflotation tests.

3 g of the sulphide mineral was weighed out into a beaker; 50 mL of NaOH stock solution at pH 9.2 was added and sonicated for 5 minutes to disperse the slurry, destroy agglomerates and to remove ultra-fines from the mineral surfaces.

The microflotation cell, with a volume of 250 cm^3, was filled with pH 9.2 solution to the recycle point and the recycle pump was started to purge air out of the system. The slurry was then poured into the microflotation cell and the cell was topped up with pH 9.2 water to the mark. Collector solution equivalent to 50% theoretical surface coverage was dosed by means of an auto pipette.

This value of coverage was chosen because some scoping tests conducted by Castelyn (2012) showed that this is the optimum collector dosage where the effect of collector addition could be observed. Dosages that are too high swamp the mineral surface with collector and differences between different strengths of collector or collector mixtures may go unobserved. SEX coverage as low as 10% of a monolayer produces a significantly high contact angle and flotation recovery of galena (Prestidge and Ralston 1996). Buckley and Woods (1997) also reported that a high galena and chalcocite recovery was produced by SEX coverages in the sub monolayer region with less than 0.2 coverage producing 50% recovery and half-monolayer coverage producing 90% recovery.

The collector conditioning time was 6 minutes. It is assumed that this time would allow the reaction between the mineral surface and the collector to proceed to completion before flotation is commenced. Air at a flow rate of 10 ml/min was introduced from the bottom of the cell. Concentrates were collected at 2, 6, 12 and 20 minutes.

2.8.2 Flotation data analysis

Chemical analysis

When mixtures of chalcopyrite and pyrite were floated, chemical analysis was conducted to determine the Cu and Fe content in the concentrates and tails. A standard mass of concentrate of 50.0 mg was microwave digested and analysed by atomic absorption spectroscopy. The results were then scaled up to determine the actual mineral compositions in the concentrates and tails assuming a chemical composition of chalcopyrite to be $CuFeS_2$ and pyrite to be FeS_2. The following equations were used to convert the assays to mineral compositions. Detailed calculation sheets are presented in the Appendix.

The number of moles of copper and the mass of chalcopyrite are calculated as follows:

$$\mathrm{n(Cu)} = \frac{\mathrm{m(Cu)}}{63.5} \tag{13}$$

$$\mathrm{n(Ccp)} = \mathrm{n(Cu)} \tag{14}$$

$$\mathrm{m(Ccp)} = \mathrm{n(Ccp)} * 183.3 \tag{15}$$

where *m(Cu)* is the mass of copper in the sample;

m(Ccp) is the mass of chalcopyrite in the sample;

n is the number of moles.

It must be noted that the total iron assayed in the concentrates, Fe_t is the sum of the iron associated with the pyrite, Fe_{Py} and the iron associated with the chalcopyrite, Fe_{Ccp}.

The total number of moles of iron assayed in the concentrates, *n(Fe_t)* was calculated as follows:

$$\mathrm{n(Fe_t)} = \frac{\mathrm{m(Fe)}}{55.8} \tag{16}$$

The iron associated with chalcopyrite, *Fe_{Ccp}* was calculated based on the fact that the stoichiometric ratio of Cu to Fe in chalcopyrite is 1:1. The calculation was as follows:

$$\mathrm{n(Fe_{Ccp})} = \mathrm{n(Cu)} \tag{17}$$

Therefore the number of moles of iron associated with pyrite, *n(Fe_{Py})* was calculated as follows:

$$\mathrm{n(Fe_{Py})} = \mathrm{n(Fe_t)} - \mathrm{n(Fe_{Ccp})} \tag{19}$$

Thus the mass of the recovered pyrite, *Py** was calculated as follows:

$$\mathrm{m(Py^*)} = \mathrm{n(Fe_{Py})} * 119.8 \tag{20}$$

Assuming a homogeneous mixture in the sample, the actual amount of chalcopyrite and pyrite in the concentrate were obtained by scaling up.

$$\mathrm{m(Ccp)_c} = \frac{\mathrm{m(Ccp)} * \mathrm{M_c}}{\mathrm{M_s}} \tag{21}$$

$$\mathrm{m(\ Py^*)_c} = \frac{\mathrm{m(Py^*)} * \mathrm{M_c}}{\mathrm{M_s}} \tag{22}$$

Where *$m(Ccp)_c$* is the actual mass of Ccp reporting in the concentrates;

$m(Py^*)_c$ is the actual mass of Py recovered from original pyrite feed reporting in the concentrates;

M_c is the total mass of the concentrate;

M_s is the mass of the sample used for chemical analysis

The above calculations were repeated in order to get the chalcopyrite and pyrite content in the tailings. *$m(Ccp)_{ta}$* and *$m(Py^*)_{ta}$* were used to denote the actual mass of chalcopyrite and pyrite reporting in the tailings respectively;

The recoveries were calculated using the following equations:

$$R_{Ccp} = \frac{M(Ccp)_c}{M(Ccp)_c \ + M(\mathrm{Ccp})_{ta}} * 100\% \tag{23}$$

$$R_{Py} = \frac{M(\mathrm{Py}*)_c}{M(Py*)_c \ + M(\mathrm{Py}*)_{ta}} * 100\% \tag{24}$$

2.9 Microflotation kinetics

The overall micro-flotation rate constants, *k* were fitted using least squares non-linear regression analysis according to the first order kinetics equation as follows:

$$\mathrm{R} = \mathrm{R_{max}}\left(1 - \mathrm{e^{-kt}}\right) \tag{25}$$

where *t* is the flotation time (min); *R* is the recovery of the mineral and R_{max} is the maximum possible recovery of the mineral. The Excel Solver function was used for curve fitting.

2.10 Investigation of the use of collector mixtures

For both microcalorimetry and microflotation, SEX: diethyl-DTC collector mixtures with 90:10 and 70:30 mole ratios were used. The total molar dosages were constant for all the experiments at a 50% monolayer mineral surface coverage. Two collectors were pre-mixed and added simultaneously in both microcalorimetry and microflotation experiments.

2.11 Investigation of mineral-mineral mixtures

The chalcopyrite and pyrite were mixed to simulate a realistic ore, which is found as an association of sulphide minerals. The calculations ensured that both pyrite and chalcopyrite contributed equal surface areas to the total available surface area in the mineral mixtures both for microcalorimetry and microflotation. The mineral mixture comprised of 51:49 wt% chalcopyrite and pyrite respectively. It follows that the 0.2000 g mineral mixture prepared for microcalorimetry comprised of 0.096 g and 0.104 g of chalcopyrite and pyrite respectively. The 3 g mineral mixture prepared for microcalorimetry also comprised of 1.53 g and 1.47 g of chalcopyrite and pyrite respectively. The same procedure for mineral mixture preparation was also used by (Rao and Finch 1988; Smart 1991).

CHAPTER 3: RESULTS

Introduction

This Section of the thesis presents the results from the microcalorimetry and microflotation experiments conducted. Different sulphide minerals were contacted with different single thiol collectors. Single sulphide minerals were also contacted with collector mixtures and mixed minerals with single collectors.

The objective of this thesis was to investigate how the collector chemical structure (i.e. alkyl chain length and ligand type) influenced the enthalpy of adsorption of the collector onto the minerals indicated and how the use of these collectors influenced microflotation recoveries. In order to ensure that the adsorption studies were indeed measuring the collector-mineral interaction, the enthalpy of adsorption corresponding to approximately ~50% monolayer coverage by the collector was determined. A collector dosage equivalent to ~50% monolayer coverage was also used throughout all the microflotation experiments. The effect of adsorbing collectors onto mixtures of minerals on the enthalpy of adsorptions and microflotation recoveries was also investigated.

When mixtures of collectors (SEX and DTC) were used the first number in the collector ratios represent the molar percentage of SEX and the second represents the molar percentage of DTC.

The results are presented in the following order:

- Reproducibility tests to investigate the reliability of the measurements made in the TAM III microcalorimeter and the UCT microflotation rig.
- The effect of changing the alkyl chain length of the collector on the enthalpy of adsorption of different xanthate homologues on different sulphide minerals.
- The effect of changing the ligand type on the enthalpy of adsorption of different thiol collectors on different sulphide minerals. Diethyl-DTC and diethyl-DTP were chosen for this investigation using SEX as the reference case.
- The microflotation results obtained when investigating the effect of changing both alkyl chain length and ligand type on the recovery of different sulphide minerals.
- The microcalorimetric and microflotation results when collector mixtures were contacted with single minerals. SEX: diethyl-DTC collector mixtures with molar ratios of 90:10 and 70:30 were contacted with chalcopyrite. The single mineral – single

collector interactions were used as the reference case to assess the performance of collector mixtures.

- The thermochemical behaviour and microflotation results when using mixed minerals with single thiol collectors and SEX: diethyl-DTC collector mixtures with molar ratios of 90:10 and 70:30. Chalcopyrite-pyrite mixtures were also investigated in this work.

3.1 Microcalorimetry

3.1.1 TAM III Microcalorimetry reproducibility tests

It was important to conduct reproducibility tests in order to investigate the suitability and reliability of the equipment and the procedure used in a mineral processing environment since there have been only limited applications in studying collector – mineral interactions in this microcalorimeter. In order to investigate the reproducibility of the TAM III equipment, SIBX was adsorbed onto chalcopyrite. The experiment was conducted three times and the average enthalpy of adsorption was determined. The procedure used has been explained in Chapter 2. The results of this investigation are shown in Figure 25.

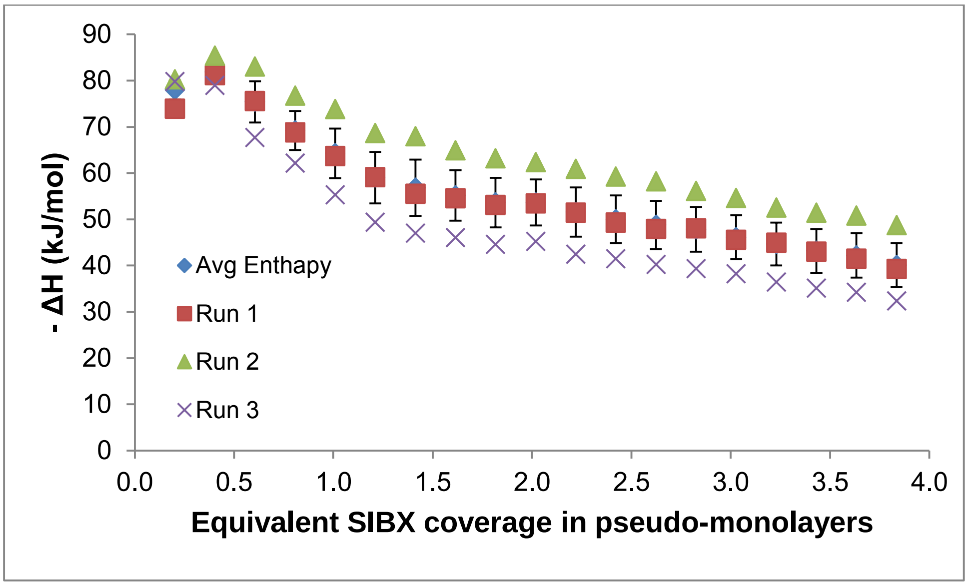


Figure 25: The thermograms for the TAM III reproducibility tests using the chalcopyrite-SIBX system. The x-axis indicates the equivalent pseudo-monolayer coverage amounts added.

The standard error (SE) was computed using the following equation:

$$\mathrm{SE} = \frac{\mathrm{SD}}{\sqrt{\mathrm{n}}} \tag{25}$$

where *SD* is the standard deviation of the population size;

n is the population size, e.g. $n = 3$ for triplicates.

Figure 25 shows that the spread gets greater at concentrations which would result in coverages greater than a monolayer. The reproducibility of collector-mineral systems was found to be between 2% and 6% relative standard error on each titration. For the purposes of this thesis, the enthalpies of adsorption corresponding to ~50% monolayer coverage were compared for different mineral-collector systems (Section 2.6.3). At this coverage, the instrument gave results which are acceptably reproducible (about 2% relative standard error), which makes the instrument suitable for the study. The heterogeneous nature of the mineral surface will inevitably result in such a relatively higher standard error for these types of systems. Nonetheless, the reproducibility provides the criterion against which differences in enthalpy from one system to another will be evaluated. Due to the fact that each experiment took around 25 hours to be completed, only one run was conducted for each investigation reported in this work.

3.2 Microflotation

The microflotation technique is used as an indicator of the hydrophobicity of a particle since it indicates the number/mass of particles which report to the concentrate in a froth-less environment as a result of the action which a collector has on enabling a particle to attach to a bubble. It is therefore suitable for determining the floatability of sulphide minerals resulting from the mineral-collector interactions. All other parameters such as bubble size, collector concentration and hydrodynamics being constant, the recovery from a microflotation experiment gives an indication of the hydrophobicity of the particle. The greater the hydrophobicity of the particle, the greater the recovery of bubble-particle aggregates. All experiments were conducted at pH 9.2 using sodium hydroxide as a pH modifier. Collectorless flotation was conducted for all the minerals to establish a baseline and to evaluate the contribution of the natural floatability of the sulphide minerals.

3.2.1 UCT Microflotation reproducibility tests

It was important to conduct reproducibility tests in order to investigate the suitability and reliability of the procedure and the equipment used for the microflotation tests. For the purpose of investigation of the UCT microflotation system, the natural flotation of pyrite, i.e. flotation without using any collector, was conducted thrice and the average recovery was computed. Concentrates were collected after 2,6,12 and 20 minutes and the measured final recoveries are shown in Table 8. The results in the form of recovery-time curves are shown graphically in Figure 26.

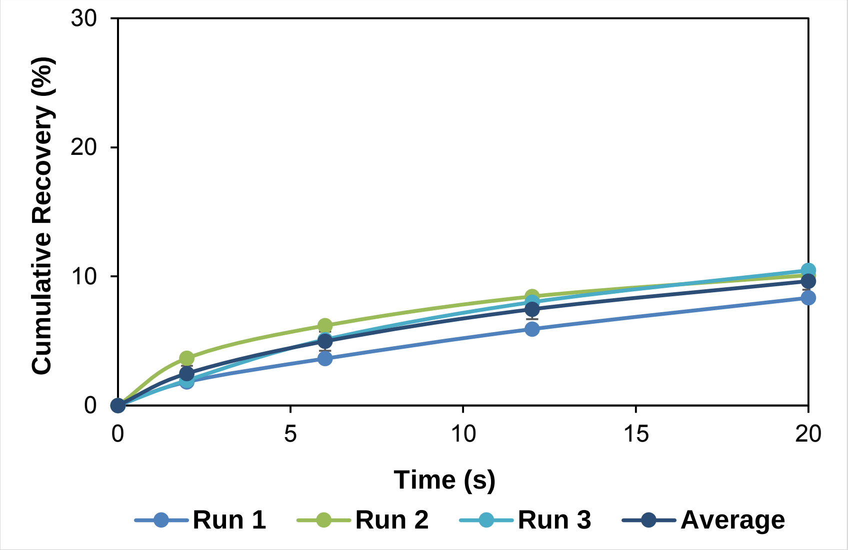


Figure 26: The investigation of the reproducibility of the UCT microflotation system using pyrite collectorless flotation.

Table 8: Pyrite recoveries and the standard deviation for collectorless flotation at pH 9.2

Time (min)	Pyrite Recovery (%)			Average Recovery (%)	Std Dev	Std Error
	1	2	3			
2	1.8	3.7	2.0	2.5	1.02	0.59
6	3.6	6.2	5.1	5.0	1.28	0.74
12	5.9	8.4	8.0	7.5	1.35	0.78
20	8.3	10.1	10.5	9.6	1.14	0.66

The results showed that both the UCT microflotation cell and the procedure gave reproducible results as evidenced by the low standard deviations, around 1.5%. Some error was expected due to differences in surface heterogeneities associated with different samples used. Experiments were done in duplicates for all microflotation tests in this work. Averages were then calculated and reported in this work. The effect of the collector would then be compared to the baseline. In all the microflotation experiments that were conducted, the relative standard error was always below ±2% and the associated errors bars were too small to be visible in the microflotation results. The actual errors are shown in Appendix B.

3.3 Effect of alkyl chain length of the collector on enthalpy of adsorption

3.3.1 Effect of chain length on the adsorption of xanthates on chalcopyrite

The initial set of experiments investigated the effect of chain length on the enthalpies of adsorption using different xanthate homologues. In the first instance the mineral used was chalcopyrite. The xanthates used, in order of decreasing alkyl chain length, were PAX (5C), PNBX (4C), SIBX (4C) and SEX (2C). It was assumed that all the thiol collectors used in this work have the same cross Sectional head area of 28.8A° (Grano et al. 1997) since this is a function of the specific ligand type and the sodium or potassium cations are unlikely to have any effect on the performance of the collector and played a role of spectator ions.

The enthalpies of adsorption corresponding to ~50% monolayer collector coverages were calculated as explained in Section 2.5. The results are shown in Figure 27.

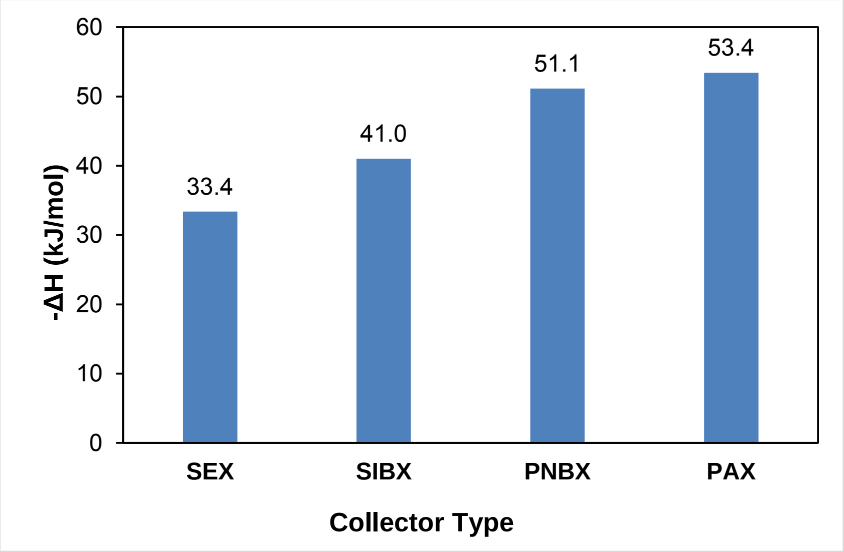


Figure 27: Effect of chain length (C2, iso-C4, n-C4, C5) on the enthalpy of adsorption of xanthate homologues on chalcopyrite, pH 9.2.

Figure 27 shows the variation of the enthalpy of adsorption with alkyl chain length, from SEX through to PAX. The measured enthalpies of adsorption were between – 30 kJ/mol and – 60 kJ/mol. Thermochemical measurements show that the enthalpy of adsorption decreased in the order: PAX > PNBX > SIBX > SEX.

3.3.2 Effect of chain length on the enthalpy of adsorption of xanthates on pyrite, galena and pyrrhotite

The effect of chain length of xanthate on the enthalpy of adsorption on pyrite, galena and pyrrhotite was investigated. This was conducted to investigate to what extent the results were mineral specific. SEX and PAX were chosen since they represent the two extreme samples in terms of alkyl chain length of those investigated in this work. Again the concentrations used equated to ~50% coverage. The enthalpies of adsorption results are shown in Figure 28.

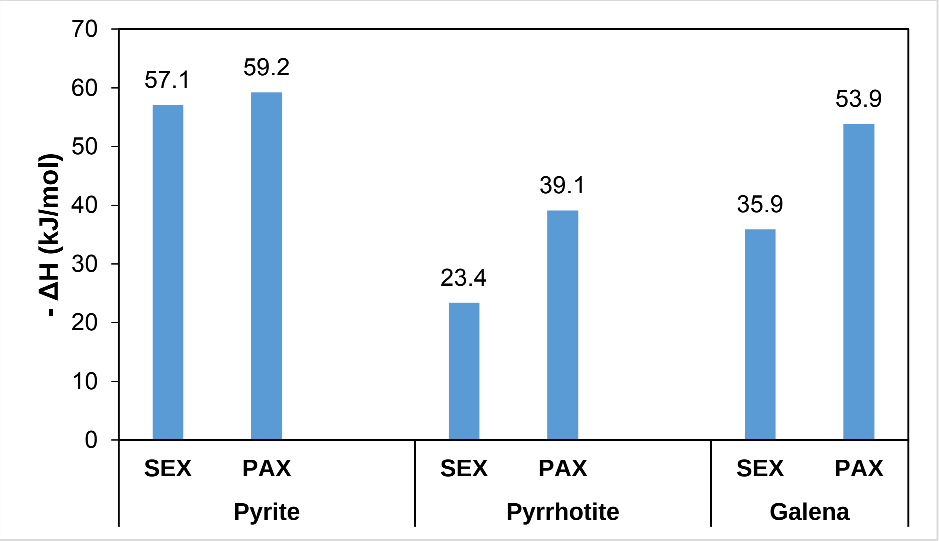


Figure 28: Effect of chain length on the enthalpy of adsorption of SEX and PAX on pyrite, pyrrhotite, and galena, pH 9.2.

Figure 28 shows that pyrite showed the most negative enthalpies of adsorption while pyrrhotite showed the least negative. It is interesting to note that the differences between the enthalpies of adsorption of SEX and PAX with the sulphide minerals was lowest for pyrite as compared to chalcopyrite, galena and pyrrhotite. The results showed that the enthalpy of adsorption was always more negative for PAX than for SEX. The results show that the enthalpy of adsorption became more negative with the alkyl chain length, independent of the mineral type. The differences between ethyl and amyl xanthates will be discussed in Chapter 4.

3.3.3 Effect of branching on the enthalpy of adsorption of collectors on chalcopyrite

The effect of the branching of the hydrocarbon chain length of the xanthates on enthalpy of adsorption of chalcopyrite was investigated. The collectors investigated were PNBX and SIBX.

The collectors have alkyl chain lengths with equivalent carbon numbers, viz. 4, though the PNBX has a straight chain and the SIBX has a branched chain. Thus this investigation provides an opportunity to investigate the effect of branching of the alkyl chain length on the enthalpy of adsorption where the carbon number of each alkyl group was the same. The enthalpies of adsorption corresponding to ~50% monolayer coverage for the interaction of PNBX and SIBX with chalcopyrite are shown in Figure 27.

Figure 27 shows that the PNBX produced a higher enthalpy of adsorption than SIBX on the chalcopyrite surface. The results show that the configuration of the alkyl chain length of the same carbon number has got an influence the enthalpy of adsorption.

The effect of the branching of the hydrocarbon chain length of the dithiocarbamates on enthalpy of adsorption on chalcopyrite was further investigated. The collectors investigated were diethyl-DTC and n-butyl DTC. The collectors have alkyl chain lengths with equivalent carbon numbers, viz. 4, though the two collectors have different chemical structures in the case of diethyl-DTC and n-butyl DTC. Thus this investigation is not a truly direct comparison. The enthalpies of adsorption corresponding to ~50% monolayer coverage for the interaction of diethyl-DTC and n-butyl-DTC with chalcopyrite are shown in Figure 29.

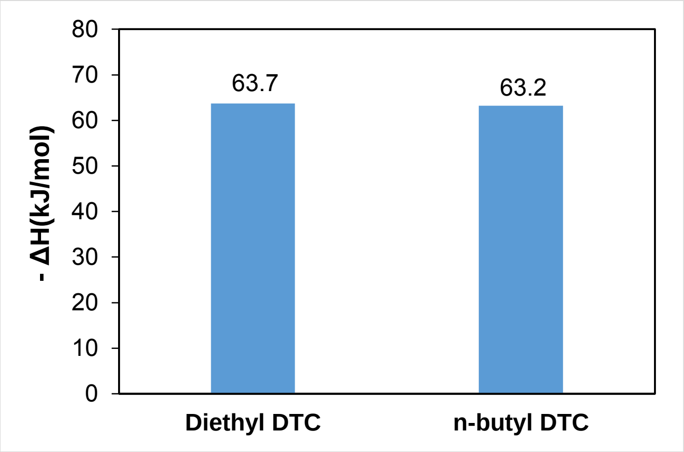


Figure 29: Effect of the branching of the hydrocarbon chain length of the dithiocarbamates on the enthalpy of adsorption on chalcopyrite, pH 9.2.

Figure 29 shows that the n-butyl DTC and diethyl-DTC produced essentially similar enthalpy of adsorptions on chalcopyrite despite having different alkyl chain length configurations.

3.4 Effect of ligand type on enthalpy of adsorption

This study investigated the effect of ligand type on the performance of thiol collectors by measuring the enthalpies of adsorption and the microflotation recoveries for different sulphide minerals. The alkyl chain length of the collectors was fixed and only the ligand type was varied. For this purpose, the dithiophosphates, xanthates and dithiocarbamates were used.

3.4.1 Effect of ligand type on the enthalpy of adsorption of thiol collectors on chalcopyrite, pyrite and pyrrhotite

The effect of ligand type on the enthalpy of adsorption on the chalcopyrite, pyrite and pyrrhotite was investigated. The collector concentrations used in this investigation equated ~50% monolayer coverage. The enthalpies of adsorption for the interaction of diethyl-DTP and diethyl-DTC with different sulphide minerals are shown in Figure 30.

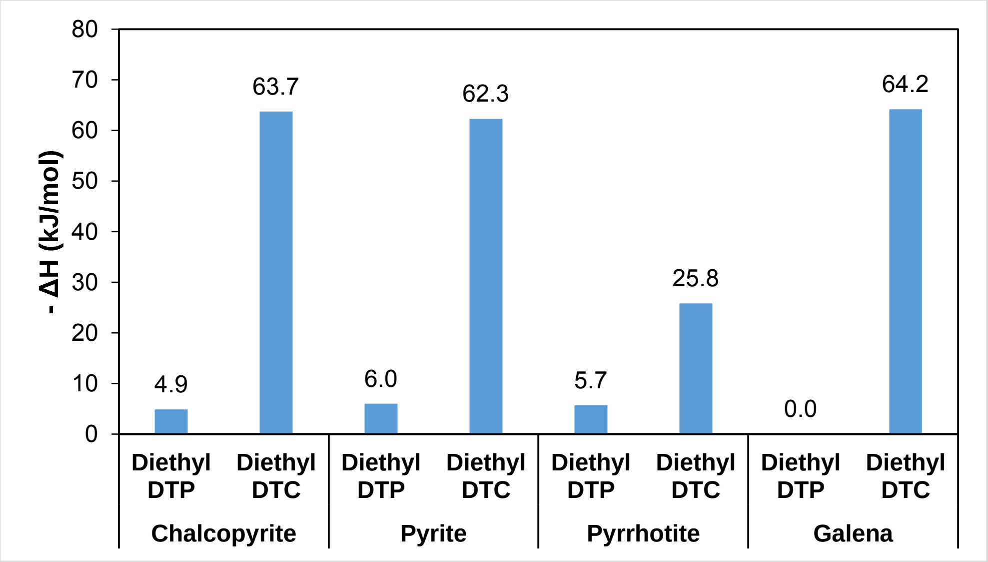


Figure 30: Enthalpy of adsorption for the interaction of diethyl-DTC and diethyl-DTP with galena, chalcopyrite, pyrite and pyrrhotite (pH 9.2).

Figure 30 shows the variation of enthalpy of adsorption with ligand type for different sulphide minerals. The results show that there was minimal enthalpy of adsorption when diethyl-DTP was dosed to all three sulphide minerals, the average value being -5 kJ/mol indicating there is hardly any surface reaction between the mineral and DTP. On the other hand the enthalpies of adsorption of diethyl-DTC with galena, chalcopyrite and pyrite were very high and quite similar being more negative than –60 kJ/mol which represented a greater exothermic reaction than for any of the xanthates. However, the enthalpy of adsorption of diethyl-DTC on pyrrhotite was less than –30 kJ/mol, approximately half that of chalcopyrite, galena and pyrite. It should thus be noted that diethyl-DTC interacts more strongly with all sulphide minerals when compared to DTP. However in the case of pyrrhotite both dithiocarbamates and xanthates have a relatively low enthalpy of adsorption compared to the other sulphides thus indicating that this sulphide behaves quite differently to the others studied here. This was similar to the observations for SEX and PAX on pyrrhotite (Figure 28).

It was clear from Figure 30 that diethyl-DTP was an outlier as it hardly reacted with all the sulphide minerals. It was thus deemed necessary to compare the enthalpies of adsorption for the interaction of PNBX and n-butyl DTC with chalcopyrite in a bid to further investigate the effect of ligand type on the enthalpy of adsorption. The two collectors have equal hydrocarbon chain length, viz. 4, but have different ligand types. The enthalpies of adsorption for the interaction of the two collectors with chalcopyrite are shown in Figure 31**.**

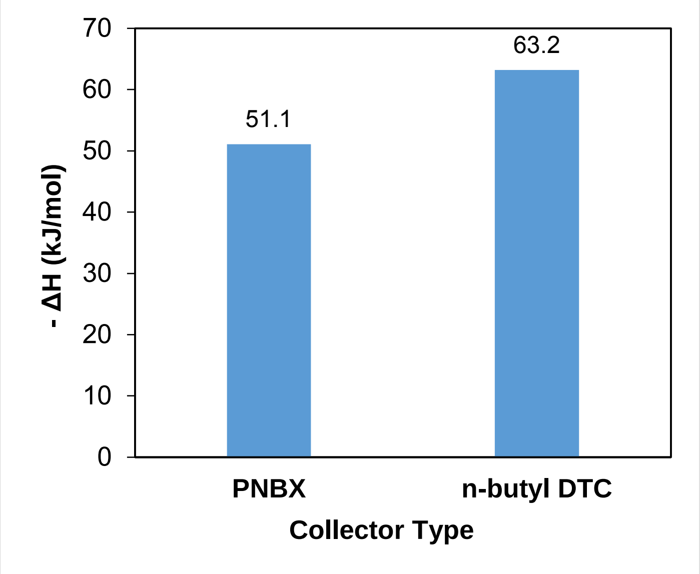


Figure 31: Enthalpy of adsorption for the interaction of PNBX and n-butyl DTC with chalcopyrite (pH 9.2).

Figure 31 shows the variation of enthalpy of adsorption with ligand type for the chalcopyrite surface. The results show that the enthalpy of adsorption for the interaction of n-butyl DTC with chalcopyrite was more exothermic than that of PNBX. This is despite the fact that the two collectors have equal hydrocarbon chain length. It should thus be noted that n-butyl DTC is a stronger adsorber than PNBX. It can be concluded that the ligand type of the collector has an effect on the enthalpy of adsorption.

3.5 Effect of collector chain length on the recovery of sulphide minerals

The second set of experiments investigated the effect of the alkyl chain length of the collectors on the floatability of the sulphide minerals. The UCT microflotation system was used to determine the pulp phase floatability of the sulphide minerals with thiol collectors of varying chain lengths. It must be stressed that the microflotation tests were conducted using collector dosages which were equivalent to ~50% collector coverage. The collectorless recovery of the sulphide minerals was first determined to establish a baseline against which the effect of collector addition would be assessed.

3.5.1 Effect of chain length of xanthates on recovery of chalcopyrite

Chalcopyrite was floated with xanthates of different alkyl chain length, from SEX through to PAX. Table 9 shows the collector dosages in equivalent grams per tonne of pure mineral. These calculations were based on the BET surface area analysis. It was assumed that all the xanthate homologues used in this work have the same cross-sectional head area and that the sodium or potassium anion did not have any influence on collector performance.

Table 9: Equimolar collector dosages corresponding to ~50% monolayer coverage (2.88 x 10^{-6} mol/m^2) in chalcopyrite flotation.

Collector	Dosage (*g/ton*)
SEX	158
SIBX	187
PNBX	206
PAX	218

The results of the microflotation tests conducted are presented graphically in Figure 32.

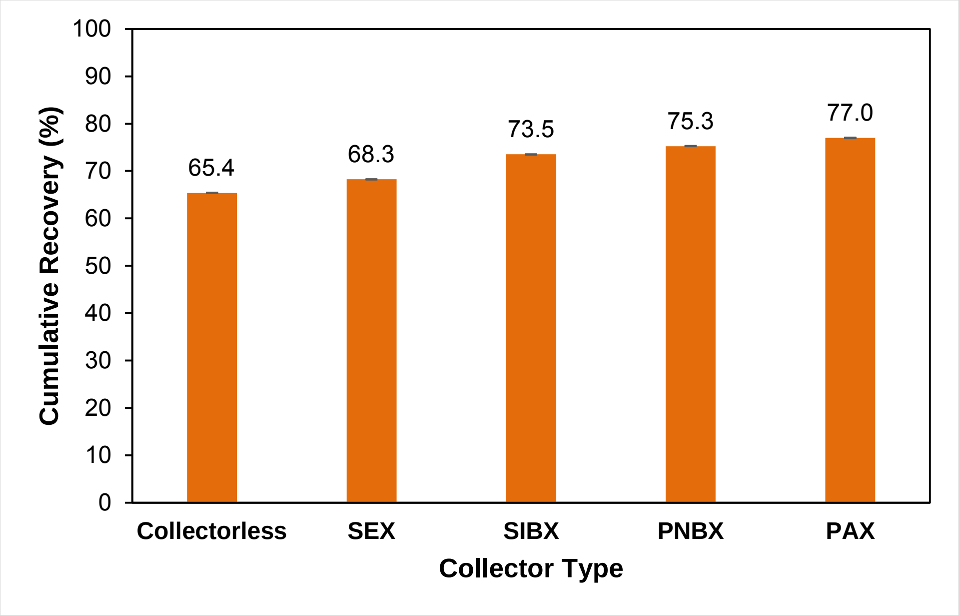


Figure 32: Effect of chain length of xanthate homologues on the recovery of chalcopyrite (pH 9.2; the relative standard error was always < ±1% hence errors bars are too small to be visible)

The results in Figure 32 show the variation of cumulative recovery with the alkyl chain length, from SEX to PAX. These results agree well with literature (Göktepe 2002; Ackerman et al. 1987; Fuerstenau 2005). The measured recoveries ranged from 65% to around 80%. It is also shown that the addition a collector in the pulp zone increased the microflotation recoveries since the recovery for the collectorless flotation was the least. The microflotation recoveries decreased in the following order: PAX > PNBX > SIBX > SEX. As expected, the results showed that PAX was the strongest collector, followed by the PNBX, SIBX and SEX. The results further show that despite having equivalent chain lengths, the PNBX gave marginally higher recoveries than the SIBX.

The recovery time curves for the flotation of chalcopyrite using the xanthate homologues are shown in Figure 33.

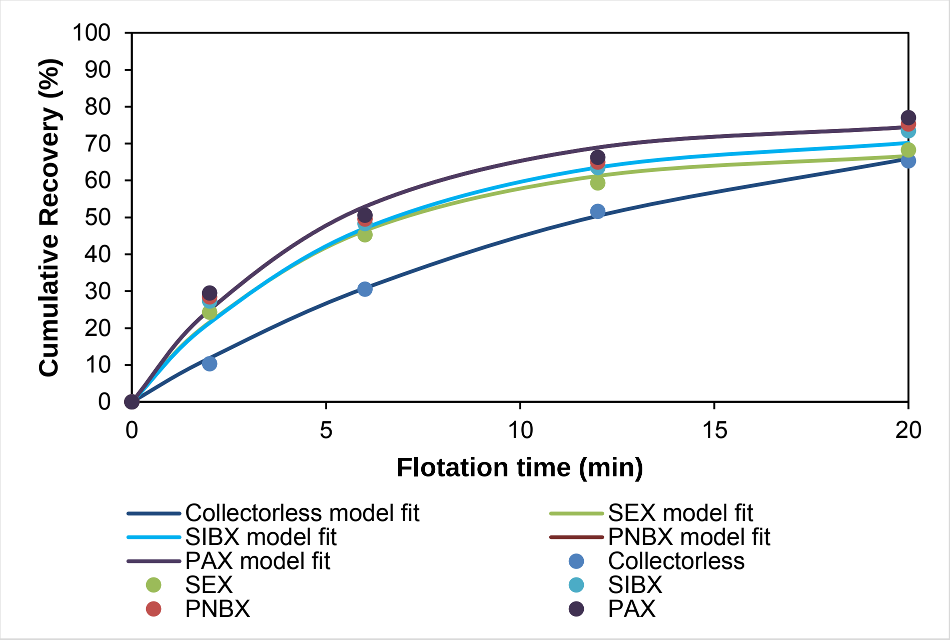


Figure 33: The recovery time curves for the flotation of chalcopyrite with xanthate homologues

The first order rate constant was determined using a standard first order model computed from the recovery-time results and are presented in

Table **10**. The results show that the first order rate constant did not differ much for SEX, SIBX and PAX but was relatively low for PNBX.

Table 10: First order rate constant for the flotation of chalcopyrite with different xanthate homologues.

Collector	First order rate constant, k (min^{-1})	Rmax
SEX	0.190	68
SIBX	0.199	76
PNBX	0.175	72
PAX	0.199	76

3.5.2 Effect of chain length of xanthate homologues on the recovery of galena, pyrite and pyrrhotite

The effect of xanthate chain length on the recovery of pyrite, galena and pyrrhotite was investigated. This was conducted to investigate whether the observed results on chalcopyrite were indicative of all sulphides or whether the results are mineral specific. SEX and PAX were chosen since they represent two extreme cases of the xanthates used in this work. The collector dosages in *g/ton* calculated for 50% pseudo-monolayer coverage are shown in Table 11.

Table 11: Collector dosages (in g/ton) calculated for the flotation of pyrite, pyrrhotite and galena with SEX and PAX. Collector dosages corresponded to ~50% monolayer coverage (2.88×10^{-6} mol/m^2).

	Collector dosages (*g/ton*) for different minerals		
Collector	Pyrite	Pyrrhotite	Galena
SEX	164	241	47
PAX	226	333	66

The results of the microflotation tests conducted for different sulphide minerals using SEX and PAX are shown in Figure 34.

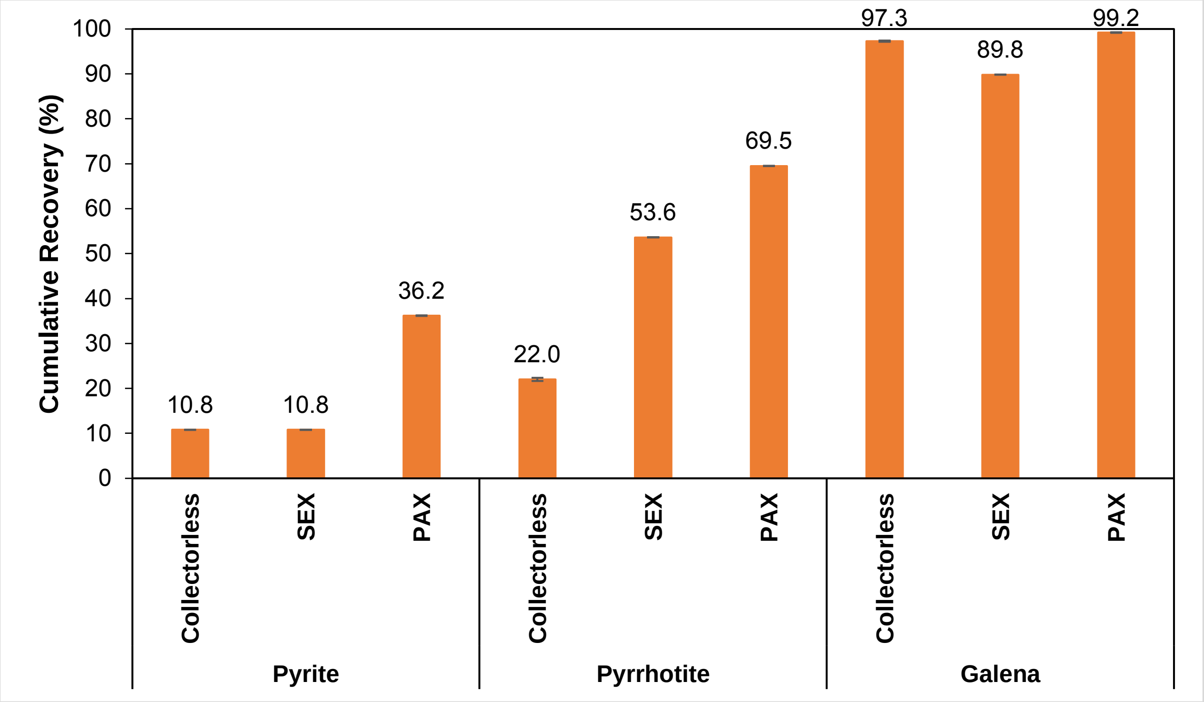


Figure 34: Effect of chain length of xanthate homologues on the recovery of pyrite, galena and pyrrhotite (pH 9.2; the relative standard error was always < ±1.5% hence error bars are too small to be visible)

Figure 34 shows that the recovery for the collectorless flotation was generally low as would be expected except in the case of galena where the collectorless recovery was remarkably high. For pyrite, the recovery for SEX was equal to that of the recovery of the collectorless flotation of pyrite. However, the addition of SEX improved pyrrhotite recovery significantly. As highlighted in Section 2.3, pyrrhotite was only about 60% pure. The 69.5% pyrrhotite recovery suggest that the floatable gangue in the form of talc reported to the concentrate. The results showed that PAX produced the highest recoveries in all cases. This was expected since it is known to be a strong collector of sulphides.

3.5.3 Effect of the branching of the hydrocarbon chain length of xanthates on the recovery of chalcopyrite

The effect of the branching of the hydrocarbon chain length of the xanthates on the recovery of chalcopyrite was investigated. The collectors investigated were PNBX and the SIBX. The collectors have the same alkyl carbon number, viz. 4 but the PNBX is a straight chain while SIBX is a branched chain. This investigation provides an opportunity to investigate the effect of branching of the alkyl chain length of constant carbon number on recovery. The equimolar collector dosages in *g/ton* calculated for ~50% pseudo-monolayer coverage are shown in Table 9.

Figure 32 shows that PNBX produced higher chalcopyrite recoveries than SIBX. This is despite the fact that the two collectors have equivalent hydrocarbon chain length. The results clearly show that the branching of the hydrocarbon chain length has an effect on the recovery of the sulphide minerals, similar to the effect on adsorption enthalpy.

The effect of the branching of the hydrocarbon chain length of the dithiocarbamates on the recovery of chalcopyrite was also investigated. The collectors investigated were diethyl-DTC and n-butyl DTC. The collectors have alkyl chain lengths with equivalent carbon numbers, viz. 4, though the two collectors have different chemical structures. Thus this investigation is not a truly direct comparison.

The equimolar collector dosages in *g/ton* calculated for 50% pseudo-monolayer coverage are shown in Table 12.

Table 12: Equimolar collector dosages (in g/ton) calculated for the flotation of chalcopyrite using n-butyl DTC and diethyl-DTC as collectors. Collector dosages corresponded to ~50% monolayer coverage (2.88×10^{-6} mol/m^2).

Collector	Collector dosages (g/ton)
Diethyl-DTC	187
n-butyl DTC	187

The microflotation results measured for the flotation of chalcopyrite using diethyl-DTC and n-butyl DTC are presented in Figure 35.

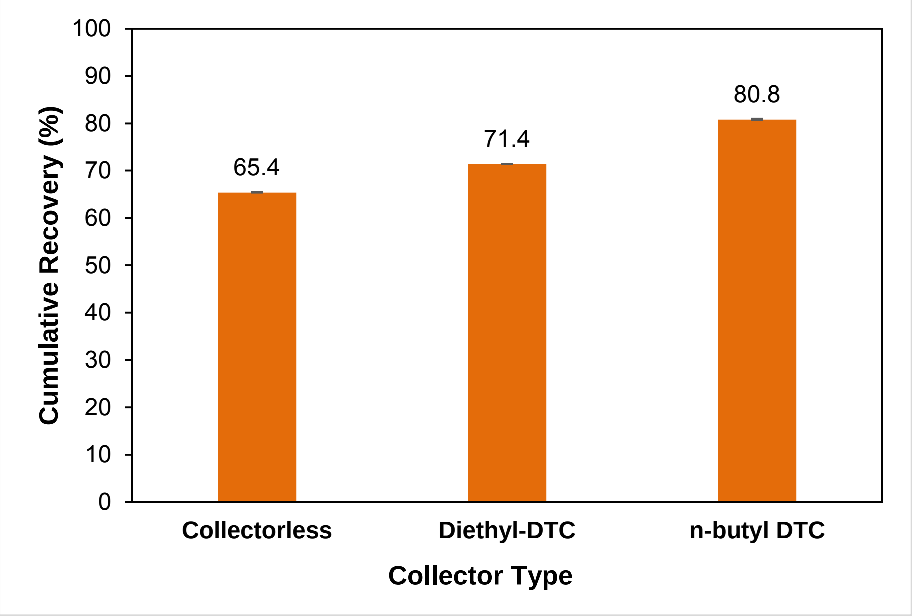


Figure 35: Effect of the nature of alkyl chain length of dithiocarbamates on chalcopyrite recovery. (pH 9.2, the relative standard error was always < ±1% hence error bars in are too small to be visible)

Figure 35 shows that the addition of the dithiocarbamates significantly improved the microflotation recoveries compared to the collectorless flotation baseline. The n- butyl DTC produced a higher chalcopyrite recovery than the diethyl-DTC. The effect of the branching of the alkyl chain will be discussed in Chapter 4.

3.6 Effect of ligand type on the floatability of sulphide minerals

The effect of ligand type on the recovery of sulphide minerals was further investigated. Similar to microcalorimetry, the collectors chosen for this investigation were the diethyl-DTC and diethyl-DTP. The collector dosages in g/ton corresponding to ~50% monolayer coverage for the flotation of different sulphide minerals with the diethyl-DTC and diethyl-DTP are shown in Table 13.

Table 13: Collector dosages (in g/ton) calculated for the flotation of sulphide minerals with diethyl-DTP and diethyl-DTC. Collector dosages corresponded to ~50% monolayer coverage (2.88 x 10^{-6} mol/m^2).

Collector	Sulphide Mineral			
	Chalcopyrite	Pyrite	Pyrrhotite	Galena
Diethyl-DTP	228	237	348	68
Diethyl-DTC	187	195	286	56

The microflotation results measured from the microflotation cell are shown in Figure 36.

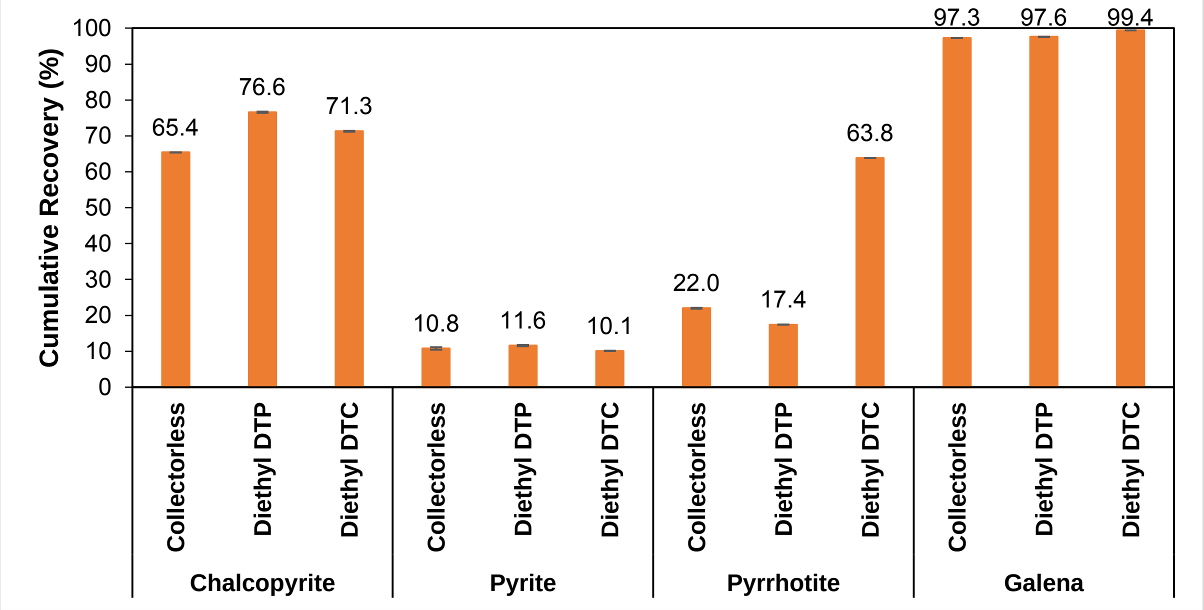


Figure 36: Microflotation recoveries for chalcopyrite, galena, pyrite and pyrrhotite using diethyl-DTC and diethyl-DTP as collectors (pH 9.2; the relative standard error was always < ±2% hence error bars are too small to be visible on the graphs).

Figure 36 shows that the recoveries when using diethyl-DTC and diethyl-DTP were very similar for chalcopyrite, galena and pyrite. However, pyrrhotite recoveries were different for the two collectors, despite the two collectors having the same hydrocarbon chains. As highlighted in Section 2.3, pyrrhotite was only about 60% pure. The 63.8% pyrrhotite recovery suggest that the floatable gangue in the form of talc reported in the concentrate. It seemed that pyrrhotite is a weakly floatable mineral and required a stronger collector (DTC) to cause an increase in recovery. Pyrite, on the other hand, is poorly floatable and neither the DTP nor the DTC was able to render it floatable. Chalcopyrite and galena were both strongly floating minerals and there was not a significant difference between the recovery when using DTP or DTC.

These results when associated with those shown in Figure 28, Figure 30 and Figure 34 provide an interesting insight into the respective roles of the ligand type vs the alkyl chain length of a thiol collector on the effectiveness of a collector for sulphide flotation. The results can provide insight into which of the two parameters - alkyl chain length or ligand type is more decisive in the flotation of sulphide minerals.

Furthermore, these results when associated with those in Figure 30 show that the enthalpy of adsorption values have no bearing on hydrophobicity i.e. DTP is a reasonably good collector despite extremely low enthalpies of adsorption with all the sulphide minerals.

Chalcopyrite was floated using PNBX and n-butyl DTC as collectors to further investigate the effect of ligand type on recovery. The microflotation results are shown in Figure 37**.**

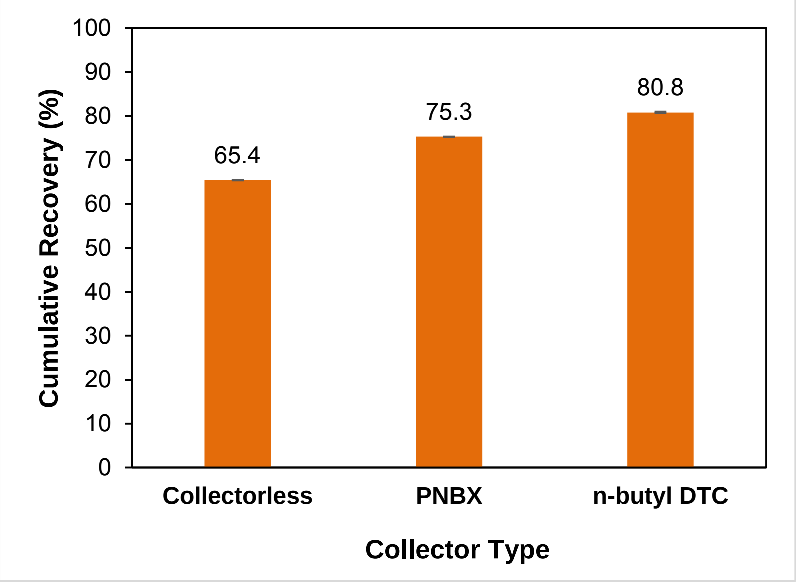


Figure 37: Microflotation recoveries for chalcopyrite using PNBX and n-butyl DTC as collectors (pH 9.2; the relative standard error was always < ±1% hence error bars are too small to be visible on the graphs).

Figure 37 shows the variation of the microflotation recoveries with ligand type in chalcopyrite flotation. The results show that the n-butyl DTC produced a higher chalcopyrite recovery than the PNBX. It should thus be noted that n-butyl DTC is a stronger collector compared to PNBX, despite the two collectors having equal hydrocarbon chain lengths. The results show that ligand type has got an effect on recovery.

3.7 COLLECTOR MIXTURES

In this study SEX: diethyl-DTC mixtures with mole ratios of 90:10 and 70:30 were adsorbed onto chalcopyrite. The collector mixture with a 70:30 mole ratio was chosen to investigate the effect of increasing the content of the secondary collector, in this case diethyl-DTC on the enthalpy of adsorption and microflotation recovery. It is important to note that although SEX is widely used in bulk sulphide mineral flotation because it is a relatively cheap and sufficiently powerful collector, it may not be very selective. This explains its use as a base or primary collector when formulating collector mixtures for use in sulphide mineral flotation while diethyl-DTC is used as a secondary collector in many plant operations. The objective of this part of the study was to compare the performance of collector mixtures to that of single collectors, as well as to investigate whether there is any synergistic effect observed. The enthalpies of adsorption and microflotation recoveries produced by collector mixtures were compared to those produced using single collectors.

3.7.1 Enthalpies of adsorption of collector mixtures on chalcopyrite

The enthalpies of adsorption corresponding to ~50% pseudo-monolayer coverage for the interaction of chalcopyrite with single and collector mixtures are shown in Figure 38. It must be emphasised that the total molar dosages used were constant for all the experiments, i.e. for single collectors and mixtures of collectors.

Figure 38 shows that the enthalpies of adsorption when using diethyl-DTC on its own or in SEX: diethyl-DTC mixtures with molar ratios of 90:10 and 70:30 were almost equal, viz. around -65 kJ/mol. The enthalpy of adsorption of SEX was lower than that of diethyl-DTC and of the two collector mixtures. However, the DTC was only present 30% or 10% of the total collector mole ratio. If the enthalpy of adsorption were purely additive, one would expect the enthalpy of the collector mixtures to be far lower (see Section 3.7.2). Therefore, this suggests that the collector mixtures have a synergistic affinity for the chalcopyrite surface.

It is clear that an increase in diethyl-DTC content above 10% did not result in any greater adsorption since the collector mixtures with mole ratios of 90:10 and 70:30 showed similar enthalpy of adsorption.

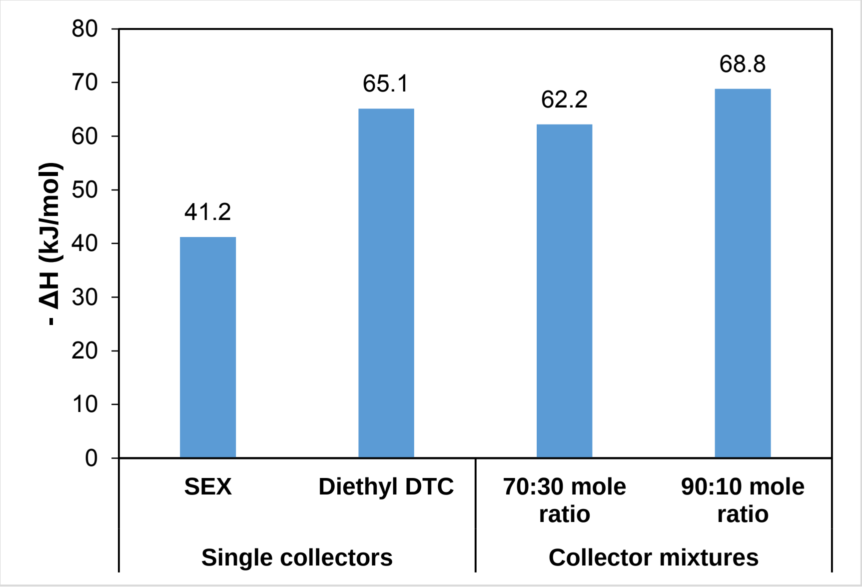


Figure 38: Enthalpies of adsorption of SEX and diethyl-DTC and their mixtures on chalcopyrite, the first number in the ratio represent molar % of SEX while the second represent the molar % diethyl-DTC (~50% pseudo-monolayer collector coverage; pH 9.2)

3.7.2 Investigation of synergism from thermochemical measurements

In order to investigate the phenomenon of synergistic interaction between SEX and diethyl-DTC, the measured enthalpies of adsorption for SEX: diethyl-DTC mixtures with mole ratios of 90:10 and 70:30 were compared with the weighted sum of the enthalpies of adsorption for the single collectors and these are shown in Figure 39.

The weighted sum of the enthalpies of adsorption was calculated based on the molar ratio of the collectors in the mixtures. Figure 38 shows that the enthalpies of adsorption for the interaction of SEX and diethyl-DTC with chalcopyrite were -41.2 and -65.1 kJ/mol respectively. The weighted sum of the enthalpy of adsorption for the interaction of the collector mixture with a 90:10 mole ratio would then be equal to (0.9 x - 41.2) + (0.1 x - 65.1). This would then give -43.6 kJ/mol as the enthalpy of adsorption for the mixture.

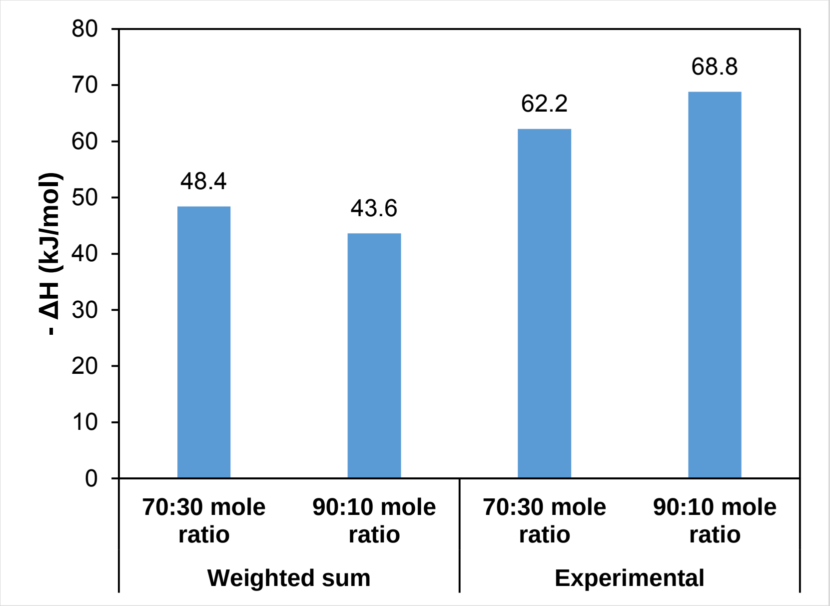


Figure 39: Comparison of the measured enthalpies of adsorption to the weighted enthalpies of adsorption for collector mixtures on chalcopyrite, the first number in the ratio represent molar % of SEX while the second represent the molar % diethyl-DTC (~50% pseudo-monolayer collector coverage; pH 9.2)

Figure 39 shows that experimentally determined enthalpies of adsorption for both collector mixtures were higher than the weighted sum of the enthalpies of adsorption. This is indicative of a possible synergistic interaction between SEX and diethyl-DTC in the collector mixture. In other words the mixture outperforms the sum of the parts. When a mixture of SEX and diethyl-DTC was contacted with chalcopyrite, higher enthalpies of adsorption were obtained above that of SEX alone as shown in Figure 38. The higher enthalpies of adsorption imply that the use of collector mixtures resulted in stronger adsorption than when pure xanthate was used alone. The thermochemical measurements showed that the maximum synergistic performance as indicated by the enthalpy of adsorption occurred when the amount DTC in the mixture was lowest.

3.7.3 Microflotation results

Chalcopyrite was floated with both single and collector mixtures in a microflotation cell. The performance of the single collectors was used as a benchmark to assess the performance of the collector mixtures. It must be emphasised that a total molar dosage of 2.88 x 10^{-6} mol/m^2 corresponding to ~50% pseudo-monolayer coverage was used in all tests. SEX: diethyl-DTC collector mixtures investigated had mole ratios of 90:10 and 70:30. The microflotation results of chalcopyrite when floated with SEX, diethyl-DTC and their mixtures are presented in Figure 40.

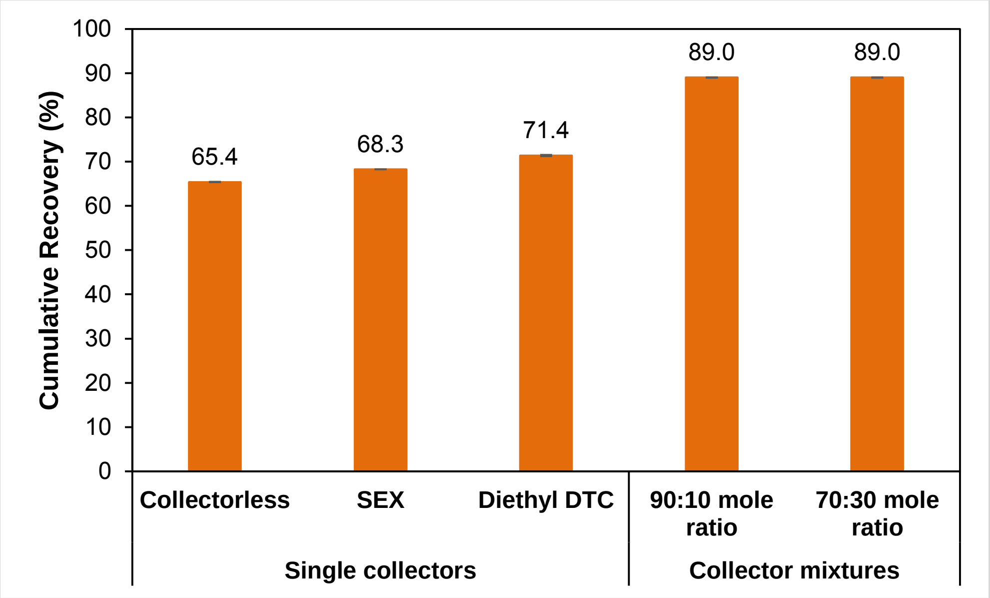


Figure 40: Chalcopyrite recoveries with SEX, diethyl-DTC and collector mixtures, the first number in the ratio represent molar % of SEX while the second represent the molar % diethyl-DTC (~50% pseudo-monolayer collector coverage; pH 9.2. the relative standard error was always < ±0.5% hence error bars are too small to be visible on the graphs)

The results in Figure 40 show that the microflotation recoveries using diethyl-DTC produced a higher chalcopyrite recovery compared to SEX and that the recoveries produced by the SEX: diethyl-DTC collector mixtures with molar ratios of 90:10 and 70:30 were equal and greater than the recovery obtained using the single collectors. The results showed that both collector mixtures produced the same hydrophobicities, bubble loading and hence recoveries.

The results showed that small quantities of diethyl-DTC (co-collector) added to SEX (base collector) in chalcopyrite flotation resulted in increased recovery. However, an increase in the molar weight of diethyl-DTC from 10% to 30% did not increase the recovery of chalcopyrite, since it was 89.0% for both collector mixtures. This could be due to the fact that the optimum hydrophobicity is already attained with 10% diethyl-DTC, such that any further increase in the diethyl-DTC content would not translate to increased hydrophobicity. This implies that an increase of the diethyl-DTC content to, for example, 30% in a collector mixture with a mole ratio of 70:30 would be costly in terms of reagent consumption without any benefit in adsorption capacity and recovery as indicated by the enthalpy of adsorption and microflotation recoveries respectively. Thus the results showed clearly that the mixtures outperformed their single components.

3.7.4 Flotation kinetics for single thiol collectors and mixtures

The recovery time curves for the flotation of chalcopyrite using the collector mixtures are shown in Figure 41.

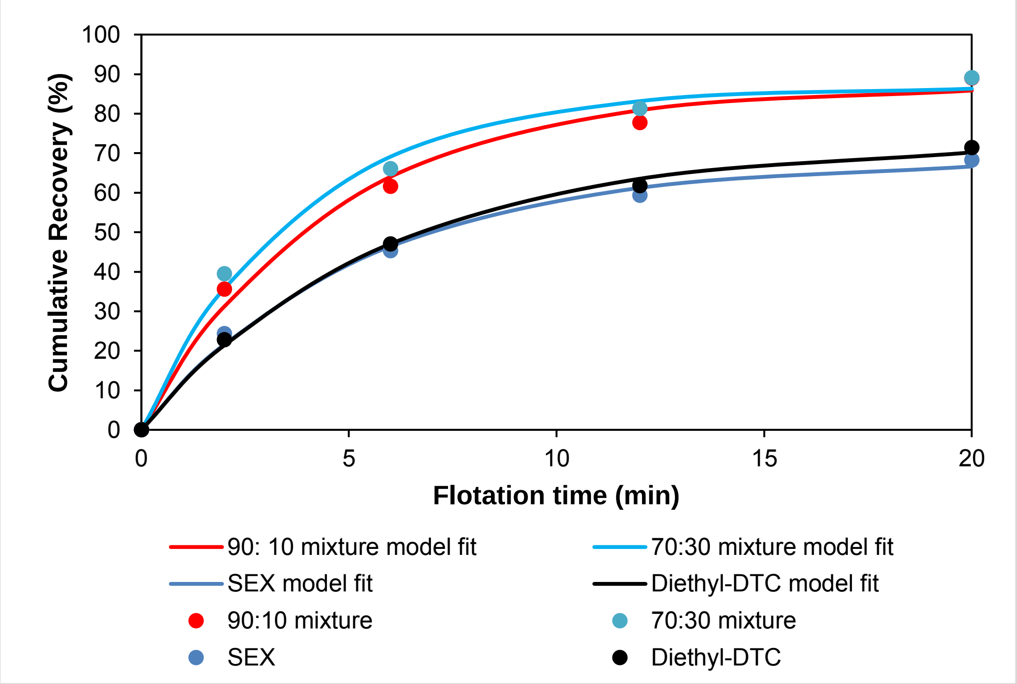


Figure 41: The recovery curves for the flotation of chalcopyrite using collector mixtures.

The first order flotation rate constant, k, for chalcopyrite flotation using single collectors and SEX: diethyl-DTC mixtures with molar ratios of 90:10 and 70:30 were calculated according to the first order kinetics (Section 2.9). The results are shown in Table 14.

Table 14: First order flotation rate constants for chalcopyrite with different collectors

Collector Type	First order rate constant, k (min^{-1})
SEX	0.19
diethyl-DTC	0.18
90:10 mole ratio	0.22
70:30 mole ratio	0.27

Table 14 shows that the first order rate constants for both collector mixtures were higher than for the single collectors. Thus the use of collector mixtures resulted in improved kinetics of flotation and in higher final recoveries in a microflotation cell.

3.8 MINERAL MIXTURES

Mixtures of sulphide minerals were used in a microcalorimetric study using single collectors. The reason behind the use of mixed minerals was to simulate a real ore which exists as an association of sulphide minerals and gangue minerals. In this study only binary mixtures of the sulphides, chalcopyrite and pyrite, were investigated. The amount of each mineral in the mixture was determined so as to have equal surface areas of each mineral. This translated to a chalcopyrite: pyrite mass % ratio of 51:49. The molar dosages for the two collectors were maintained constant at 2.88×10^{-6} moles/m^2.

3.8.1 Thermochemical behaviour of SEX, diethyl-DTC with chalcopyrite, pyrite and mineral mixtures.

The enthalpies of adsorption corresponding to ~50% pseudo-monolayer coverage for the interaction of chalcopyrite, pyrite and the mineral mixtures with SEX and diethyl-DTC are shown Figure 42.

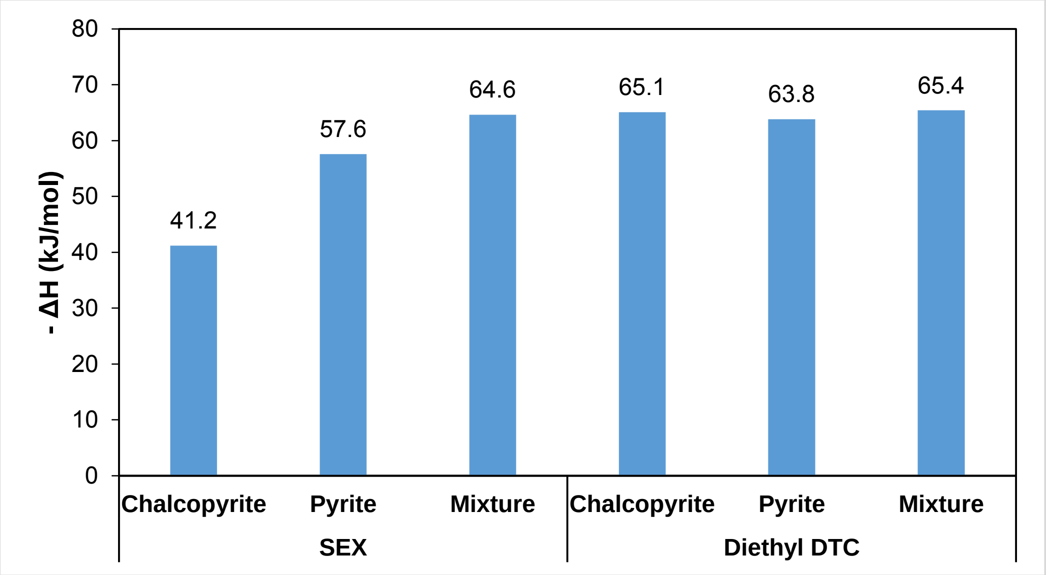


Figure 42: Enthalpies of adsorption of SEX and diethyl-DTC on chalcopyrite, pyrite and mixtures of these minerals at pH 9.2 (The amount of each mineral in the mixture was determined so as to have equal surface areas of each mineral).

Figure 42 shows that the enthalpies of adsorption for the interaction between SEX with both single minerals and mineral mixtures decreased (less negative) in the following order: mixture > pyrite > chalcopyrite. The enthalpies of adsorption for the mineral mixtures were significantly greater compared to that of the pure minerals alone. It appears that the behaviour of the two pure minerals changes once they are in a mixed system.

With respect to di-ethyl DTC, the thermochemical measurements in Figure 42 show that the enthalpies of adsorption with single minerals and mineral mixtures were almost equal, around – 65 kJ/mol. When diethyl-DTC was reacted with a mineral mixture, the magnitude of reaction was equal to that of the individual constituent minerals that make up the mineral mixture. This is different to the findings on SEX.

3.8.2 Microflotation of chalcopyrite, pyrite and mineral mixture with SEX

Mixtures of sulphide minerals were floated to simulate the behaviour of the real ore. As in the case of the enthalpy of adsorption studies only binary mixtures of chalcopyrite and pyrite were investigated. Chalcopyrite and pyrite were floated with SEX to establish a baseline reference to which the floatability of the mixed minerals was compared. As in the adsorption studies the mineral mixture comprised of 51:49 mass% chalcopyrite and pyrite respectively to ensure that equivalent surface areas of each mineral were used. Collector dosage was equivalent to ~50% pseudo-monolayer coverage, translating to 191 g/ton (2.88 x 10^{-6} mol/m^2). The microflotation results of the mineral mixtures using SEX as collector are shown in Figure 43.

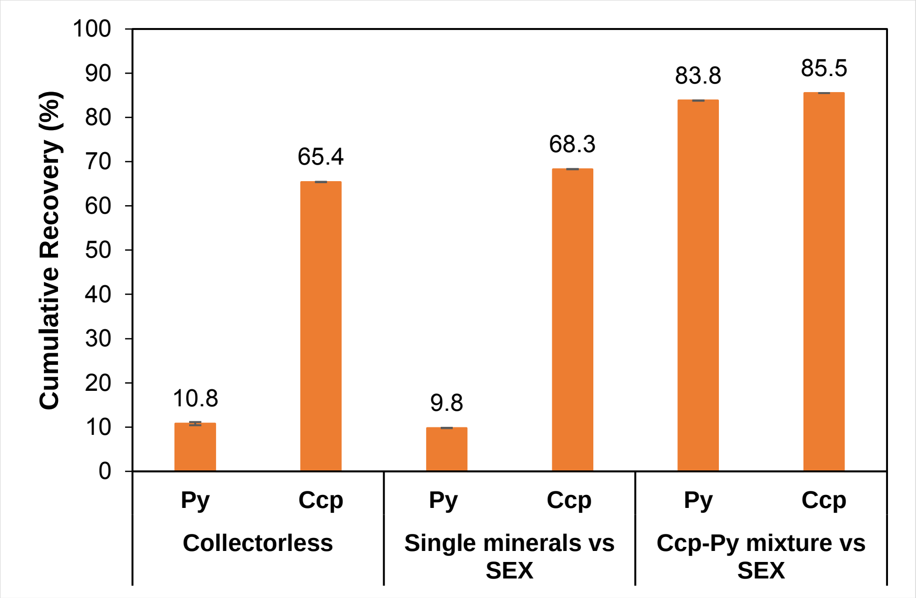


Figure 43: Microflotation results when pure Ccp, Py and Ccp-Py mixtures were floated using SEX as the collector at pH 9.2. For Ccp-Py mixture, the reported recoveries refer to the pure component minerals as described in Section 2.8.2 (the relative standard error was always < ±0.5% hence error bars are too small to be visible on the graphs)

Figure 43 shows that the collectorless recoveries of pyrite and chalcopyrite were quite different at 10.8% and 65.4%, respectively. The addition of SEX increased the chalcopyrite recovery slightly. Pyrite however hardly responded to the addition of SEX collector since there was no improvement in recoveries compared to the collectorless recovery. However, when pyrite and chalcopyrite were combined and reacted with SEX, there was a dramatic improvement in pyrite recovery from 10.8% to 83.8%. There was also an increase in the recovery of chalcopyrite by 18% when it was mixed with pyrite. It follows that the hydrophobicity of both chalcopyrite and pyrite increased significantly once in a mixture.

3.8.3 Microflotation of chalcopyrite, pyrite and mineral mixture with diethyl-DTC

Chalcopyrite and pyrite were floated with diethyl-DTC to establish a baseline reference to which the floatability of the mixed minerals was compared. The mineral mixture comprised of 51:49 mass percent chalcopyrite and pyrite, respectively. Collector dosage was equivalent to ~50% pseudo-monolayer coverage, translating to 191 g/ton ($2.88*10^{-6}$ mol/m^2). The microflotation results for chalcopyrite, pyrite and mixed minerals with diethyl-DTC are shown in Figure 44.

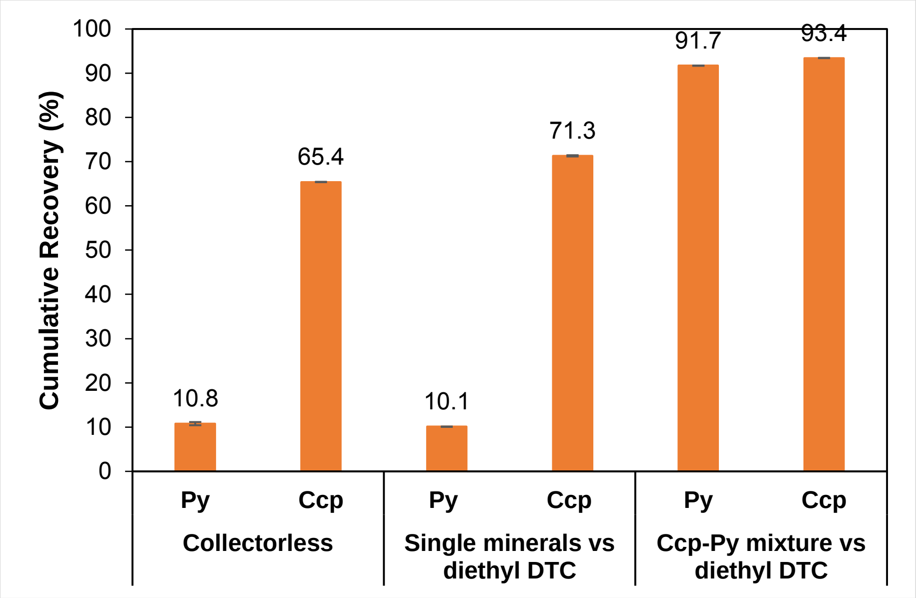


Figure 44: Microflotation results when pure Ccp, Py and Ccp-Py mixtures were floated using diethyl-DTC as the collector at pH 9.2. For Ccp-Py mixture, the reported recoveries refer to the pure component minerals as described in Section 2.8.2 (the relative standard error was always < ±0.5% hence the error bars are too small to be visible on the graphs).

Figure 44 again shows poor recovery of pyrite in collectorless flotation. The addition of diethyl-DTC slightly increased the hydrophobicity of the chalcopyrite as shown by improved recoveries. However, similar to SEX, pyrite did not respond to the addition of the diethyl-DTC collector, since there was no improvement in recoveries above the collectorless recovery. Once again, there was a dramatic increase in pyrite recovery once it was mixed with chalcopyrite, from 10% to 92%. Chalcopyrite recovery also increased by 22% when it was mixed with pyrite.

The results indicate that the flotation behaviour of chalcopyrite and pyrite is completely changed once the two minerals are contacted in a mixture. It was evident from the microflotation tests that the flotation behaviour of chalcopyrite and pyrite in mineral mixtures were quite different from their behaviour as the single minerals.

3.8.4 Microflotation kinetics for mineral mixtures

The first order flotation rate constant, k, for the flotation of chalcopyrite, pyrite and a chalcopyrite-pyrite mixture using SEX and diethyl-DTC were calculated according to the first order kinetics (Section 2.9). The results are shown in Table 15.

Table 15: Average overall microflotation rate constants for chalcopyrite, pyrite and mineral mixtures.

	First order rate constant, k (min^{-1})		
Collector Type	**Chalcopyrite**	**Pyrite**	**Mineral mixture**
SEX	0.19	0.42	0.10
diethyl-DTC	0.18	0.09	0.30

Table 15 shows that when using SEX, the rate constant for pyrite flotation was almost double that for chalcopyrite flotation. However, this is not a significant finding since the pyrite recovery were extremely low. The opposite was true for diethyl-DTC. Flotation of the mineral mixture with SEX resulted in slower kinetics than the pure minerals. However, the flotation of the mineral mixture with diethyl-DTC resulted in significantly improved kinetics than for pure minerals.

3.9 MIXED MINERALS

3.9.1 Thermochemical measurements of mixed minerals with single collectors and collector mixtures

Thermochemical measurements of mixed minerals with single collectors and collector mixtures were studied. SEX: diethyl-DTC mixtures with molar ratios of 90:10 mole percent and 70:30 mole percent were used. The enthalpies of adsorption of the collector suites were compared with the enthalpies of adsorption of single, constituent collectors. The enthalpies of adsorption corresponding to ~50% monolayer coverage are shown in Figure 45.

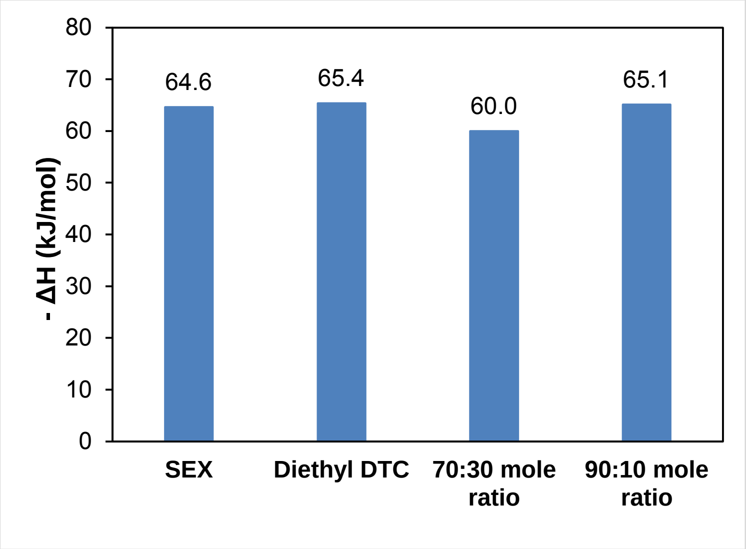


Figure 45: Enthalpy of adsorptions for SEX, diethyl-DTC and SEX: diethyl-DTC with molar ratios of 90:10 and 70:30 using a mixed mineral with a 51:49 wt% Ccp and Py respectively (~50% pseudo-monolayer collector coverage; pH 9.2)

Figure 45 shows that the enthalpies of adsorption were almost equal, independent of the collector type, collector mixture or collector molar ratios. The results show that in this case the use of collector mixtures did not result in stronger adsorption of collector mixtures compared to single collectors.

3.9.2 Microflotation tests of mixed minerals with single and collector mixtures

Mixed minerals were floated in a microflotation cell using mixed thiol collectors. SEX: diethyl-DTC mixtures with molar ratios of 90:10 and the 70:30 were used. The microflotation of the collector mixtures were compared with the microflotation recoveries of single, constituent collectors. The recoveries corresponding to ~50% monolayer coverage (2.88×10^{-6} mol/m^2) are shown in Figure 46.

Figure 46 shows that diethyl-DTC produced the best recoveries, especially in terms of chalcopyrite recovery, as compared to SEX and both collector mixtures. The results also show that the collector mixture with a 70:30 mole ratio produced a higher recovery than its 90:10 counterpart. In fact the 90:10 collector mixture produced similar recoveries to SEX. It is thus clear from the results that there was no benefit arising from the use of collector mixtures in the flotation of mixed chalcopyrite and pyrite.

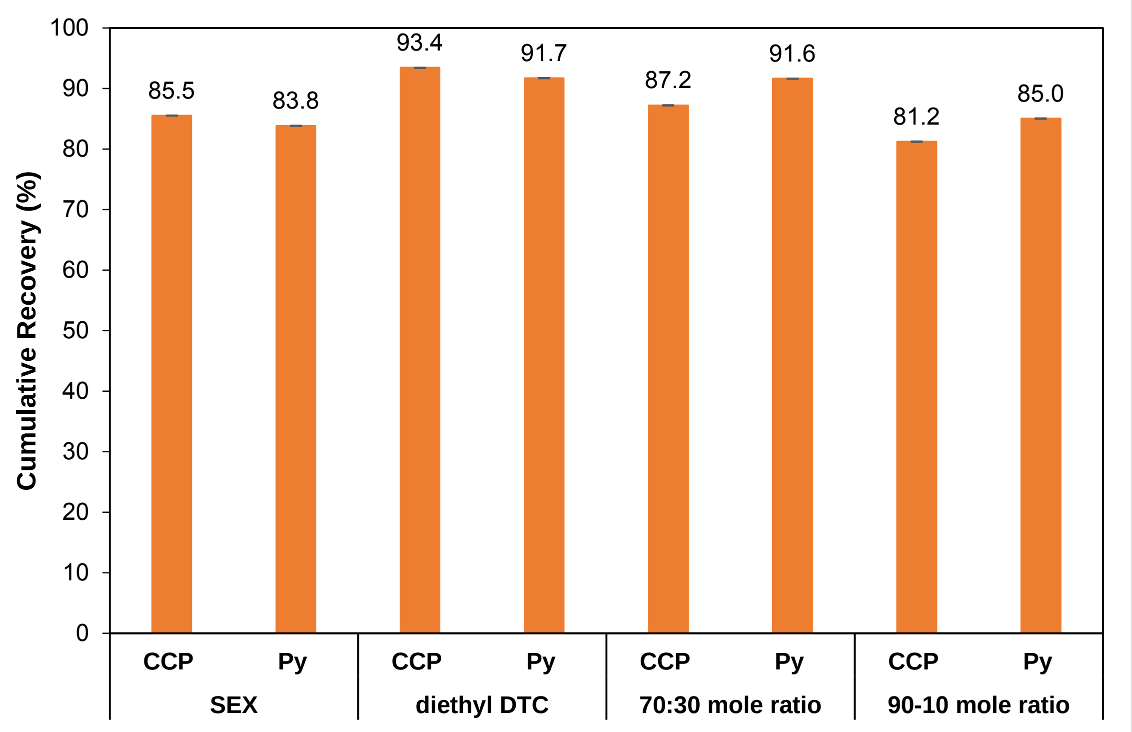


Figure 46: Microflotation results when Ccp-Py mixtures were floated using SEX, diethyl-DTC and SEX: diethyl-DTC with molar ratios of 90:10 and 70:30. The reported recoveries refer to the pure component minerals as described in Section 2.8.2. The relative standard error was always < ±0.5% hence error bars are too small to be visible (pH 9.2).

3.9.3 Microflotation kinetics for mineral mixtures using collector mixtures

The first order flotation rate constant, k, for the flotation of chalcopyrite-pyrite mixture using single collectors and SEX: diethyl-DTC mixtures with 90:10 molar ratios and 70:30 molar ratios were calculated according to the first order kinetics (Section 2.9). The results are shown in Table 16.

Table 16 shows that the use of collector mixtures in the flotation of mineral mixtures resulted in relatively slower kinetics compared to the use of single collectors. However, the collector mixture with a mole ratio of 70:30 floated the mineral mixture almost three times faster than its counterpart with a mole ratio of 90:10. Furthermore, Table 18 shows that the use of collector mixtures did not improve the overall microflotation recoveries in the flotation of mineral mixtures.

Table 16: Average overall micro-flotation rate constants for mineral mixtures using single collectors and collector mixtures

Collector mixture ratios	**First rate constant, k (min^{-1})**	**Terminal recovery (%) of mineral mixture**
SEX	0.10	76.6
Diethyl-DTC	0.30	87.8
90:10 mole ratio	0.09	77.5
70:30 mole ratio	0.24	84.5

CHAPTER 4: DISCUSSION

Introduction

This Section of the thesis discusses the results presented in Chapter 3, relating them to the objectives of the study. The effect of alkyl chain length and ligand type on the enthalpy of adsorption of collector onto a sulphide mineral surface and on the floatability of sulphide minerals was investigated. The enthalpy of adsorption of collectors onto sulphide minerals was determined using microcalorimetry while pulp phase floatability (or hydrophobicity) was characterised using the microflotation technique.

It is frequently reported that using mixtures of collectors in flotation results in improved flotation performance in sulphide mineral flotation. This phenomenon is considered to be a result of a synergistic interaction between the roles of the reagents in the mixture. In other words the performance of the collector mixtures is, on a weighted molar basis, greater than what would be expected if the performance was simply a result of the additive effects of each reagent in the mixture.

Flotation studies which investigate single minerals are quite simplistic since real ores consist of an association of sulphide minerals. In light of this, the effect of using mixtures of minerals, as well as pure minerals, on the enthalpy of adsorption and pulp phase floatability was investigated using microcalorimetry and microflotation.

Pure chalcopyrite, pyrite, galena and pyrrhotite were used in this study. The collectors investigated were the xanthates of different chain lengths from sodium ethyl xanthate through to potassium amyl-xanthate. The cationic species, i.e. sodium or potassium, is not considered to play any significant role. Diethyl-DTC and n-butyl DTC were used to investigate the effect of the alkyl chain length (both with respect to carbon number and linearity vs branching) on the collector – mineral adsorption characteristics and floatability of the sulphide minerals. Pre-mixed SEX: diethyl-DTC collector mixtures with mole ratios of 90:10 and 70:30, respectively, were investigated. In those studies the total molar dosage was kept constant and was the same as that used in the single collector case.

4.1 Effect of alkyl chain length on the enthalpy of adsorption of thiol collectors on sulphide minerals

Key question: Do differences in alkyl chain length have any effects on the enthalpies of adsorption?

The results of the effect of chain length of xanthates on the enthalpies of adsorption on chalcopyrite (Figure 27) and on galena, pyrite and pyrrhotite (Figure 28) have shown that an increase in chain length of the xanthates resulted in an increase in the enthalpies of adsorption for all the minerals.

This is an important observation since the ligand is the same in all cases and therefore the effect is due to the role of the alkyl group. This has not been shown previously through the use of directly measured enthalpies of adsorption. The increase of the enthalpies of adsorption with increasing alkyl chain length is intuitively to be expected since longer alkyl chain lengths are associated with a stronger positive inductive effect, releasing electrons towards the head/ligand/functional group and thereby increasing the electron density around the functional group rendering the collector more reactive (McMurry 1996). Thus the collectors with a longer chain length will result in a more exothermic reaction than those with shorter chain lengths.

The enthalpy of adsorption results are also consistent with decreasing trends of the pKa with the increasing alkyl chain lengths for the xanthate homologues (Hayashi et al. 1984). The pKa values of the collectors have been reported in Table 2. The electron donating or withdrawing effects of the substituent groups in a collector molecule not only affects the electron density around the donor atom but also the pKa of the collector (Somasundaran and Nagaraj 1984). Collectors with a larger pK_a should have greater electron donating capacity and have stronger bonds with the mineral surface and hence a more negative enthalpy of adsorption. The assumption here is that the collector anion reacts with the metal cations on the mineral surface. The pH versus zeta potential values will be discussed in Section 4.8.3 and 4.8.4.

4.2 Effect of alkyl chain length on the recovery of sulphide minerals

Key question: Do differences in alkyl chain length have any effects on the microflotation recoveries?

The results of the effect of chain length of xanthates on the recoveries of chalcopyrite (Figure 32) and of galena, pyrite and pyrrhotite (Figure 34) showed that an increase in chain length of the xanthates resulted in an increase in recoveries for all the minerals.

The increasing order of hydrophobicity of the mineral surface with increasing chain length is consistent with the early work of Wark and Wark (1932), which showed that an increase in the collector chain length of the collector resulted in an increase in contact angle on chalcopyrite, pyrite, sphalerite, bornite and galena. The increase in the alkyl chain length of the thiol collectors has been shown to increase the contact angle between the galena surface and the air bubble, independent of the collector species formed in the system (Rao 1982).

The increase of the contact angle with the alkyl chain length might be explained in terms of the hemi-micelle formation (Rao 2004; Bulatovic 2007). At low collector concentrations, collector ions adsorb as individual collectors while at higher concentrations collector ions interact through van der Waals forces forming hemi-micelles (Rao 2004; Bulatovic 2007). The contact angle formed between the mineral surface and the air bubble is enhanced by the hemi-micelle formation (Rao 2004). Fuerstenau (2005) reported that the contact angle induced between the mineral surface and the air bubble increases with the alkyl chain length. This is because hemi-micelles are formed due to the removal of alkyl group from the aqueous phase by expelling more water leading to a higher contact angle. Longer chain collectors are associated with enhanced hemi-micelle formation. This could explain the accepted phenomena that longer chain collectors are associated with higher contact angles.

It is also known that there is a direct correlation between particle contact angle and the flotation recovery in the galena-SEX system (Prestidge and Ralston 1996). Other studies have demonstrated the correlation between collector hydrocarbon chain length and recovery (Göktepe 2002; Gaudin 1974; Ngobeni and Hangone 1998).

The increase in recoveries with an increase in collector chain length can also be explained in terms of the decrease in the solubility of the hydrophobic species with increasing collector chain length. It is reported that there is a close relationship between the adsorption of a collector and the insolubility of its heavy metal salts (Wark and Wark 1932). For the metal thiolate species in the case of chalcopyrite, it is reported that an increase in collector chain length results in a decrease in the solubility of the metal thiolate formed (Kim et al. 2012).

In cases where the collector species formed is dixanthogen, it was also found that the solubility of dixanthogen for the xanthate homologues decreased with increasing chain length (Hamilton and Woods 1979). It has been established that the mechanism of interaction does not change with the alkyl chain length (Alison et al. 1972; Fuerstenau et al. 1968). It follows that the lower the solubility of the collector species formed (whether metal thiolates or dixanthogen), the higher the recovery produced by the collector.

4.3 Effect of the branching of the hydrocarbon chain length of the collectors on enthalpy of adsorption of sulphide minerals.

The microcalorimetric results in Figure 27 showed that the PNBX produced a higher enthalpy of adsorption than SIBX on the chalcopyrite surface, despite the two collectors having equivalent alkyl chain length, viz. 4 carbon atoms. PNBX has a straight chain while SIBX has a branched chain and their structures are shown in Figure 47.

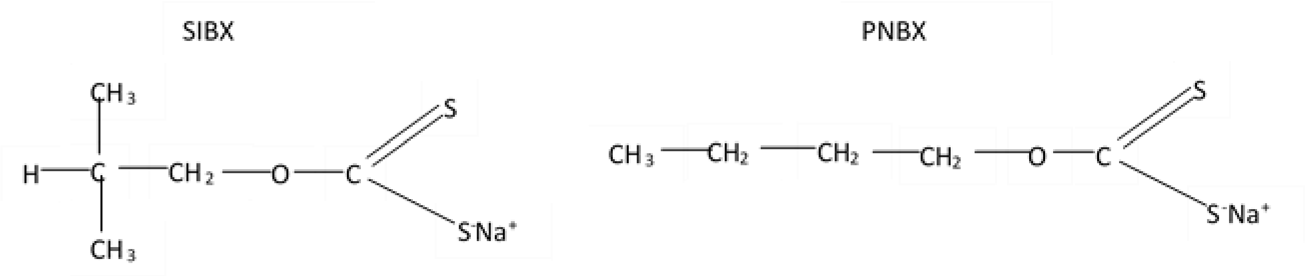


Figure 47: The chemical structures of SIBX and PNBX

This is consistent with the expectation that a branched chain collector has more positive inductive effect than its linear chain counterpart of equivalent chain length (McMurry 1996).

A comparison of diethyl-DTC and n-butyl DTC showed that both the diethyl-DTC and n-butyl DTC produced similar enthalpies of adsorption on the chalcopyrite surface (Figure 29). Both collectors have 4 carbon atoms in their hydrocarbon chains, but diethyl-DTC has a two ethyl chains attached to the nitrogen atom, while n-butyl DTC has a linear 4-carbon chain attached to the nitrogen atom. The structures of the two collectors are shown in Figure 48.

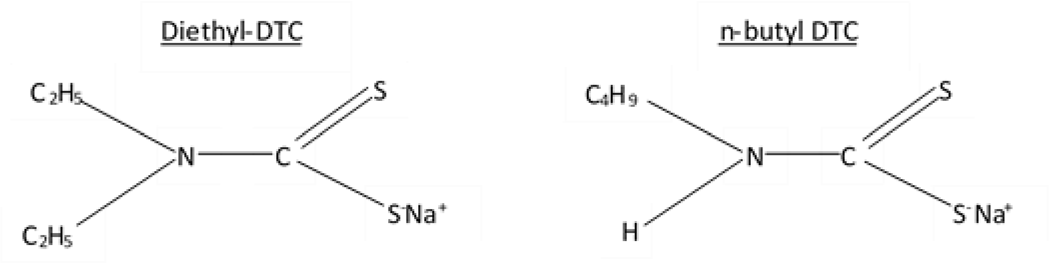


Figure 48: The chemical structures of diethyl-DTC and n-butyl DTC

This configuration of the carbon chains resulted in a similar enthalpy of adsorption of the collectors onto the chalcopyrite surface, although it may have been expected that the diethyl configuration may have had a slightly greater positive inductive effect than the n-butyl configuration (McMurry 1996). This highlights the fact that differences in strength of adsorption due to changes in carbon chain length are slight, whereas differences due to changes in the reactive head group may be considerable. This is in line with the larger differences in pK_a for different ligand types.

4.4 Effect of the branching of the hydrocarbon chain length of the collectors on the recovery of sulphide minerals.

The results of the microflotation tests in Figure 32 showed that the PNBX produced a higher recovery of chalcopyrite than the SIBX (77.0% versus 73.5%). Furthermore n-butyl DTC produced a higher recovery of chalcopyrite (80.8%) than diethyl-DTC (71.3%) (Figure 35). These results are consistent with other findings in literature. Ackerman et al. (1987) compared the flotation performance of straight chain versus branched chain collectors and they found that straight chain collectors outperformed their branched counterparts in chalcopyrite, covellite and chalcocite flotation. The higher recovery produced by the linear chain (n-butyl DTC and PNBX) might be attributed to enhanced hemi-micelle formation associated with longer alkyl chains (Rao 1982; Bulatovic 2007; Fuerstenau 2005). The other possible explanation for the lower recovery associated with the branched chain is the greater steric hindrance experienced by the branched collector on the surface, which leads to lower surface coverage and consequently lower hydrophobicity (Rao 1982).

4.5 Effect of ligand type on the enthalpy of adsorption of thiol collectors on sulphide minerals

Key question: Do differences in collector types have any effect on the magnitude of the mineral-collector enthalpies of adsorption?

The effect of the type of ligand on the enthalpy of adsorption was also investigated and results were shown in Figure 30. The diethyl-DTP and diethyl-DTC were initially chosen for this investigation. It must be emphasised that the alkyl chain length was fixed so that only the effect of collector type could be investigated. The investigations were conducted on chalcopyrite, galena, pyrite and pyrrhotite.

Thermochemical measurements showed that the diethyl-DTC produced a higher enthalpy of adsorption compared to the diethyl-DTP with all the sulphide minerals. In fact, diethyl-DTP showed essentially no interaction with any sulphide mineral as evidenced by the extremely low enthalpies of adsorption. It is interesting to note that the enthalpy of adsorption of the diethyl-DTC on chalcopyrite, galena and pyrite were more than twice that for the pyrrhotite indicating how mineral specific such interactions are. From Figure 30, it can be seen that the enthalpies of adsorption of diethyl-DTC on chalcopyrite, pyrite and galena were almost equal, viz., around –63 kJ/mol. This value is close to that found by Bradshaw et al. (1995) who found that the heat of reaction between pyrite and cyclo-hexyl DTC was -67 kJ/mol. The slight difference can be attributed to the differences in pH conditions under which the experiments were carried out and the differences in the chain length of the collectors investigated. Bradshaw et al. (1995) conducted their work at pH 4 while this work was conducted at pH 9.2.

The main difference in the enthalpy of adsorption of the collectors for a sulphide mineral is probably due to the differences in the electronegativity of the O, C, P and N atoms in the polar head group (Somasundaran and Nagaraj 1984; McMurry 1996; Lotter and Bradshaw 2010). The DTP is less reactive than the diethyl-DTC because of the two RO groups which are electron-withdrawing and the more electropositive phosphorous, thus reducing electron density around the donor sulphur atoms. The electron releasing tendency of the R_2N in DTC increases the electron density around the donor S atom, rendering DTC more reactive (Raju and Forsling 1997). Hence, the reactivity decreases in the following order: DTC > DTP (Somasundaran and Nagaraj 1984; Lotter and Bradshaw 2010). Thus, the observed trends in enthalpies of adsorption can be attributed to the differences in reactivities of diethyl-DTC and diethyl-DTP arising from different structure-related inductive effects.

The results agree with the fact that the pKa value of diethyl-DTP (~0) is lower than that of diethyl-DTC (7.5) (Raju and Forsling 1991; Hayashi et al. 1984). The very low pKa value of diethyl-DTP indicates that it is more electron withdrawing than diethyl-DTC, implying that diethyl-DTP forms weaker bonds with the mineral surface.

Since diethyl-DTP barely reacted with all the sulphide minerals (Figure 30), the enthalpies of adsorption for the interaction of PNBX and n-butyl DTC with chalcopyrite are compared here to further investigate the effect of ligand type on the enthalpy of adsorption. The two collectors have equal hydrocarbon chain length, viz. 4, but have different reactive head groups. Figure 31 showed that n-butyl DTC produced a higher enthalpy of adsorption compared to PNBX on the chalcopyrite surface. This is despite the fact that the two collectors have equivalent hydrocarbon chain lengths.

It is reported that the reactivity decreases in the following order: DTC > X (Somasundaran and Nagaraj 1984; Lotter and Bradshaw 2010). This is in keeping with the more electron-withdrawing effect of the single O atom of the xanthate compared to the electron-releasing effect of the N atom of the DTC. Thus the observed trends in enthalpies of adsorption can be attributed to the differences in reactivities of n-butyl DTC and PNBX arising from different structure-related inductive effects.

The results agree with the fact that the pKa value of butyl xanthate is lower than that of diethyl-DTC (Raju and Forsling 1997; Rao 1982). Unfortunately the actual pKa value of n-butyl DTC could not be found in literature hence it was assumed that the pKa of diethyl-DTC was closer to that of n-butyl DTC since the two collectors have equivalent number of carbon atoms. The pKa of diethyl-DTC is 7.5 while that of butyl xanthate is 2.23 (Raju and Forsling 1991; Hayashi et al. 1984). The lower pKa value of PNBX indicates that it is more electron withdrawing than DTC, implying that PNBX forms weaker bonds with the mineral surface.

4.6 Effect of ligand type on the flotation of sulphide minerals

Key question: Do differences in collector types have any effect on the microflotation recoveries?

The microflotation results for chalcopyrite, galena, pyrite and pyrrhotite using diethyl-DTC and diethyl-DTP are shown Figure 36. The results showed that the final recoveries produced by both diethyl-DTC and diethyl-DTP were similar for each of the minerals except pyrrhotite. The galena sample was not deemed suitable for investigation of the effect of ligand type on recovery since its recovery in the absence of a collector was already nearly 100%.

The microflotation results for chalcopyrite using n-butyl-DTC and PNBX are shown in Figure 37. The results showed that the n-butyl DTC and PNBX produced similar chalcopyrite recoveries, despite the fact that the two collectors have different types of ligands. These results are consistent with the previously referenced findings in Wark and Wark (1932) where it was observed that the contact angle induced by different collector types with the same alkyl chain length was the same, independent of mineral type.

The results show that recoveries were independent of ligand type for a specific mineral. The results also show that the alkyl chain length is the decisive parameter in determining the flotation performance of the collector and not the ligand type. Though the ligand type was different, the microflotation recoveries were similar for a particular mineral. Obviously it is important that the ligand is able to establish a bond between the collector and the mineral before any flotation can occur.

Pyrrhotite was an exception in that the measured recoveries for diethyl-DTC and diethyl-DTP were different, with a difference in recovery of 47%. Despite having identical alkyl chain lengths and structures, diethyl-DTC produced a higher pyrrhotite recovery. This implies the diethyl-DTC induced a higher contact angle than the diethyl-DTP. This result does not agree with Wark and Wark (1932) who found that collectors with the same alkyl chain length induced the same contact angle, independent of the ligand type. On the other hand this may indicate that the bond formed between the DTP and the pyrrhotite was inadequate for flotation to occur since the recovery was even less than in the case of collectorless flotation.

The natural hydrophobicity of the mineral seems to have some bearing on how well the collector will perform. In the case of chalcopyrite and galena, the minerals were both naturally hydrophobic as shown by their collectorless recoveries of 65.4% and 97.3%, respectively. In these cases, both DTP and DTC were able to improve recoveries to an approximately equivalent extent. In the case of pyrrhotite, the natural hydrophobicity was less, with collectorless flotation of 22.0%. In this case only the “stronger” collector, DTC, was able to improve on the collectorless flotation. Finally, pyrite had poor natural floatability, with a collectorless recovery of 10.8%. In this case, neither DTC nor DTP was able to improve recovery, although, incidentally, the long chain PAX was able to induce some hydrophobicity (36.2% recovery, Figure 34).

4.7 Relationship between the enthalpy of adsorption and microflotation recovery

Key question: Is there a relationship between the enthalpy of adsorption and microflotation recovery?

4.7.1 Collectors with same ligand type but different alkyl chain length

It can be concluded that there exists a direct positive correlation between the enthalpy of adsorption and the alkyl chain length for the xanthates and also between recovery of the sulphide minerals and the chain length of the xanthates. The plot of the enthalpy of adsorption and cumulative recovery as a function of the number of carbon atoms for linear-chained xanthates is shown in Figure 49.

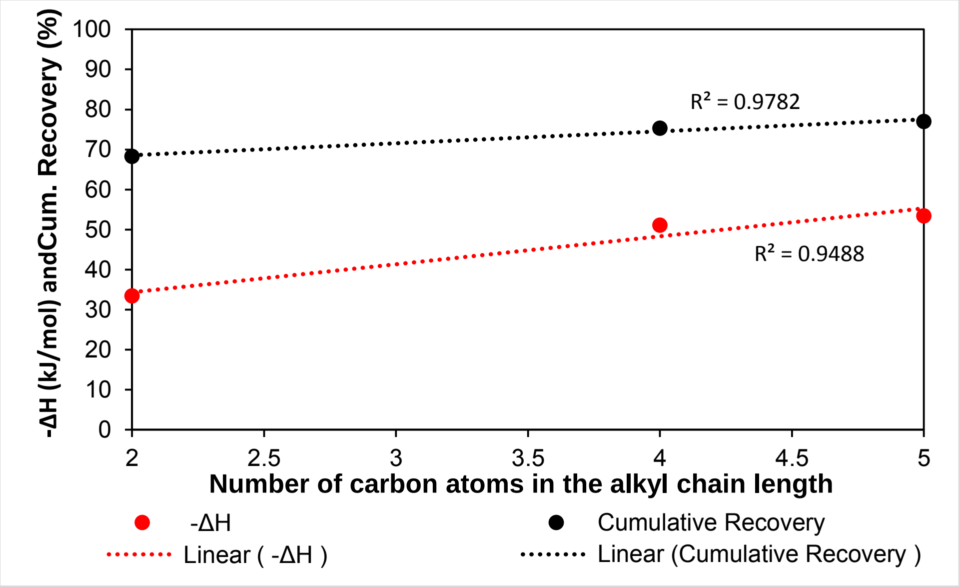


Figure 49: The variation of the enthalpy of adsorption and microflotation recovery as a function of the number of carbon atoms for linear chained xanthates.

From Figure 49, it was evident from the experiments conducted that there is a positive correlation between the enthalpy of adsorption and the imparted hydrophobicity for collectors with the same ligand type but different alkyl chain length. This shows that the alkyl chain length is an important parameter in enhancing hydrophobicity in the flotation of sulphide minerals.

4.7.2 Collectors with different ligand type but same alkyl chain length

When comparisons were made between the enthalpies of adsorption and recoveries for collectors with the same alkyl chain length but different ligand type, the relationship between the enthalpy of adsorption and recovery was not sustained. The enthalpy of adsorption of diethyl-DTC on all the sulphide minerals except pyrrhotite was an order of magnitude greater than that of diethyl-DTP (Figure 30). On the contrary, the two collectors produced similar recoveries for each of the sulphide minerals except for pyrrhotite (Figure 36). Therefore, there is no connection between the enthalpy of adsorption of the collector on the mineral surface and the imparted hydrophobicity.

The relationship between enthalpy of adsorption and recovery noted for the xanthates of increasing chain length in Section 4.7.1 was not sustained for different ligand types. In the case of increasing chain length for the same reactive head group, the driving force for the increase in enthalpy is the same as the driving force for the increase in hydrophobicity (the increasing chain length). However, in the case of different ligand types the main driving force for the enthalpy value is the reactive head group, whereas the main driving force behind the imparted hydrophobicity is the carbon chain length.

Despite little or no interaction between diethyl-DTP and the sulphide minerals, microflotation tests showed that the diethyl-DTP produced very high recoveries of chalcopyrite and galena. It was not clear how diethyl-DTP improved the recoveries, however, since it is a froth-less system, it is speculated that diethyl-DTP may be adsorbing at the air-water interface, enhancing the particle-bubble interaction resulting in stronger particle-bubble agglomerates. This would then translate to higher recoveries in a microflotation cell.

4.7.3 Different collectors producing similar enthalpy of adsorption

An interesting scenario would be to investigate whether different collectors producing the same enthalpy of adsorption produced the same microflotation recoveries of the same mineral. The enthalpies of adsorption of the interaction of PAX and diethyl-DTC with pyrite were similar, viz. -59 kJ/mol and -62 kJ/mol (Figure 28 and Figure 30 respectively). However, the microflotation recoveries produced by PAX and diethyl-DTC were 36% and 10% respectively (Figure 34 and Figure 36). It might be expected that PAX (5C) would produce a higher enthalpy of adsorption than diethyl-DTC (4C) since PAX has a longer alkyl chain length which is associated with stronger positive inductive effects making it more reactive (McMurry 1996). However, the diethyl-DTC has a more reactive head group than PAX and this explains why the two collectors gave similar enthalpies of adsorption (Somasundaran and Nagaraj 1984; Lotter and Bradshaw 2010). These results reinforce the fact that the enthalpy of adsorption is not necessarily an indication of imparted hydrophobicity.

In summary, it can be generally concluded that there is no correlation between the enthalpy of adsorption and hydrophobicity for sulphide minerals. The correlation only exists in collectors of same ligand type but with different alkyl chain length. Fundamentally, therefore, this study has shown that the enthalpy of adsorption cannot be used to predict hydrophobicity in sulphide minerals flotation.

4.8 Mechanisms

Although microcalorimetry does not give the identity of the actual collector species formed from mineral-collector interactions, an attempt is made to propose a possible mechanism of interaction between the sulphide minerals in light of the microcalorimetric and microflotation results. It is generally accepted that chemisorption occurs when the enthalpy is more negative than -40 kJ/mol while physisorption occurs when the enthalpy of reaction is more positive than

-40 kJ/mol (Wang et al. 2012). The microflotation results obtained in this work are compared with the flotation behaviour in literature.

The majority of the measured enthalpies of adsorption of xanthates and DTC's on galena, chalcopyrite and pyrite were more negative than -40 kJ/mol, suggesting that chemisorption was taking place to form the metal thiolates (Wang et al. 2012). The enthalpies of adsorption of various thiol collectors on pyrrhotite were less negative than -40 kJ/mol, indicative of a physical interaction. The proposed mechanisms are presented below.

4.8.1 Chalcopyrite

The agreement in established literature is that the mechanism involves the oxidation of the sulphur in chalcopyrite, liberating copper (II) ions into the bulk solution.

$Cu^{2+} + 2X^{-} \rightarrow CuX_2$ (26)

The CuX_2 is believed to be very unstable and would then be converted to Cu(I) and dixanthogen

$2CuX_2 \rightarrow 2CuX + X_2$ (27)

It has been established when chalcopyrite is interacted with xanthate, copper xanthate (Valli and Persson 1994; Raju and Forsling 1997; Finkelstein and Goold 1972) and dixanthogen (Alison et al. 1972; Yoon and Basilio 1993; Leppinen et al. 1989) and mixture of copper xanthate and dixanthogen (Leppinen 1990) are the hydrophobic species formed.

The SEX and PAX enthalpies of adsorption are similar for chalcopyrite and galena (-33.4 and -53.4 kJ/mol for chalcopyrite versus -35.9 and -53.9 kJ/mol for galena). As discussed in Section 4.8.2, the mechanism for xanthate adsorption onto galena is proposed to be similar to that of chalcopyrite. The similarities in enthalpies of adsorption may be confirmation of similarities in the mechanisms of reaction.

4.8.2 Galena

Similar to chalcopyrite, the mechanism involves the oxidation of galena, liberating lead (II) ions into the bulk solution, since oxidised lead species such as PbS_2O_3 are more soluble than PbS.

$Pb^{2+} + 2X^{-} \rightarrow PbX_2$ (28)

Many researchers agree that the metal thiolate is responsible for the flotation of galena (Woods and Gardener 1997; Valli and Persson 1994; Persson 1994; Finkelstein and Goold 1972; N. Finkelstein and Poling 1977; Alison et al. 1972).

The microflotation results of galena in the absence of a collector in Figure 34 showed that galena is naturally hydrophobic, with almost 97% recovery. This value is consistent with the work conducted by (Kelebek and Yoruk 2002) shown in Figure 50.

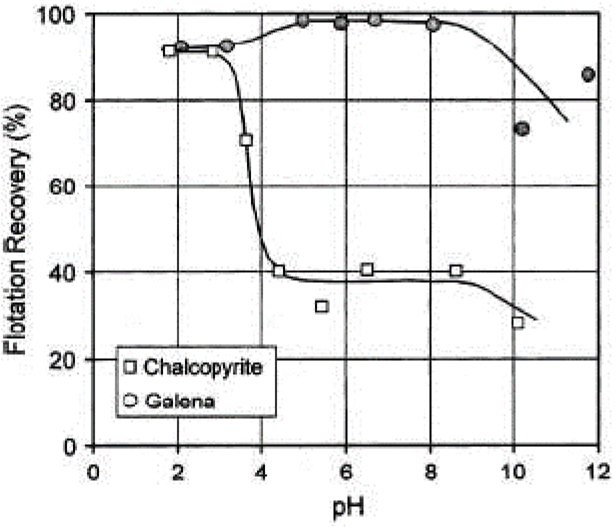


Figure 50: Flotation behaviour of galena and chalcopyrite as a function of pH in the absence of a collector (Kelebek and Yoruk 2002).

It was therefore difficult to investigate the effect of collector addition on the effect of galena flotation. It must be pointed out that the microflotation behaviour of chalcopyrite obtained in this work (Figure 32) was not consistent with the work conducted by Kelebek and Yoruk (2002) shown in Figure 50, where recoveries of less than 40% were obtained at pH 9.

4.8.3 Pyrite

Thermochemical measurements showed that pyrite produced relatively higher enthalpies of adsorption compared to galena and chalcopyrite (Figure 27, Figure 28 and Figure 30). The proposed mechanism is that a metal thiolate is formed first when the xanthate ion adsorbs at metal sites in a chemisorption reaction (equation 29). The second step would be the oxidation of the metal thiolate to dixanthogen (equation 30). The anodic reactions are given below:

$Py + X^{-} \rightarrow PyX + e^{-}$ (29)

$PyX + X^- \rightarrow PyX_2 + e^-$ (30)

The coupled cathodic reaction is:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (4)

This proposed mechanism is in agreement with established mechanisms in literature. It is well established in literature that pyrite forms dixanthogen when interacted with the xanthate collector (Finkelstein and Goold 1972; Lo et al. 2005; Alison et al. 1972; Finkelstein and Poling 1977; Yoon and Basilio 1993; Valli and Persson 1994; Fuerstenau et al. 1968; Bradshaw et al. 1995; Leppinen et al. 1989). Some researchers showed that both an iron complex and dixanthogen coexist as hydrophobic species (Nagaraj and Brinen 2001; Leppinen 1990).

The pyrite recoveries produced by SEX, diethyl-DTP and diethyl-DTC were around 10%, equal to the pyrite recovery in the absence of collector (Figure 34 and Figure 36). This value was obtained at pH 9.2 and collector concentrations of 10^{-5} M. This result is consistent with other pyrite recoveries reported in literature for the same conditions (Kongolo et al. 2005; Hanson and Fuerstenau 1993; Lo et al. 2005; Fuerstenau et al. 1968). The flotation behaviour of pyrite as a function of pH using SEX of different concentrations was studied by Hanson and Fuerstenau (1993) and their results are presented in Figure 51.

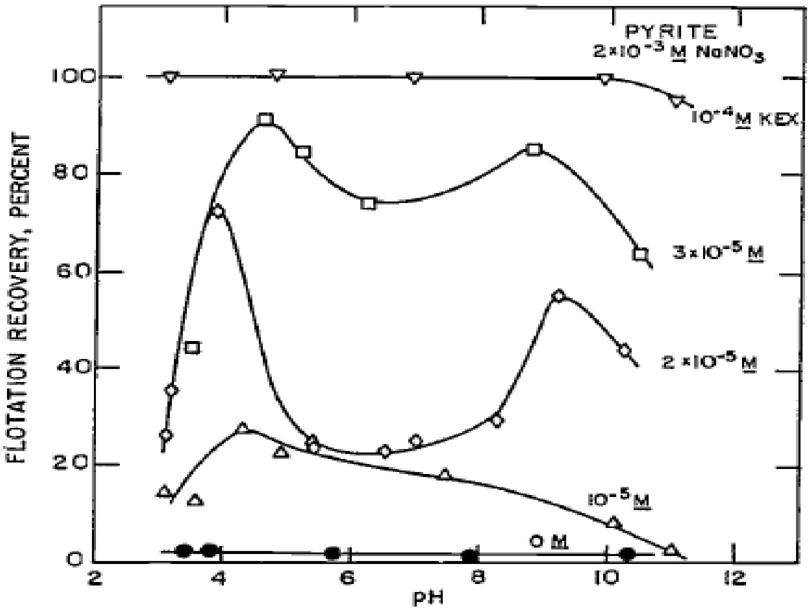


Figure 51: Pyrite recoveries as a function of pH at different concentrations of SEX (Hanson and Fuerstenau 1993)

Their results show that the floatability of pyrite varies as a function of pH and collector concentrations. At 10^{-5} M SEX concentration and pH 9, their pyrite recovery was around 10%, which is similar to the value obtained in this work.

The fact that the recoveries for SEX, diethyl-DTP and diethyl-DTC collectors were similar to the collectorless flotation of pyrite suggest that the pyrite surface did not respond to the different collectors. This is despite the fact that thermochemical measurements in Figure 28 and Figure 30 showed that there was an interaction between the pyrite and the thiol collectors. It is evident that whatever reactions occurred, did not impart sufficient hydrophobicity to the pyrite surface. It was established from zeta potential experiments that SEX ions adsorb onto the pyrite surface at pH 9 (Hanson and Fuerstenau 1993). Their results are shown in Figure 52.

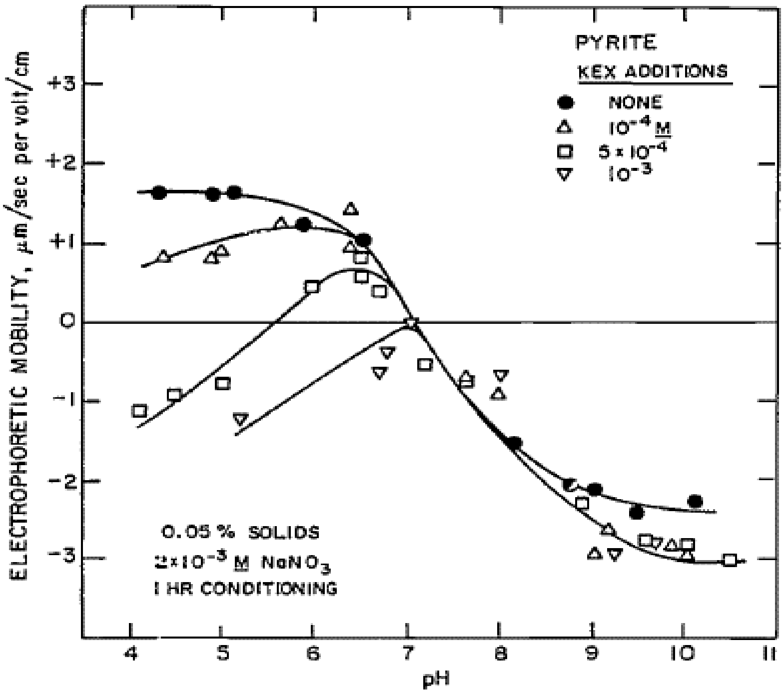


Figure 52: Variation of Electrophoretic mobility with pH for pyrite in the presence of SEX at different concentrations (Hanson and Fuerstenau 1993)

Figure 52 shows that there is some interaction between pyrite and SEX at pH 9.2, although the interaction is more pronounced in the acidic region. The combination of microflotation tests and electro-kinetic measurements conducted by Hanson and Fuerstenau (1993) show that SEX does adsorb onto the pyrite surface at pH 9, and that the recovery was a function of the collector concentration. Furthermore a significant pyrite recovery of 36.2% produced by PAX in Figure 34 is evidence that the collectors adsorb onto the pyrite surface at pH 9.2.

The possibility of the formation of ferric xanthate has been postulated according to equation 29. However ferric thiolates are believed to be very unstable beyond pH 5 (Hanson and Fuerstenau 1993). Ferric xanthate is also said to be highly soluble, thus it cannot form at moderate collector additions (Gaudin 1974). Woods and Gardener (1997) found that the pyrite surface was hydrophilic except in cases where dixanthogen was formed. They went further to establish that pyrite flotation started to occur at a pH when significant amounts of dixanthogen were formed. Again they attributed this to the presence of hydrated iron oxide (ferric hydroxide) on the pyrite surface.

In alkaline conditions, dixanthogen is believed to be formed by the oxidation of the xanthates by the ferric hydroxide or amphoteric iron hydroxide sites present on the pyrite surface (Hanson and Fuerstenau 1993). Pyrite contains disulphide ions that are able to oxidise xanthates to corresponding dixanthogen (Persson 1994). Thus pyrite requires dixanthogen to float. The dixanthogen is formed according to the following equation:

$$2X^- \rightarrow X_2 + 2e^- \qquad (31)$$

The coupling cathodic reaction is:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (4)$$

The hydroxyl ions react with the ferric ions producing ferric hydroxide according to the following equations:

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \qquad (32)$$

Ferric hydroxide is believed to be the stable iron species at pH 9 and may prevent dixanthogen from imparting sufficient hydrophobicity onto the pyrite surface.

The results show that even though a chemical reaction may have taken place with a corresponding heat of reaction, the species formed may not impart hydrophobicity. This discussion has shown that a possible reaction was the formation of ferric xanthate, which did not impart sufficient hydrophobicity with which to float the pyrite. Only the formation of dixanthogen, in the case of PAX, imparted sufficient hydrophobicity onto the pyrite surface to render it floatable. The longer the alkyl chain length, the more readily oxidisable is the collector and therefore PAX may have been oxidised to dixanthogen rendering the pyrite surface hydrophobic

4.8.4 Pyrrhotite

It is interesting to note that the enthalpies of adsorption for pyrrhotite with different thiol collectors were between 50 and 70% of those measured for chalcopyrite, galena and pyrite (Figure 27, Figure 28 and Figure 30). These results are consistent with the XRD results highlighted in Section 2.3, which showed that pyrrhotite was only about 60% pure. The implication of this finding is that when pyrrhotite is contacted with different collectors, only 60% of the mineral sample reacts, while the remaining 40% (made up non-sulphide minerals) remains unreacted. This translates to enthalpies of adsorption that are nearly 60% of the expected value had the pyrrhotite sample been 100% pure. This explains why the enthalpies of adsorption on pyrrhotite were between 50 and 70% of those measured for other minerals.

The proposed mechanism of the interaction of pyrrhotite and the xanthates is the formation of dixanthogen as given by Bozkurt and Xu (1998) and Miller et al. (2005)

The first step is shown in the equation below:

$$\mathrm{Po} + \mathrm{H_2O} \rightarrow \mathrm{Po(OH)[S]^+} + \mathrm{H^+} + 2e- \qquad (33)$$

The collector ions then electrostatically interact with ferrous ions on the surface forming ferrous or ferric hydroxyl xanthates according to equation 34.

$$\mathrm{Po(OH)[S]^+} + \mathrm{X^-} \rightarrow \mathrm{Po(OH)[S][X]} \qquad (34)$$

The hydroxyl xanthates form favourable sites as anchors to accommodate more collector ions, forming dixanthogen, according to equation 35.

$$\mathrm{Po(OH)[S][X]} + \mathrm{X^-} \rightarrow \mathrm{Po(OH)[S][X_2]} + e- \qquad (35)$$

The microflotation recoveries produced when pyrrhotite was floated using thiol collectors were relatively lower, compared to the galena and chalcopyrite recoveries produced by the same collectors (Figure 32, Figure 34 and Figure 36). This result is consistent with literature as it is reported that pyrrhotite recoveries are relatively lower than other sulphide minerals and this results in loss of PGMs in concentrators when PGMs are associated with pyrrhotite (Miller et al. 2005). The microflotation recovery of pyrrhotite using SEX at pH 9.2 was found to be 54% (Figure 34). This pyrrhotite recovery agrees very well with the microflotation behaviour of pyrrhotite using SEX reported by Montalti (1994) at different pH values shown in Figure 53. It can be seen from Figure 53 the pyrrhotite recovery was around 50% at pH 9, at collector concentrations above 1M.

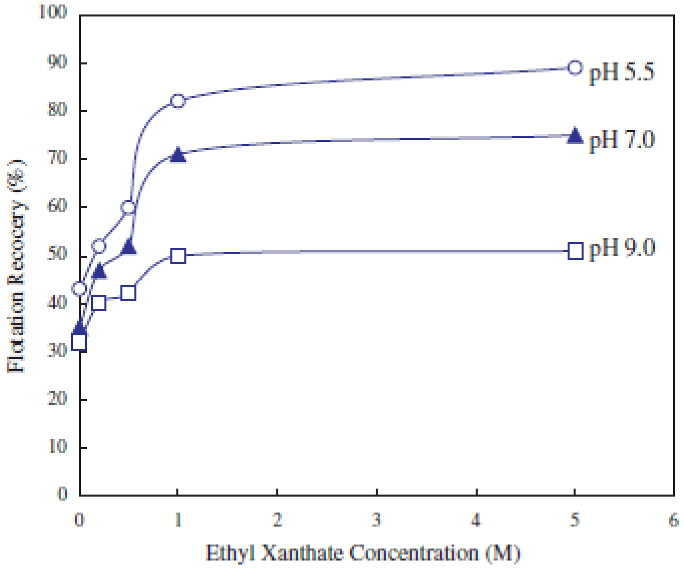


Figure 53: Pyrrhotite recoveries at different pH values using SEX (Miller et al. 2005).

The relatively lower pyrrhotite recoveries obtained in this work were probably a result of the fact that pyrrhotite was only about 60% pure as shown by XRD results highlighted in Section 2.3. It was shown that the pyrrhotite samples contained 8% talc, which is a naturally floating gangue mineral. The implication of this result is that the rest of the mineral sample (29.5%) did not float at all. The 63.8% and 69.5% pyrrhotite recoveries produced by diethyl-DTC and PAX, respectively, suggest that the floatable gangue in the form of talc reported in the concentrate. Overall, these results indicate that pyrrhotite is a weakly floating mineral that requires a strong collector in order to float.

4.9 COLLECTOR MIXTURES

The interaction of collector mixtures with chalcopyrite was investigated using microcalorimetry. The microflotation technique was also used to investigate the pulp phase floatability of chalcopyrite using the collector mixtures. The thermochemical and microflotation behaviour of chalcopyrite with single collectors was initially established to assess the performance of collector mixtures. SEX: diethyl-DTC collector mixtures with molar ratios of 90:10 and 70:30 were adsorbed on chalcopyrite.

Key question: Is the thermochemical behaviour and flotation performance of mixtures of thiol collectors different from single collectors?

4.9.1 Thermochemical behaviour SEX, diethyl-DTC and mixtures thereof with chalcopyrite

Chalcopyrite was interacted with SEX, diethyl-DTC and mixtures of the two collectors. Thermochemical measurements in Figure 38 showed that the enthalpies of adsorption when using diethyl-DTC on its own or in SEX: diethyl-DTC mixtures with molar ratios of 90:10 and 70:30 were similar, viz. around -65 kJ/mol. The enthalpy of adsorption of SEX was lower than that of diethyl-DTC and of the two collector mixtures. Figure 38 showed that diethyl-DTC adsorbed more strongly on chalcopyrite than SEX. The differences in the enthalpies of adsorption arise from the differences in the electronegativity of the O, C and N atoms in the polar head groups, which affect the reactivity of the collector (Somasundaran and Nagaraj 1984). This was discussed in Section 4.5. The results agree with the fact that the pKa value of SEX (2.20) is lower than that of diethyl-DTC (7.5) (Raju and Forsling 1997; Hayashi et al. 1984). The lower pKa value of SEX indicates that it is more electron withdrawing than diethyl-DTC, implying that SEX forms weaker bonds with the mineral surface.

Figure 38 shows that addition of small amounts of diethyl-DTC to SEX in a mixture resulted in synergistically higher enthalpies of adsorption, similar to that of 100% diethyl-DTC. Synergism is a phenomenon whereby the observed performance of a collector mixture is greater than that of the weighted sum of the individual constituent collectors. If there was an additive effect, it would be expected that the enthalpies of adsorption of the collector mixtures be far lower than that of 100% diethyl-DTC because of the very small amounts of diethyl-DTC in the collector mixtures (90:10 and 70:30 mole ratios). On the other hand, it would also be expected that the enthalpies of adsorption of both collector suites to be close to that of 100% SEX since SEX constituted a large proportion in the collector mixtures. However, these were not the case as the enthalpies of adsorption of both collector suites were similar to that of 100% diethyl-DTC.

Furthermore, in order to quantitatively investigate the likelihood of synergistic interactions between SEX and diethyl-DTC, the measured enthalpies of adsorption of both collector mixtures were compared to the weighted sum of the enthalpies of adsorption for the single collectors. The results were presented in Figure 39. The results showed that the measured enthalpies of adsorption for both collector mixtures were higher than the molar weighted sum of the enthalpies of adsorption of the single collectors.

This suggests that there was synergistic interaction between SEX and diethyl-DTC in the collector mixtures. The results are consistent with thermochemical measurements conducted by Bradshaw et al. (1995) which showed that a higher reaction enthalpy was obtained when the mixture of butyl xanthate and cyclohexyl dithiocarbamate was interacted with pyrite at pH 4 than in the case of the single constituent collectors.

It is important to note that SEX is used in bulk sulphide mineral flotation because it is a relatively cheaper and powerful collector (Chen et al. 2013). This explains its use as a base or primary collector when formulating collector mixtures for use in sulphide mineral flotation. However, since SEX: diethyl-DTC collector mixtures with molar ratios of 90:10 and 70:30 showed equal enthalpies of adsorption, it follows that an increase in diethyl-DTC content above 10% does not result in any greater adsorption and thus would be costly in terms of reagent consumption without any benefit in adsorption capacity. This result suggests that optimum adsorption would be already attained at 10% diethyl-DTC content. The thermochemical measurements also suggest that the maximum synergistic performance, as indicated by the enthalpy of adsorption, occurred when the amount DTC in the mixture was lowest.

4.9.2 Microflotation of chalcopyrite using SEX, diethyl-DTC and collector mixtures

Chalcopyrite was floated with SEX, diethyl-DTC and their mixtures with SEX: diethyl-DTC mole ratios of 90:10 and 70:30. The flotation performance of the two collector mixtures were compared with that of single collectors. The results were shown in Figure 40.

Similar to thermochemical measurements, microflotation tests showed that the final recoveries for SEX: diethyl-DTC collector mixtures with mole ratios of 90:10 and 70:30 were equal. The collector mixtures produced higher recoveries (89.0%) than either SEX or DTC alone (68.3% and 71.4%). This may have been expected given the higher experimental enthalpy values compared to the expected values from adding the weighted sum of the individual components. Overall microflotation recovery of chalcopyrite increased from 71.4% to 89.0% when collector mixtures were used. The same phenomenon of synergistic performance associated with collector mixtures has also been reported in literature (Bradshaw and O’Connor 1994; Hangone et al. 2000; Makanza et al. 2008; Mcfadzean et al. 2012). Similar results were obtained by Bradshaw and O’Connor (1994) when a PNBX: Cyclo-hexyl DTC mixture with molar ratio of 90:10 was found to produce the highest pyrite recovery. Hangone et al. (2000) also found increased recoveries when using a SEX: diethyl-DTC mixture with molar ratio of 90:10 to float copper sulphide ore from Okiep.

The results showed that small quantities of diethyl-DTC mixed with SEX in chalcopyrite flotation resulted in increased recovery. Thus as mentioned earlier with thermochemical measurements, the character of diethyl-DTC dominates in the collector mixture. However, an increase in the mole fraction of diethyl-DTC from 10 mole% to 30 mole% did not increase the recovery of chalcopyrite, since the microflotation recovery was 89.0% for both collector mixtures. Thus, it follows again that an increase in diethyl-DTC content above 10 mole% would be costly in terms of reagent consumption without any benefit in recovery.

Figure 40 showed that the flotation of chalcopyrite using the collector mixtures resulted in higher recoveries of than in the case of single collectors. This implies the collector mixtures imparted a higher hydrophobicity onto the chalcopyrite surface than the single minerals. This will be discussed in detail in the following Section. The results showed that the behaviour of single collectors change once they are contacted in a mixture since collector mixtures behaved differently from the single constituent collectors. The results showed synergistic interactions between SEX and diethyl-DTC, which resulted in recoveries that were greater than that obtained with the individual collector at the same total molar dosage.

Table 14 showed that the overall first order flotation rate constants for both collector suites were higher than those observed for the single collectors. Thus the use of collector mixtures also resulted in improved rates of flotation compared to the case of pure single collectors. The same results were reported by Bradshaw and O'Connor (1994) who found that collector mixtures improved the overall flotation rates in pyrite flotation. The SEX: diethyl-DTC collector mixture with a 70:30 mole ratio showed faster rates than its counterpart with a 90:10 mole ratio although they produced the same chalcopyrite final recoveries. The results show that increasing the DTC content in the collector mixture improves the flotation rates without increasing the final recoveries. The significance of these findings is that for a slow floating mineral, increasing DTC could improve its flotation rate for a fixed residence time.

Overall, the results showed that when mixtures of collectors are used to float chalcopyrite, each constituent collector in the mixture has a synergistic effect on the performance of the other, resulting in improved recoveries and rates.

4.9.3 Mechanism of interaction of collector mixtures with chalcopyrite

The combination of thermochemical measurements and microflotation tests can be helpful to elucidate the mechanism whereby collector mixtures adsorb on a mineral surface. The rate of dixanthogen production is limited by the rate of oxygen reduction in the corresponding half-reaction. Although the free energy of oxygen reduction coupled to xanthate oxidation is negative the reaction is kinetically hindered due to the necessity for the simultaneous transfer of 2 or 4 electrons. However, it has been shown that catalysts can increase the rate of oxidation of xanthate to dixanthogen and that this increases the flotation recovery (Chanturiya and Vigdergauz 2009). Catalysts such as a complex heterocyclic, substituted cobalt phthalocyanine have been shown to catalyse the auto oxidation of thiols to their corresponding dithiolates (Chanturiya and Vigdergauz 2009). In addition, certain minerals favour the production of dixanthogen over the metal-xanthate reaction at the mineral surface as discussed in Section 1.4.3. Therefore, it is postulated that DTC acts as a catalyst in the formation of dixanthogen resulting in an increased hydrophobicity. The DTC may not directly catalyse the oxidation of xanthate by oxidation but the adsorption of DTC onto the mineral surface may increase the electron density on the mineral surface, promoting the catalytic capacity of the mineral surface. It is thus postulated that when chalcopyrite is contacted with collector mixtures, dixanthogen is formed via a two-step process, viz.:

a. Initial adsorption of xanthate;
b. Subsequent oxidation of xanthate to dixanthogen.

This explains why the enthalpies of adsorption for the collector mixtures were unexpectedly higher than that of SEX, which represented the majority of the collector present. The enthalpies of adsorption for the collector mixtures are the sum of two components, (a) and (b). The formation of dixanthogen results in improved hydrophobicity, which in turn increases the chalcopyrite recoveries (Figure 40).

4.10 MINERAL MIXTURES

Key question: Do mixtures of minerals respond to thiol collectors in the same way as single minerals?

4.10.1 Mineral mixtures versus single collectors and collector mixtures

Mixtures of sulphide minerals were also investigated in a microcalorimetric study using single collectors as well as collector mixtures. Binary mixtures of chalcopyrite and pyrite were used and the amount of each mineral in the mixture was determined so as to have equal surface areas of each mineral. SEX: diethyl-DTC mixtures with mole ratios of 90:10 and 70:30 were investigated. Total molar dosages per injection for SEX, diethyl-DTC and both collector mixtures were maintained constant.

4.10.1.1 Thermochemical behaviour of mineral mixtures using SEX, diethyl-DTC and mixtures thereof.

Thermochemical measurements in Figure 42 show that the enthalpies of adsorption for the interaction between SEX and the mineral mixture was greater than for either of the pure minerals alone. It can be concluded that when SEX is added to a mixture of chalcopyrite and pyrite, the magnitude of reaction was higher than that measured for the pure mineral alone. The behaviour of the two pure minerals changed once they are in a mixed system. The enthalpies of adsorption suggest that SEX has a higher affinity for pyrite after mixing with chalcopyrite

Figure 42 shows that the enthalpies of adsorption for the interaction of diethyl-DTC with both single minerals and mineral mixtures were similar, viz. around -65 kJ/mol. It is clear that the magnitude of interaction of diethyl-DTC was equal for chalcopyrite, pyrite and the mineral mixture. It follows that the thermochemical behaviour of the mineral mixture was the same as that of the pure minerals that make up the mineral mixture. Thus the findings on diethyl-DTC are opposite that of SEX.

Thermochemical measurements in Figure 45 showed that the enthalpies of adsorption for SEX, diethyl-DTC and both collector mixtures onto the mineral mixtures were similar. This suggests that the mechanism of interaction of the single collectors and collector mixtures with mixed minerals was the same.

4.10.1.2 Microflotation of the mineral mixtures using SEX and diethyl-DTC and mixtures thereof

Figure 43 and Figure 44 shows that the addition of SEX and diethyl-DTC in the pulp zone slightly increased the recoveries of chalcopyrite and did nothing to the pyrite recovery. However, when pyrite and chalcopyrite were combined and reacted with either SEX or DTC, there was a dramatic improvement in pyrite recovery by around 70-80%. There was also an increase in the recovery of chalcopyrite by about 20% when it was mixed with pyrite.

Figure 46 shows that similiar chalcopyrite and pyrite recoveries were produced by single collectors and collector mixtures in the flotation of mixed minerals. There was no synergistic performance observed as diethyl-DTC outperformed both collector suites.

The microcalorimetric and microflotation results indicate that there were interactions between chalcopyrite and pyrite and these interactions significantly affected the adsorption of the collectors and the floatability of chalcopyrite and pyrite.

Similar results were observed by Ekmekci (1997) who showed that the chalcopyrite-pyrite interactions significantly affected the floatability of the pure minerals. Peng et al. (2003) also observed that pyrite floatability was very poor, around 10%, but its recovery was significantly enhanced after it was mixed with chalcopyrite.

The overall first order flotation rate constants presented in Table 15 show that the flotation rate constant for pyrite using SEX was almost double that of chalcopyrite flotation using the same collector. However, the flotation rate constant for pyrite using diethyl-DTC was half that of chalcopyrite using the same collector. It is important to note that the flotation of the mineral mixture with SEX resulted in slower kinetics than the pure minerals. However, this was insignificant compared to the large improvements in recovery. The flotation of the mineral mixture with diethyl-DTC resulted in significantly improved kinetics than pure minerals.

4.10.1.3 Mechanisms

It has been noted that the thermochemical and flotation behaviour of the chalcopyrite-pyrite mixtures using either single collectors or collector mixtures were similar. It can thus be postulated that the mechanism of interaction of the single collectors as well as the collector mixtures with the chalcopyrite-pyrite mixture was the same.

Since it is accepted that sulphide minerals are semi-conductors (Rao 2004), it follows that when two different sulphide minerals are brought into contact there will be an electrochemical interaction with electrons flowing from the anodic mineral to the cathodic mineral.

There are two possible phenomena to explain the interactions between chalcopyrite and pyrite:

A. Galvanic interaction between chalcopyrite and pyrite;
B. Copper activation of pyrite.

A. Galvanic interaction

Pyrite has been shown to have a higher rest potential than chalcopyrite in distilled water at pH 9.2, making pyrite less electrochemically active than chalcopyrite (Rao and Finch 1988; Mielczarski and Mielczarski 2003). Rao and Finch (1988), using rest potential measurements found that the combination potentials of pyrite in contact with chalcopyrite were lower than that of pyrite alone, implying that there was electrochemical interaction between chalcopyrite and pyrite. Their results at pH 9.2 are shown in Table 17.

Table 17 : Electrochemical measurements with mineral electrodes in distilled water (Rao and Finch 1988)

Mineral	Rest potential mV vs S.H.E. at pH 9.2
Pyrite	336
Chalcopyrite	288
Mineral mixture	312-326

In the galvanic cell set up between chalcopyrite and pyrite, electrons flow from chalcopyrite (anodic) to pyrite (cathodic). Thus chalcopyrite would be oxidised while oxygen is reduced on the pyrite. A schematic of the model of the electrochemical interaction between chalcopyrite and pyrite was proposed by Ekmekci (1997) and is shown in Figure 13.

The galvanic coupling will allow for electron flow between the minerals to enhance the oxidation of the species present in the chalcopyrite by depolarizing the reduction of oxygen to water on the additional surface area provided by the pyrite. The additional copper released may also catalyse the reduction of oxygen or activate the pyrite as will be discussed in the next Section. The more positive mixed potential relative to that of chalcopyrite on its own may also favour the oxidation of xanthate on the chalcopyrite.

$$2X^- \rightarrow X_2 + 2e^- \qquad (8)$$

The dixanthogen formed is the preferred species in the flotation of both chalcopyrite (Alison et al. 1972; Yoon and Basilio 1993; Leppinen et al. 1989) and pyrite (Finkelstein and Goold 1972; Lo et al. 2005; Alison et al. 1972; Finkelstein and Poling 1977; Yoon and Basilio 1993; Valli and Persson 1994; Fuerstenau et al. 1968; Bradshaw et al. 1995; Leppinen et al. 1989). This explains the unexpectedly high pyrite recovery once contacted with chalcopyrite and the increase of chalcopyrite recovery once contacted with pyrite. This is the preferred mechanism since it explains both increases in pyrite and chalcopyrite recovery.

B. Pyrite activation

In terms of the mechanisms whereby pyrite became floatable once contacted with chalcopyrite in a mixture, Ekmekci (1997) using EDTA extraction and XPS suggested that improved pyrite hydrophobicity might be due to two mechanisms:

1. Pyrite oxidation resulting in the metal-deficient, sulphur rich hydrophobic layers forming on the pyrite surface;
2. Indirect copper activation of the pyrite surface.

The first mechanism is highly unlikely since rest potential measurements showed that chalcopyrite is more electrochemically active than pyrite hence chalcopyrite is more susceptible to oxidation than pyrite (Rao and Finch 1988). Furthermore, if the mechanism was responsible, the pyrite would have shown considerable hydrophobicity in the absence of chalcopyrite. However, this was not the case since the collectorless recovery of pyrite was extremely poor, around 10%.

The second mechanism involves the favouring of the oxidation of chalcopyrite by its coupling to pyrite. The oxidation of the chalcopyrite surface would release copper (II) ions into the bulk solution. Owusu et al. (2014) reported that the amount of EDTA extractable Cu (II) ions increased from 5.1% to 8.7% with an increase in pyrite content from 20 to 80 wt% in the mixture. Using XPS and ToF-SIMS, Owusu et al. (2014) showed that the Cu (II) ions are transferred from the chalcopyrite surface to the pyrite surface and would activate the pyrite surface. They found that this inadvertent copper activation of the pyrite increased with increasing pyrite content in the mineral mixture.

Copper activation promotes the adsorption of collector ions on the pyrite surface, enhancing its flotation in alkaline conditions (Finkelstein 1997). Thus once activated, the pyrite surface becomes hydrophobic, translating to improved recoveries.

Smart (1991) studied surface layers on metal sulphides as single and mineral mixtures and showed that copper dissolves from chalcopyrite surfaces equilibrating in solution as copper (II) ions, adsorbing on the pyrite surface via an electrochemical mechanism as copper (I). The Copper (I) ions then complex with the collector ions, thereby activating the hydrophilic pyrite surface. It is further reported that the pyrite activation is due to the deposition of a copper sulphide phase onto the pyrite through the reduction of copper (II) to copper (I) (Peng et al. 2003). XPS experiments conducted by Owusu et al. (2014) showed that surface copper was mainly in the form of Cu(I) while EDTA extraction showed the bulk copper in the form of Cu(II). This reinforces the possibility of the reduction of Cu(II) to Cu(I) at the pyrite surface.

To investigate the activation of pyrite by copper ions, microflotation experiments were conducted in the presence of a copper sulphate activator. The copper sulphate was assumed to have a cross Sectional head area of 20 Å (Malysiak 2003). A dosage of copper sulphate equivalent to two monolayers was used. The results are shown in Figure 54.

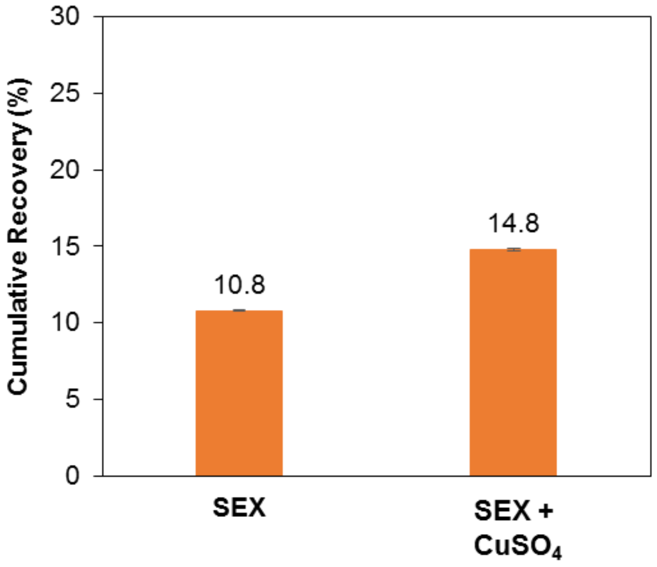


Figure 54: Comparison of pyrite recoveries using SEX as collector in the presence and absence of $CuSO_4$ activator (pH 9.2; the standard error was always below ±1% hence the error bars were too small to be visible).

Figure 54 shows that there was a small increase in the pyrite recoveries in the presence of the $CuSO_4$ activator. This implies that the marked increase in pyrite recovery noted in this study once it is mixed with chalcopyrite is partly a result of inadvertent activation of pyrite by Cu^{2+} ions (produced through the dissolution of chalcopyrite) as well as through the mechanism discussed in A.

In summary, the increase of the chalcopyrite and pyrite recoveries are a result of the galvanic interactions between chalcopyrite and pyrite which are the driving force for the dimerisation of the collector anions. Furthermore, the increased floatability of pyrite is also a result of the indirect activation of pyrite by Cu^{2+} ions released from the dissolution of chalcopyrite through oxidation.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The enthalpies of adsorption of the interaction of sulphide minerals with single thiol collectors and collector mixtures were determined using microcalorimetry. The resultant hydrophobicity has been determined using microflotation. Mineral mixtures were also investigated with both single collectors and collector mixtures. All experiments were conducted at pH 9.2.

Sulphide minerals investigated were chalcopyrite, pyrite, pyrrhotite and galena. Thiol collectors investigated were xanthates of varying chain length (SEX, SIBX, PNBX and PAX) as well as dithiocarbamates (diethyl-DTC and n-butyl DTC) and diethyl-DTP. Collector dosages were determined based on the BET surface area of the minerals. SEX: diethyl-DTC collector mixtures with mole ratios of 90:10 and 70:30 were investigated. Chalcopyrite-pyrite mixtures were used to simulate real ore although a real ore would include gangue. The mineral mixture comprised of 51:49wt% chalcopyrite and pyrite respectively to ensure that equivalent surface areas of each mineral were used.

The enthalpy of adsorption was found to increase with increasing collector chain length of xanthates on chalcopyrite. The same observation was made when pyrite, pyrrhotite and galena were interacted and floated with SEX and PAX. The microflotation recoveries were found to increase with increasing collector chain length for chalcopyrite, pyrite, galena and pyrrhotite (Göktepe 2002; Ackerman et al. 1987; Fuerstenau 2005). It was observed that there is a positive correlation between the enthalpy of adsorption and hydrophobicity for xanthates of different chain length on sulphide minerals. It was concluded that increasing alkyl chain length promotes both collector-mineral interaction, as well as the resultant hydrophobicity of the mineral.

The effect of the branching of the hydrocarbon chain length on the enthalpy of adsorption was dependent on the ligand type. For the xanthates, PNBX produced a higher enthalpy of adsorption than SIBX on the chalcopyrite surface. However, n-butyl DTC and diethyl-DTC produced similar enthalpies of adsorption on the chalcopyrite. From microflotation tests, the linear collectors outperformed their branched counterparts for collectors with equivalent alkyl chain length.

The enthalpy of adsorption of diethyl-DTC was always greater than diethyl-DTP for chalcopyrite, pyrite, galena and pyrrhotite. In fact, diethyl-DTP showed barely any interaction with all the sulphide minerals, since extremely low enthalpies of adsorption, viz. around -5 kJ/mol were obtained. Diethyl-DTP showed unexpectedly high recoveries for galena, chalcopyrite and pyrrhotite despite low enthalpies of adsorption. Since the microflotation experiments excluded the froth phase, it was speculated that the diethyl-DTP stabilised the bubble-particle agglomerates, translating to higher recoveries. Diethyl-DTC and diethyl-DTP produced equal recoveries for each of the minerals studied, except for pyrrhotite. These results indicate that that there is no correlation between the enthalpy of adsorption and hydrophobicity for collectors with the same alkyl chain length but different ligand type. The results further indicate that the alkyl chain length generally is the decisive parameter in imparting hydrophobicity in flotation.

It can be concluded that generally there is no correlation between the enthalpy of adsorption and hydrophobicity. The magnitude of the collector-mineral interactions do not necessarily translate to hydrophobicity. The enthalpy of adsorption cannot be used to predict the recovery of sulphide minerals. This was substantiated by the fact that diethyl-DTP hardly reacted with all the sulphide minerals, and yet produced unexpectedly high chalcopyrite and galena recoveries. Furthermore, PAX and diethyl-DTC produced similar enthalpies of adsorption when contacted with pyrite but produced markedly different recoveries of the same mineral.

An interesting result was that pyrite did not respond to SEX and diethyl-DTC in a microflotation cell although microcalorimetry showed that there was interaction between pyrite and the two collectors. This suggested that, although reactions were occurring with a resultant heat associated with them, these reactions did not result in sufficient hydrophobicity for flotation to occur. This is an interesting observation and from an economic perspective would result in the consumption of reagent with no recovery benefit.

It is interesting to note that the enthalpies of adsorption for pyrrhotite with different thiol collectors were about half of those measured for chalcopyrite, galena and pyrite. This implies that the magnitude of the reaction between these collectors and pyrrhotite was relatively lower than on pyrite, galena and chalcopyrite. The explanation for this behaviour was simply attributed to the purity of the pyrrhotite sample that was used. The purest sample available was composed of only about 60% pyrrhotite. The microflotation recoveries produced when pyrrhotite was interacted with thiol collectors were relatively lower, which were attributed to the same fact – the lower pyrrhotite purity.

The enthalpy of adsorption for SEX: diethyl-DTC collector mixtures with mole ratios of 90:10 and 70:30 were similar to those of pure diethyl-DTC on chalcopyrite. However, these enthalpies of adsorptions were higher than those of SEX on the same mineral.

Thermochemical measurements showed that synergistically higher enthalpies of adsorption were produced when a small amount of diethyl-DTC was contacted with SEX in a mixture. Microflotation tests showed that the use of collector mixtures resulted in improved kinetics and recoveries than in the case of pure collectors. Overall, the results showed that when mixtures of collectors are used to float chalcopyrite, synergistic performance takes place, resulting in improved recoveries and rates. The optimum ratio of the collectors in the collector mixtures was 90:10 as there was neither an increase in enthalpy of adsorption or terminal recovery when the diethyl-DTC content was raised from 10 mole% to 30 mole% in the mixture. The SEX: diethyl-DTC collector mixture with a mole ratio 70:30 resulted in faster kinetics than its 90:10 counterpart in chalcopyrite flotation. The significance of these findings is that for a slow floating mineral, increasing DTC could improve its flotation rate for a fixed residence time.

It was postulated that dixanthogen was formed when SEX: diethyl-DTC collector mixtures were contacted with chalcopyrite. It is proposed that the reaction is catalysed by diethyl-DTC. Thermochemical measurements showed that collector mixtures produced unexpectedly higher enthalpies of adsorption. This was attributed to the initial adsorption of the DTC and xanthate and the subsequent oxidation of the xanthate to dixanthogen by the DTC-modified chalcopyrite surface. The mechanism of dixanthogen formation was reinforced by the increase in chalcopyrite recoveries produced by collector mixtures above those produced by single collectors.

When SEX was interacted with a mixture of chalcopyrite and pyrite, the heat of reaction was higher than that measured for the reaction of SEX with the pure mineral alone. However, with diethyl-DTC, the magnitude of reaction was equal to that of the DTC reaction with pyrite. SEX, diethyl-DTC and SEX: diethyl-DTC mixtures with mole ratios of 90:10 and 70:30 produced similar enthalpies of adsorption and microflotation recoveries when interacted with chalcopyrite-pyrite mixtures. It was thus concluded that the mechanism of interaction of the single collectors and collector mixtures with the mixed mineral was the same. Pyrite showed extremely poor flotation behaviour singly, but showed improved and significant flotation behaviour once it was mixed with chalcopyrite, using both single and collector mixtures. Chalcopyrite recoveries were also improved once it was mixed with pyrite. There was no evidence of synergistic interaction when collector mixtures were used to float mixed minerals. Both thermochemical measurements and microflotation tests showed that the behaviour of the pure minerals changes significantly once they are brought into contact in a mixture. It can be concluded that the changes in the thermochemical behaviour and floatability of minerals once they are contacted in a mixture are a result of the galvanic interactions between chalcopyrite and pyrite which is the driving force for the dimerisation of the collector ions and the indirect activation of pyrite by Cu^{2+} ions released from the dissolution of chalcopyrite through oxidation.

5.2 Recommendations

Since this study focussed only on processes taking place in the pulp phase, it follows that the findings obtained in this study only hold for the pulp phase. It would be useful to investigate whether these findings are sustained when the froth phase is introduced. The following recommendations are made:

a. Using a batch flotation cell in which the froth phase is introduced.
b. The use of a real ore to find out whether the findings hold true for a real ore.
c. Use of surface science techniques to identify the actual species formed from the mineral-collector interactions.
d. Investigate the effect of the chalcopyrite: pyrite ratio on the thermochemical behaviour and floatability of the minerals.
e. Investigate the effect of water type on the enthalpy of adsorption and floatability of sulphide minerals.

CHAPTER 6: REFERENCES

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APPENDIX A: Microcalorimetry

Collector dosage calculations

An example of the Pyrrhotite – amyl xanthate system

Mass of pyrrhotite (g)	0.2002
Surface area of mineral (m2/g)	1.267
Specific surface area of mineral (m2)	0.254
One molecule collector head (m2)	2.88E-19
Number of molecules required for 100% coverage	8.81E+17
Number of molecules required for 50% coverage	4.40E+17
Number of molecules required for 25% coverage	2.20E+17
Mass of PAX used (g) in 50 ml	1.854
Concentration of collector (mol/dm3)	0.186
Collector purity	0.982
Active mass of PAX	1.821
Active concentration collector (mol/dm3)	0.183
Number of moles of collector required for 25% coverage	3.66E-07
Volume of collector required for 25% coverage (L)	2.00E-06
Volume of collector required for 25% coverage (μL)	1.998
No of moles required for 100% coverage	1.46E-06

Enthalpies of adsorption for different mineral-collector systems (corresponding to ~50% monolayer coverage, pH 9.2)

Chalcopyrite

No of injection	Cumulative mol added	Fraction of monolayer	-Specific enthalpy of adsorption (kJ/mol)						
			SEX	SIBX	PNBX	PAX	Diethyl-DTC	Diethyl-DTP	n-butyl DTC
1	1.93E-07	0.25	33.6	41.2	51.5	53.6	67.0	4.0	63.1
2	3.86E-07	0.50	33.5	40.8	50.7	53.2	60.5	5.7	63.3
3	5.79E-07	0.75	26.8	40.3	48.8	57.3	49.9	3.3	60.7
4	7.71E-07	1.00	26.0	38.1	49.5	49.0	42.0	2.4	56.6

Pyrite

No of injection	Cumulative mol added	Fraction of monolayer	-Specific enthalpy of adsorption (kJ/mol)			
			SEX	PAX	Diethyl-DTC	Diethyl-DTP
1	1.79E-07	0.25	58.6	59.7	62.3	5.4
2	3.59E-07	0.50	55.6	58.9	62.5	6.6
3	5.38E-07	0.75	51.4	60.2	62.4	6.0
4	7.18E-07	1.00	47.7	62.7	64.1	6.0

Pyrrhotite

No of injection	Cumulative mol added	Fraction of monolayer	-Specific enthalpy of adsorption (kJ/mol)			
			SEX	PAX	Diethyl-DTC	Diethyl-DTP
1	3.66E-07	0.25	23.3	37.3	26.2	7.4
2	7.32E-07	0.50	23.6	41.0	26.9	9.7
3	1.10E-06	0.75	20.9	38.4	27.7	10.2
4	1.46E-06	1.00	20.3	36.3	26.3	10.3

Galena

No of injection	Cumulative mol added	Fraction of monolayer	-Specific enthalpy of adsorption (kJ/mol)			
			SEX	PAX	Diethyl-DTC	Diethyl-DTP
1	1.00E-07	0.25	43.3	56.0	63.5	-1.5
2	2.01E-07	0.50	28.5	51.9	65.2	1.6
3	3.01E-07	0.75	25.8	44.0	68.0	1.1
4	4.01E-07	1.00	29.8	39.1	69.4	-4.0

Chalcopyrite vs collector mixtures

No of injection	Cumulative mol added	Fraction of monolayer	-Specific enthalpy of adsorption (kJ/mol)	
			90:10	70:30
1	1.93E-07	0.25	74.9	70.0
2	3.86E-07	0.50	62.8	54.5
3	5.78E-07	0.75	51.7	48.1
4	7.71E-07	1.00	42.5	39.3

Mineral mixtures

No of injection	Cumulative mol added	Fraction of monolayer	- Specific enthalpy of adsorption (kJ/mol)			
			SEX	Diethyl-DTC	90:10	70:30
1	1.86E-07	0.25	65.9	66.2	65.6	62.6
2	3.72E-07	0.50	63.3	64.7	64.7	57.3
3	5.58E-07	0.75	65.5	65.8	65.8	49.1
4	7.44E-07	1.00	64.6	62.4	62.4	43.5

APPENDIX B: Microflotation

Chalcopyrite

Collectorless

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	10.3	10.3	10.3	0.006	0.004
C2	6	30.6	30.5	30.6	0.033	0.023
C3	12	51.7	51.6	51.7	0.077	0.055
C4	20	65.4	65.3	65.4	0.115	0.082

SEX

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	24.4	24.3	24.3	0.108	0.076
C2	6	45.3	45.3	45.3	0.012	0.009
C3	12	59.3	59.4	59.3	0.049	0.035
C4	20	68.3	68.3	68.3	0.009	0.006

SIBX

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	27.4	27.3	27.4	0.110	0.078
C2	6	48.5	48.2	48.3	0.166	0.118
C3	12	63.5	63.5	63.5	0.020	0.014
C4	20	73.5	73.4	73.5	0.049	0.035

PNBX

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	28.5	28.4	28.5	0.030	0.021
C2	6	49.5	49.5	49.5	0.010	0.007
C3	12	64.9	65.0	65.0	0.060	0.043
C4	20	75.3	75.3	75.3	0.019	0.013

PAX

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	29.5	29.6	29.5	0.068	0.048
C2	6	50.5	50.7	50.6	0.158	0.112
C3	12	66.3	66.4	66.3	0.072	0.051
C4	20	77.1	76.9	77.0	0.121	0.086

Diethyl-DTC

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	22.7	22.8	22.8	0.035	0.025
C2	6	46.6	47.4	47.0	0.592	0.419
C3	12	61.5	62.0	61.8	0.324	0.229
C4	20	71.3	71.5	71.4	0.111	0.079

Diethyl-DTP

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	17.8	17.4	17.6	0.292	0.207
C2	6	45.8	46.7	46.2	0.590	0.417
C3	12	65.2	65.5	65.4	0.192	0.136
C4	20	76.6	76.8	76.7	0.156	0.111

Galena flotation

Collectorless

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	7.8	7.8	7.8	0.032	0.022
C2	6	37.8	37.8	37.8	0.003	0.002
C3	12	70.9	70.9	70.9	0.023	0.017
C4	20	97.3	97.2	97.2	0.020	0.014

SEX

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	11.0	11.0	11.0	0.025	0.017
C2	6	31.2	31.3	31.3	0.059	0.042
C3	12	59.5	59.5	59.5	0.034	0.024
C4	20	89.8	89.9	89.9	0.033	0.023

PAX

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	40.3	40.3	40.3	0.029	0.021
C2	6	79.4	79.4	79.4	0.019	0.013
C3	12	95.5	95.5	95.5	0.012	0.009
C4	20	99.3	99.3	99.3	0.007	0.005

Diethyl-DTC

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	49.6	49.6	49.6	0.006	0.004
C2	6	84.9	84.9	84.9	0.021	0.015
C3	12	97.3	97.4	97.3	0.012	0.009
C4	20	99.5	99.5	99.5	0.010	0.007

Diethyl-DTP

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	6.1	6.3	6.2	0.123	0.087
C2	6	18.0	18.0	18.0	0.026	0.019
C3	12	41.6	41.7	41.7	0.025	0.017
C4	20	78.9	78.9	78.9	0.030	0.021

Pyrite

Collectorless

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	3.7	2.0	2.8	1.206	0.853
C2	6	6.2	5.1	5.6	0.766	0.542
C3	12	8.4	8.0	8.2	0.311	0.220
C4	20	10.1	10.5	10.3	0.265	0.187

SEX

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	5.6	5.6	5.6	0.015	0.011
C2	6	7.6	7.5	7.6	0.028	0.020
C3	12	8.6	8.7	8.6	0.037	0.026
C4	20	9.8	10.0	9.9	0.184	0.130

PAX

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	7.5	7.7	7.6	0.125	0.089
C2	6	18.0	17.9	17.9	0.040	0.028
C3	12	28.6	28.4	28.5	0.100	0.071
C4	20	36.2	36.1	36.2	0.080	0.057

Diethyl-DTP

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	2.3	2.2	2.3	0.073	0.052
C2	6	4.7	4.6	4.6	0.099	0.070
C3	12	7.7	8.4	8.0	0.479	0.339
C4	20	11.6	12.3	11.9	0.496	0.351

Diethyl-DTC

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	3.0	2.8	2.9	0.148	0.105
C2	6	4.9	4.8	4.9	0.128	0.090
C3	12	7.0	6.9	7.0	0.111	0.079
C4	20	10.1	10.0	10.1	0.047	0.033

Pyrite with $CuSO_4$ activator

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	2.7	2.9	2.8	0.118	0.083
C2	6	5.4	5.5	5.4	0.089	0.063
C3	12	10.1	10.2	10.2	0.122	0.087
C4	20	14.8	14.9	14.8	0.076	0.054

Pyrrhotite

Collectorless

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	2.2	1.9	2.1	0.258	0.182
C2	6	6.7	6.2	6.5	0.308	0.217
C3	12	12.7	12.3	12.5	0.231	0.163
C4	20	22.0	21.8	21.9	0.186	0.131

SEX

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	11.0	11.0	11.0	0.009	0.007
C2	6	24.8	24.8	24.8	0.022	0.016
C3	12	40.7	40.5	40.6	0.144	0.102
C4	20	53.6	53.4	53.5	0.128	0.090

PAX

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	13.9	14.0	14.0	0.061	0.043
C2	6	31.6	31.6	31.6	0.036	0.025
C3	12	51.7	51.5	51.6	0.114	0.081
C4	20	69.5	69.3	69.4	0.109	0.077

Diethyl-DTP

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	9.7	9.7	9.7	0.013	0.009
C2	6	28.0	28.0	28.0	0.028	0.020
C3	12	47.7	47.7	47.7	0.010	0.007
C4	20	63.8	63.7	63.8	0.017	0.012

Diethyl-DTP

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	2.5	2.6	2.6	0.077	0.054
C2	6	6.5	6.6	6.5	0.107	0.076
C3	12	9.9	10.0	10.0	0.018	0.013
C4	20	17.4	17.2	17.3	0.132	0.093

Chalcopyrite floated with collector mixtures (SEX + diethyl-DTC)

90:10 mole ratio

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	35.6	35.6	35.6	0.017	0.012
C2	6	61.7	61.6	61.6	0.071	0.050
C3	12	77.8	77.6	77.7	0.120	0.085
C4	20	89.0	89.0	89.0	0.019	0.013

70:30 mole ratio

	Time (min)	Run 1	Run 2	Avg	SD	SE
C0	0	0	0	0	0	0
C1	2	39.6	39.3	39.5	0.224	0.159
C2	6	66.0	66.1	66.1	0.079	0.056
C3	12	81.3	81.2	81.3	0.051	0.036
C4	20	89.0	89.1	89.0	0.027	0.019

Chalcopyrite-Pyrite mixtures

SEX

	CONCENTRATES	**TAILINGS**
Mass of sample (mg)	**51.4**	**49**
% Cu	**11.9**	**6.62**
Mass of Cu (mg)	6.117	3.244
Moles of Cu (mmol)	0.096	0.051
Moles of chalcopyrite (mmol)	0.0963	0.051
Mass of chalcopyrite (mg)	17.66	9.36
Fe associated with Ccp		
1:1 Cu:Fe		
Moles Fe (mmol)	0.096	0.051
Total Fe (Ccp + Py)		
Mass of sample (mg)	**51.4**	**49**
% Fe	**37.93**	**23.29**
Mass of Fe (mg)	19.50	11.41
Moles of Fe (mmol)	0.3494	0.205
Fe associated with pyrite		
Fe from pyrite (mmol)	0.253	0.153
Mass of pyrite, Py* (mg)	30.32	18.38

Scale up		
Total concentrates (g)	2.211	0.674
Chalcopyrite recovered	0.759	0.129
Pyrite recovered	0.0108	0.0021
Chalcopyrite recovery	**85.5**	
Pyrite recovery	**83.8**	

Diethyl-DTC

	CONCENTRATES	**TAILINGS**
Mass of sample (mg)	**52.5**	**48.2**
% Cu	**14.19**	**7.3**
Mass of Cu (mg)	7.450	3.519
Moles of Cu (mmol)	0.117	0.055
Moles of chalcopyrite (mmol)	0.117	0.055
Mass of chalcopyrite (mg)	21.50	10.16
Fe released from Ccp		
1:1 Cu:Fe		
Moles Fe (mmol)	0.117	0.055
Total Fe (Ccp + Py)		
Mass of sample (mg)	**52.5**	**48.2**
% Fe	**39.37**	**23.92**
Mass of Fe (mg)	20.669	11.529
Moles of Fe (mg)	0.370	0.207
Fe from pyrite		
Fe from pyrite (mmol)	0.253	0.151
Mass of pyrite, Py* (mg)	30.321	18.115

Scale up		
Total concentrates (g)	2.491	0.345
Chalcopyrite recovered	1.020	0.073
Pyrite recovered	0.012	0.001
Chalcopyrite recovery	**93.4**	
Pyrite recovery	**91.7**	

90:10 mole ratio

	CONCENTRATES	**TAILINGS**
Mass of sample (mg)	**50.6**	**52.1**
% Cu	**11.31**	**9.06**
Mass of Cu (mg)	5.723	4.720
Moles of Cu (mmol)	0.090	0.074
Moles of chalcopyrite (mmol)	0.090	0.074
Mass of chalcopyrite (mg)	16.52	13.63
Fe released from Ccp		
1:1 Cu:Fe		
Moles Fe (mmol)	0.090	0.074
Total Fe (Ccp + Py)		
Mass of sample (mg)	**50.6**	**52.1**
% Fe	**37.66**	**24.98**
Mass of Fe (mg)	19.056	13.015
Moles of Fe (mmol)	0.342	0.233
Fe from pyrite		
Fe from pyrite (mmol)	0.251	0.159
Mass of pyrite, Py* (mg)	30.12	19.04

Scale up		
Total concentrates (g)	2.136	0.617
Chalcopyrite recovered	0.697	0.161
Pyrite recovered	0.011	0.002
Chalcopyrite recovery	**81.2**	
Pyrite recovery	**84.9**	

70:30 mole ratio

	CONCENTRATES	**TAILINGS**
Mass of sample (mg)	**51.6**	**68.1**
% Cu	**11.22**	**8.97**
Mass of Cu (mg)	5.790	6.109
Moles of Cu (mmol)	0.091	0.096
Moles of chalcopyrite (mmol)	0.091	0.096
Mass of chalcopyrite (mg)	16.71	17.63
Fe released from Ccp		
1:1 Cu:Fe		
Moles Fe (mmol)	0.091	0.096
Total Fe (Ccp + Py)		
Mass of sample (mg)	**51.6**	**68.1**
% Fe	**35.97**	**20.98**
Mass of Fe (mg)	18.561	14.287
Moles of Fe (mg)	0.333	0.256
Fe from pyrite		

Fe from pyrite (mmol)	0.241	0.160
Mass of pyrite, Py* (mg)	28.93	19.15
Scale up		
Total concentrates (g)	2.407	0.442
Chalcopyrite recovered	0.780	0.114
Pyrite recovered	0.011	0.001
Chalcopyrite recovery	**87.2**	
Pyrite recovery	**91.6**	