The effect of mixing thiol collectors in the flotation of pure sulphide ores

by

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Synopsis

Using mixtures of xanthate with either dithiophosphate (DTP) or dithiocarbamate (DTC) has been reported to increase the flotation performance of several sulphide flotation operations. The increased flotation performance has often been termed synergistic. Synergism is defined as the effect exceeding the *pro rata* contribution of either constituent in the mixture.

This thesis aims to investigate the effects that mixtures of either xanthate and di-alkyl DTP or xanthate and di-alkyl DTC have on the pulp phase floatability of pure galena and pyrite by means of microflotation. Both minerals were chosen because they have been widely studied in sulphide flotation, and to determine whether flotation results with mixtures were mineral specific.

All collectors were investigated at both the ethyl and isobutyl alkyl chain lengths. 90:10 and 10:90 molar ratios of xanthate:DTC or xanthate:DTP were investigated. The total molar dosage was based on the BET surface area of each mineral and the cross – sectional area of a typical reagent molecule. This molar dosage was kept constant at an estimated 50% pseudo monolayer coverage. Pure collector tests were done to establish a baseline from which to assess changes in flotation behaviour when using mixtures of collectors. Deionised water was used to eliminate any possible affect of mineral activation by dissolved ions. The investigation was carried out at pH 9, which simulates common concentrator conditions.

Pulp phase floatability of both minerals was divided into the three limiting particle size regions of flotation, viz. coarse, intermediate and fine. The coarse fraction was chosen as -150 +75μm, intermediate as -75 +38μm and the fine as -38μm. The fine fraction was proposed to be recovered mainly by entrainment as it did not respond to different collector conditions, whereas the intermediate and coarse fraction did. The coarse fraction was found to be the least amenable to flotation and thus was used as the indicator for increased hydrophobicity.

Pure collector test findings showed that an increase in alkyl chain length, regardless of collector, resulted in increased flotation performance for both minerals. The findings validated the experimental method used in this study, as these results were consistent with accepted results recorded in literature. The general order of collector strength for both minerals was found to be xanthate > dithiophosphate > dithiocarbamate. DTC was expected to be the strongest collector according to general literature, but was found to have virtually no collecting properties under the conditions used in this study. Xanthate and DTP were found to have similar flotation behaviour at the ethyl alkyl chain length. It was also found that galena was more amenable to flotation than pyrite.

Galena flotation was observed to increase synergistically in three cases. The first case was the use of a 10:90 ethyl xanthate : di-ethyl DTP mixture resulted in a 17% (overall), 49% (coarse) and 39% (intermediate) improvement in galena recovery above that of the case where only ethyl xanthate was used. Due to the marked increase in the coarse fraction recovery, which is thought to require the most hydrophobicity to float, it is proposed that the use of this mixture may have resulted in a more favourable distribution of reagents on the mineral surface, which resulted in increased hydrophobicity.

An increase in flotation performance was also observed for 90:10 and 10:90 ethyl xanthate : di-ethyl DTC mixtures for galena. The 10:90 mixture resulted in a 13% (over all), 26% (coarse) and 31% (intermediate) improvement in galena recovery. The 90:10 mixture resulted in a 30% (overall), 77% (coarse) and 51% (intermediate) improvement in galena recovery. Both increases were measured relative to the case where only ethyl xanthate was used. Again the coarse fraction was observed to have the largest increase in flotation recovery indicating markedly increased hydrophobicity. These increases in flotation were a strong indication of either a more favourable distribution or arrangement of collector species on the galena surface or a change in the actual collector species adsorbed on the mineral surface may have occurred.

The improvements in flotation performance when using mixtures of collectors for pyrite flotation followed the same trends as for galena, but were not as significant. There was one exception, a 10:90 mixture of SEX:SEDTP increased pyrite flotation by 4.3% from using SEDTP only. The standard deviation of the SEDTP result was 3% and so the increase was only slight at a maximum of 1.3%.

Three sequences of reagent addition were investigated, viz. xanthate first, DTP or DTC first and simultaneous addition of both collectors. The three mixtures mentioned in previous paragraphs were the result of xanthate being added first. The simultaneous addition of reagents resulted in a poorer flotation response of galena than with either pure collector. The addition of either DTP or DTC first resulted in a flotation response similar to using the pure collectors. These findings supported the arguments proposed for the observed increases in pulp phase floatability observed for galena.

The use of isobutyl mixtures did not result in improved flotation performance for either galena or pyrite. Isobutyl xanthate was found to be the superior collector and it was proposed that under these conditions a more favourable distribution of collector species on the mineral surface when using collector mixtures was not probable. This was due to the already significant hydrophobicity that SIBX had induced on the mineral. Previously observed improvements reported in literature of flotation performance with higher alkyl chain lengths (above ethyl) may have been due to froth phase effects. This is plausible because froth behaviour is known to be influenced by collectors such as di-isobutyl DTP, but not shorter alkyl chain lengths. For both X:DTP and X:DTC mixtures at the isobutyl chain length, the collecting action of SIBX was diluted by the presence of the secondary collector. This effect was more pronounced with DTC than it was with DTP.

The findings in this thesis have shown that shorter chain lengths of collector mixtures can result in synergistically increased particle hydrophobicity on galena. However mixtures consisting of longer alkyl chain length collectors did not exhibit this same behaviour, pointing to the fact that froth phase effects would need to be investigated.

Preliminary batch flotation tests of a synthetic ore, made up (by mass) of 5% galena, 47.5% plagioclase-rich ore (gangue) and 47.5% pyroxene-rich ore (gangue), were carried out to determine whether observations made in microflotation tests for galena were sustained when a froth phase was present. The 90:10 ethyl xanthate : di-ethyl DTC mixture, ethyl xanthate only, di-ethyl DTC only and collectorless condition were investigated. The use of the 90:10 mixture resulted in increased solids and lead recovery when compared to using SEX only. The order of collector strength was similar to that observed for galena in microflotation tests, viz. SEDTC < SEX < 90:10 SEX:SEDTC. Increased water recovery when using the 90:10 mixture, compared to when using SEX only, pointed to a froth stabilisation effect of the mixture and thus increased mass pull.

There could be potential for the use of collector mixtures in mixed sulphide flotation, in that a mixture of ethyl collectors markedly increased the hydrophobicity of a mineral such as galena to a similar extent as if an isobutyl xanthate were used. Whereas a gangue mineral such as pyrite continued to exhibit low flotation performance relative to the use of pure ethyl collectors. This would result in a potentially better separation of the two minerals, as selective collector adsorption between two minerals such as pyrite and galena is hard to achieve. It is appreciated that the effects observed on a pure mineral may be confounded when a mixture of minerals or real ore is used. The huge importance of the role that the froth phase plays in flotation is also recognised even though this study focused on the pulp phase phenomenon.

Plagiarism declaration

I declare that this thesis, submitted for the degree of Master of Science in Engineering at the University of Cape Town, is my own work and has not been submitted prior to this for any degree at this university or any other institution. I understand the meaning of plagiarism and declare that all the work in the document, save for that which is properly acknowledged, is my own.

Daniel Gregory Castelyn

Acknowledgements

> "*What is more, I consider everything a loss compared to the surpassing greatness of knowing Christ Jesus my Lord, for whose sake I have lost all things. I consider them rubbish, that I may gain Christ.*" Philippians 3:8

My hope and gratitude belong to God whose love is greater than the vastness of the universe.

I am grateful for the parents, Mike and Veronika, God has blessed me with, who love me and so have sacrificed a great deal to bring me to this point. My sister Gabi and brother Timmy, thanks for always being awesome siblings. While this is again just the step to another journey, it has been a hell of a step! Danke Papa und Mama!

I could not have stayed presentable to society if it were not for Zara Rindel, thank you, your love is amazing. I hope this experience has not traumatised you too much.

I would like to thank Dr. Belinda McFadzean and Prof. Cyril O'Connor for their supervision throughout this thesis. I consider Prof O'Connor to be one of the great minds of Mineral Processing. It is truly a privilege to be your student. And Belinda who has soldiered through the details and groundwork with me, I appreciate all your help and effort.

Last but not least, I owe my ease in times of stress to the game of Rugby and the men who played for Turtle's Rugby under the tenure of Ben Lowe as captain - *Heroes in a half shell... Turtle power*!

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Nomenclature

d_p particle diameter

d_b bubble diameter

$\mathbf{E}_{coll}$ Collection efficiency

$\mathbf{E}_c$ Particle-bubble collision efficiency

$\mathbf{E}_a$ Adhesion efficiency

$\mathbf{E}_s$ Stability or detachment efficicny

FF particle form factor

$\Delta\mathbf{G}_S$ Change in Gibbs free energy

J_g superficial gas velocity

K or k is the flotation rate constant, in this thesis it is a first order rate constant

MB is the difference between the calculated and the actual mass recovery

n population size, e.g. for a duplicate $n = 2$

P Feed ore flotability

R particle roundness

R_f Froth phase recovery

S_b bubble surface area flux

SD Standard error of the mean, all error bars shown in Figures are the standard error of the mean

Greek letters

θ_Y - Young contact angle

θ - contact angle

μ - micron or 10^{-6}m

σ - the standard deviation of the sample population

τ - flotation time [min]

List of abbreviations

BET - initials of the surnames of the authors of the gas adsorption surface area estimation technique.

C$_{2-8}$ - number of carbon atoms in the collector alkyl chain length

CCC - critical coalescence concentration

DTC - di-alkyl dithiocarbamate

DTP - di-alkyl dithiophosphate

EC - electrochemical mechanism

esd - equivalent sphere diameter

FTIR - Fourier transform infra-red spectroscopy

ICP - inductively couple plasma optical emission spectroscopy

MIBC - methyl iso-butyl carbinol

MX$_z$ - is the metal thiol salt

PAX - potassium amyl (normal pentyl) xanthate

PNBX - potassium normal butyl xanthate

pK$_a$ - acid dissociation constant or stability constant

ppm - part per million *or* $1/1e^6$

PSD - particle size distribution

R - alkyl group

SEM - scanning electron microscope

SEX - sodium ethyl xanthate

SIBX - sodium isobutyl xanthate

SEDTP - sodium di-ethyl dithiophosphate

SIBDTP - sodium di-isobutyl dithiophosphate

SEDTC - sodium di-ethyl dithiocarbamate

SIBDTC - sodium di-isobutyl dithiocarbamate

SIMS - secondary ion mass spectrometry

ToF-SIMS - time of flight secondary ion mass spectrometry

UCT - University of Cape Town

XRD - X-ray diffraction

$\mathbf{X}^-$ - xanthate radical

$\mathbf{X}_2$ - xanthate dimer, dixanthogen

Chapter 1

Introduction and literature review

1.1 Introduction

1.1.1 Mining and flotation

To introduce the topic of flotation it is best to start with the reason this technology exists. The need for hard commodities such as base and precious metals is the root of all technology involved in the extraction of valuable minerals from the earth's crust. Mining and the processing of ore has been a part of humanity's technological development from pre-historic times to the present day and age. Mining in a way is the embodiment of humanity's progression from the stone age through to the bronze age, iron age and into our modern age or contemporary era.

As time has progressed the amount of extractable minerals has become less concentrated in ore bodies around the world and so the technology used to extract it has had to develop significantly. From being able to smelt copper mined with stone and bone tools, to the present day processing plants and open pit mines such as the Bingham Canyon Mine copper mine in Utah (USA) (seen in Figure 1.1.1). Flotation research is part of addressing the challenge that the world's minerals are becoming less concentrated as rich ore bodies are being mined out, yet at the same time demand for base and precious metals increases as global population and economic wealth continue to grow.

Figure 1.1.1: An illustration of the worlds deepest open pit copper mine - Kennecott Copper Mine in Utah.

Mining is the up-stream process of extractive metallurgy as illustrated in the Figure 1.1.2. Extractive Metallurgy covers all processes used in the recovery of metals from their ores and is broadly made up of four main fields viz. Pyrometallurgy, Hydrometallurgy, Electrowinning and Mineral Processing. These are however not independent of each other and are often used in combination to process the same ore. Comminution, or size reduction and classification is commonly the first step, regardless of the processing type chosen. Mineral processing is mainly concerned with the comminution and concentration of the mineral(s) in an ore. The method of concentration used by the metallurgist depends on the mineral that needs to be recovered. Each process makes use of physical and/or chemical differences between the value bearing mineral and the gangue.

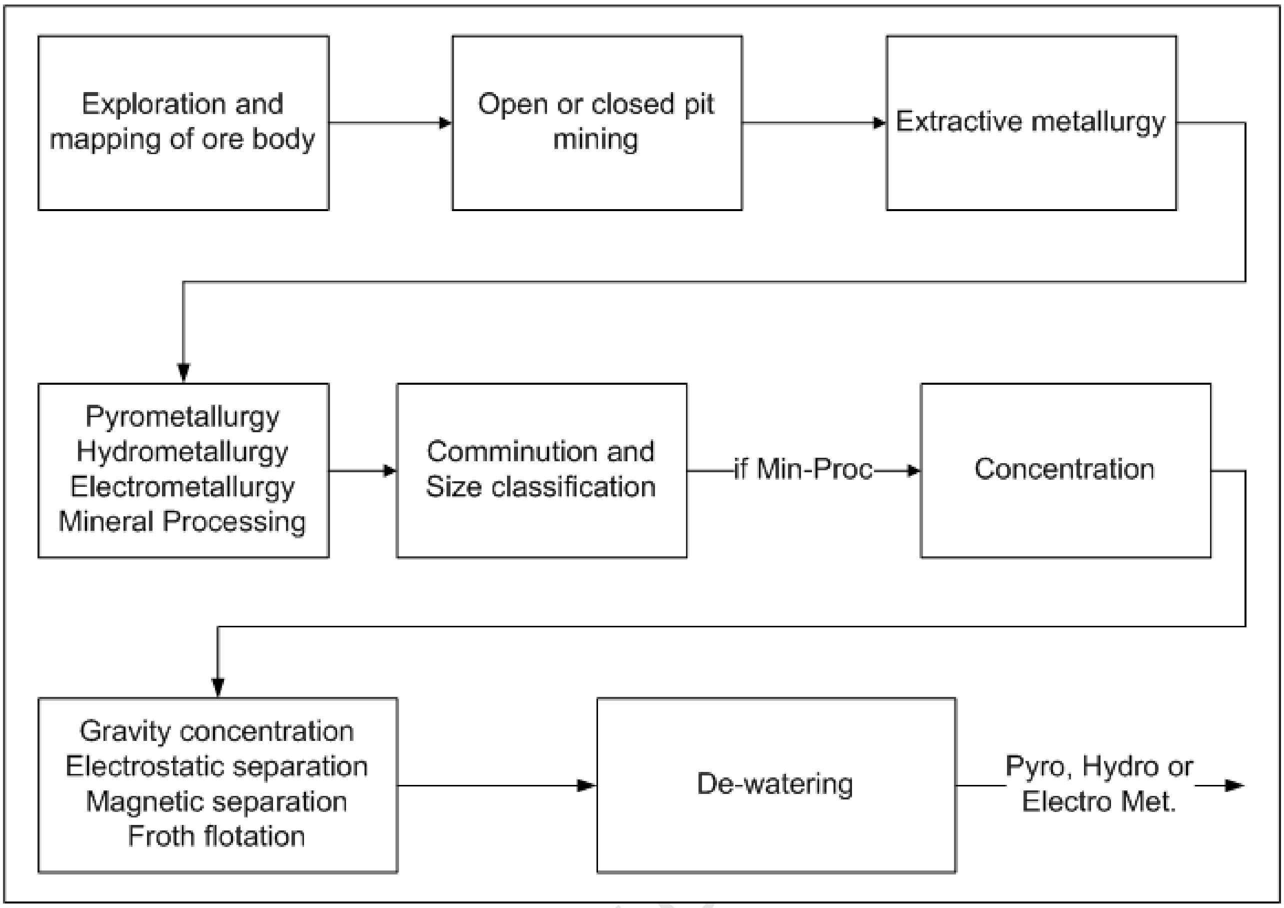


Figure 1.1.2: A diagram illustrating the cradle to gate life cycle of Minerals mining.

Froth flotation is one of the most common technologies used in the processing of ores today. It has also found application in industries outside mining such as water treatment and paper recycling. Flotation cells use water and air to selectively separate hydrophobic from hydrophilic materials. There are two operational phases present, the pulp and froth phase. The pulp phase ensures the floated particles are transported out of the cell. The convention is for valuable minerals to be floated and gangue to remain depressed in the pulp. The reverse is, however, also possible. Figure 1.1.3 represents the cross section of a flotation cell. There are several different cell designs, each with its own advantages and disadvantages. For a detailed account of the development and history of the flotation cell (and its different designs) the reader is referred to *History of Flotation* by Lynch et al. (2010).

The most basic and arguably important step in flotation is for hydrophobic particles to attach to rising air bubbles and be successfully collected in the froth phase. This is known as true flotation, which is a selective process based on the physical and chemical characteristics of the particle. Undesired materials can also be recovered by entrainment, which is unselective as it is just material being entrained in water reporting to the froth phase. Careful control of the froth phase can ensure that the effect of entrainment is minimised by allowing the flotable gangue to drain out of the froth before it is collected (Wills and Napier-Munn, 2006).

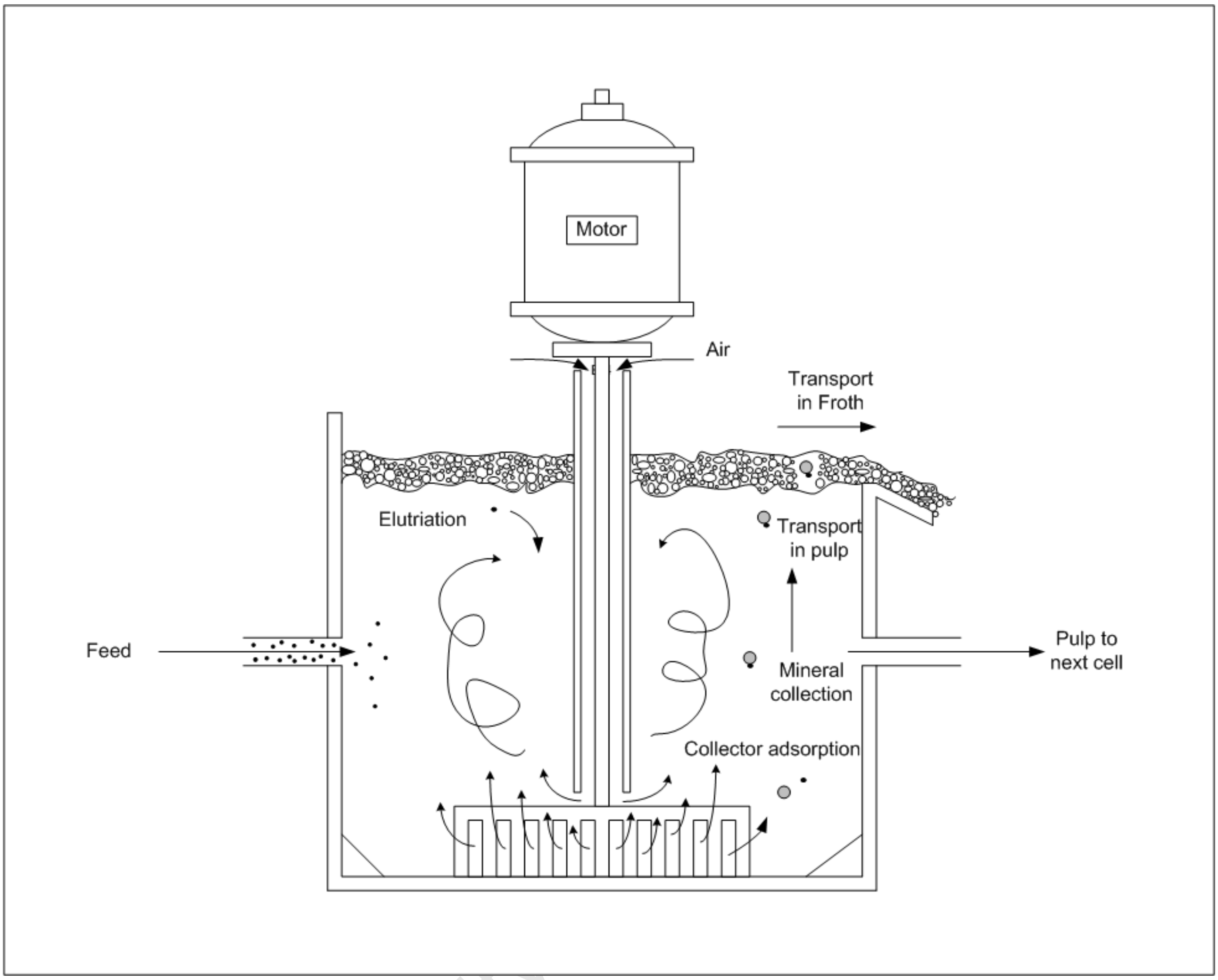


Figure 1.1.3: Cross section of a flotation cell

As with any chemical reactor or separations unit there is almost always the need for more than one unit to achieve an operational line as close to physical equilibrium of separation as possible (and an economically viable product). These circuits or banks of flotation cells (in series) are designed to maximise recovery of the valuable mineral. An example of a simple flotation circuit is shown in Figure 1.1.4.

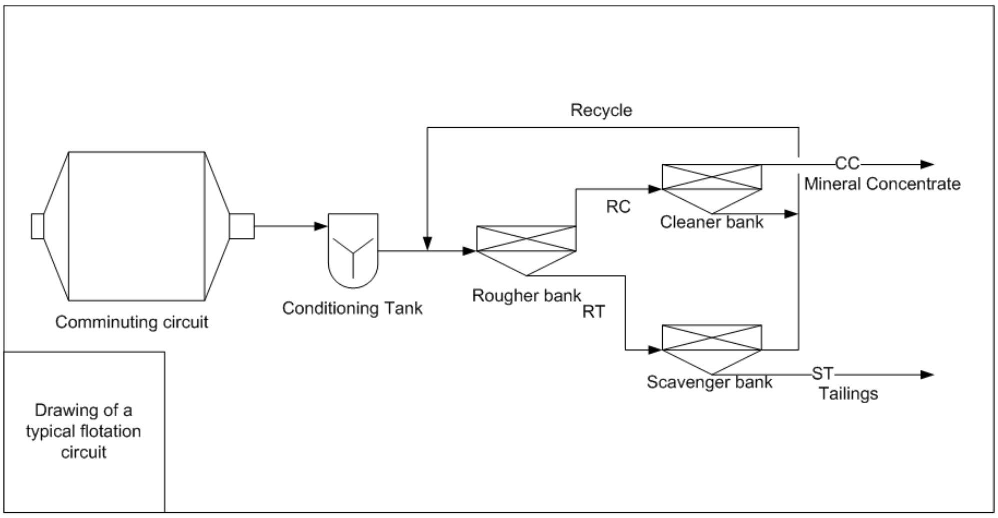


Figure 1.1.4: A typical flotation circuit consisting of a grinding circuit, pulp conditioning tank, rougher, cleaner and scavenger banks.

There are numerous factors which affect the efficiency of separation within a flotation cell. These factors have been aptly summarised in Figure 1.1.5 by Klimpel (1988). The triangle illustrates the point that while these factors can be categorised, they are mutually inter-dependent (Nagaraj, 2005).

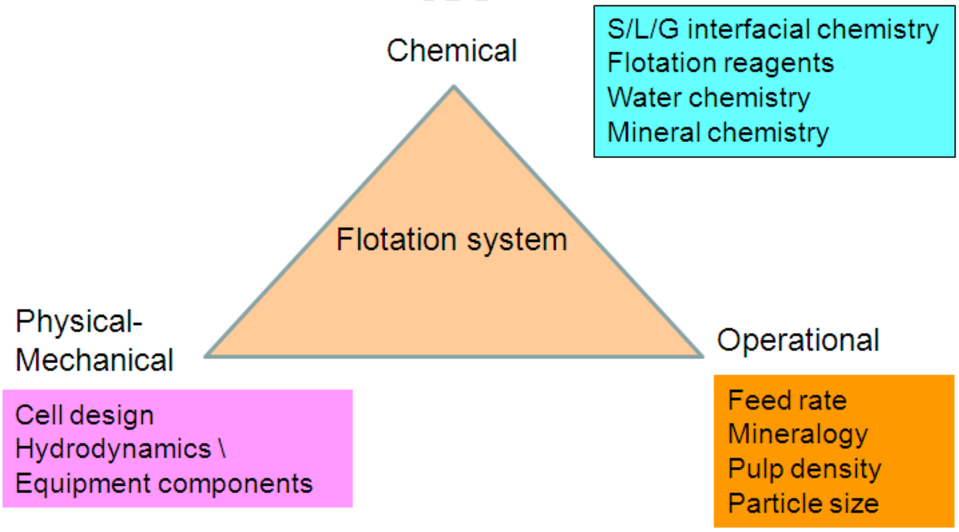


Figure 1.1.5: Flotation system schematically represented by a triangle, indicating the mutual importance of each factor involved; Adapted from Klimpel (1988).

Most important for the purpose of this thesis are the chemical effects on flotation, specifically collectors, a class of flotation reagents designed to enhance the hydrophobicity of valuable minerals and thus their use is central to the success of achieving selective flotation. The triangle in Figure 1.1.5 was expanded by Nagaraj (2005) to include the reagent optimisation in a holistic view as seen in Figure 1.1.6, most importantly highlighting the interaction between frothers, modifiers and collectors.

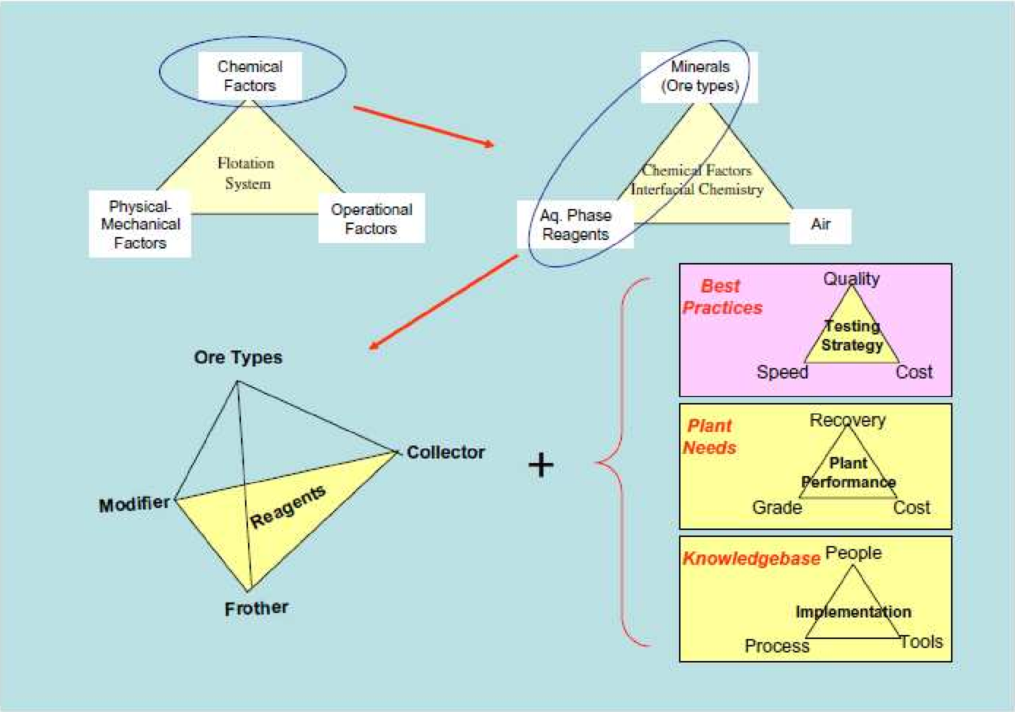


Figure 1.1.6: The expanded holistic view of the flotation system in reagent selection and optimisation. Copied from Nagaraj (2005).

1.2 The sub-process of flotation

Froth flotation is comprised of a variety of sub processes all of which have a role in the ultimate efficiency and success of recovering and separating the value bearing minerals from the gaunge. These sub-processes are generally described as follows (Bradshaw, 1997):

1. The mineral particle surface of interest is rendered hydrophobic by adsorption of a reagent. Adsorption is controlled by the hydrodynamics and properties of the pulp (pH, pulp potential etc.).
2. Bubbles of a specific size and distribution are introduced into the pulp.
3. The bubble and mineral collide with a possibility of particle attachment. Particle detachment may also occur.
4. The loaded bubble is transported through the pulp phase.
5. Particles are transferred from the pulp to the froth phase, this can occur by bubble transport and entrainment. Elutriation can occur, whereby particles fall back into the pulp phase from the froth.

6. Loaded bubbles are collected from the froth phase and recovered.

1.3 Physical effects on flotation

1.3.1 Particle collection

The third step described in the last section is quantitatively characterised by the collection efficiency (E_{coll}) into the froth. The concept was first proposed by Schumann (1942) and then later extended by Derjaguin and Dukhin (1961) to be made up of a further three sub-processes; Efficiency of particle-bubble collision (E_c), adhesion (E_a) and stability or detachment (E_s).

where

$$E_{coll} = E_c\, E_a\, E_s \tag{1.3.1}$$

Each sub-process takes into account variables such as contact angle, system turbulence, particle and bubble size (Duan et al., 2003). They are briefly discussed. Extensive research has gone into understanding E_{coll} and its constituent efficiencies. The literature has been reviewed (Dai et al., 2000).

1.3.1.1 Collision

A particle must collide with a bubble for it to attach. Hydrodynamics of the system determine how particles approach and interact with bubbles. Fine particles tend to skirt around the edges of the bubble instead of directly coming into contact with it (King, 1982) because of a lack of momentum. Models exist to predict the collision efficiency of particles and bubbles. Taking into account variables such as particle trajectory and inertial forces (Duan et al., 2003). The conclusion is that the smaller the particle is the less efficient the bubble/particle collision tends to be. This is simply a result of the momentum of such particles.

1.3.1.2 Attachment

Once a particle has come into contact with a bubble it must attach to it. Attachment occurs by the water film between the particle and bubble thinning and eventually rupturing. The ability to do this depends on how hydrophobic the particle is. The amount of time the particle has to rupture the film and attach to the bubble is referred to as the induction time. Attachment will be unsuccessful if the induction period is longer than the time it takes the particle to sweep over the bubble surface and back into the bulk.

1.3.1.3 Stability

The particle must remain attached to the bubble as it rises to the surface for it to be successfully collected. There will be a fraction of particles which detach from the bubble. A particle will detach when the strain caused by gravity and turbulence exceeds the bubble's skin stress threshold. The conclusion is that a bubble has a maximum load it can successfully collect.

1.3.2 Hydrophobicity

Hydrophobicity or wettability of a particle is a key thermodynamic property which affects separation. Thermodynamics cannot predict grade and recovery in flotation as there is no state of equilibrium reached within a cell (Fuerstenau, 1982a). Hydrophobicity is an important parameter in flotation but its application in predicting overall flotation behaviour is a point of contention.

1.3.2.1 Contact angle

Contact angle was identified early on by Wark (1932) as an important measure of the wettability of a particle. The three phases present at the mineral surface viz. solid, liquid and gas form an angle of contact. The classic way of understanding the contact angle is by using the Young equation. Young described the relationship between the contact angle and tension at each one of the three interfaces as seen below:

$$cos\,\theta_Y = \frac{\gamma_{s/a} - \gamma_{s/l}}{\gamma_{l/a}} \tag{1.3.2}$$

where $\gamma_{s/a}$ = solid-air surface tension

$\gamma_{s/l}$ = solid-liquid interfacial tension

$\gamma_{l/a}$ = liquid air surface tension

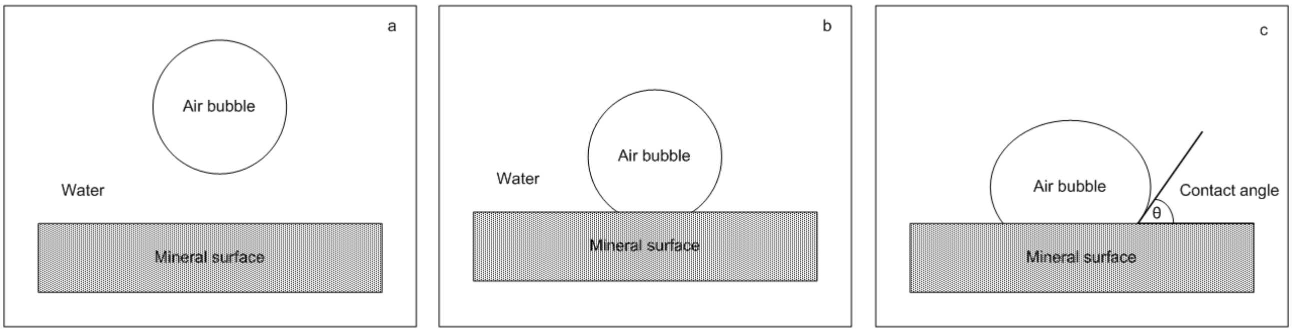


Figure 1.3.1: Picturing contact angle - a) air bubble approaching mineral surface. b) thinning of liquid film until it ruptures and the bubble forms a gas/solid film. c) bubble and mineral surface form a three phase contact angle.

There are numerous estimates which relate the Young contact angle (θ_Y) to factors which affect it. These factors were reviewed by Chau et al. (2009) and include surface roughness and heterogeneity. Contact angle is a good indicator of surface hydrophobicity but not a measure in itself (Leja, 2004).

1.3.2.2 Hydrophobicity

Hydrophobicity of a particle cannot be interchangeably used with contact angle. Hydrophobicity of a surface is an indication of its ability to repel water, shown by the change in Gibbs energy in Equations 1.3.3 and 1.3.4. As seen in Figure 1.3.1 when a bubble attaches to the solid surface the air-water and solid-water interfaces are disrupted. The air bubble must first thin and then rupture the water film before it can attach to the mineral surface. The change in free energy accompanied by the replacing of the solid-liquid by an air-solid interface is given below by Dupre's equation:

$$\Delta G = \gamma_{s/a} - (\gamma_{s/l} + \gamma_{l/a}) \tag{1.3.3}$$

this can be combined with Young's equation to yield

$$\Delta G_S = \gamma_{l/a} (cos \theta - 1) \tag{1.3.4}$$

Free energy change ΔG_S must be less than zero for bubble adhesion to take place in whichever liquid medium is being considered, thus for any contact angle greater than zero, adhesion of the bubble on the mineral surface should in theory be possible (Fuerstenau, 1982a). Hydrophobicity has also been called the thermodynamic probability of flotation (Fuerstenau, 1982a).

Prestidge and Ralston (1996) measured the powder contact angle and related it to surface hydrophobicity. The work related particle size of the galena particles and collector surface coverage measured in equivalent monolayers with the contact angle. As the monolayers increased so did the powder contact angle θ_p. The second significant finding was that as the contact angle increased so did the flotation recovery. This seems like an intuitive result as hydrophobic particles will be more thermodynamically stable out of the water phase and in contact with the air phase.

1.3.3 Particle size effects

Particle size effects are most important to the efficiency of any flotation. It is affected by both physical and chemical factors of the flotation system. Particle size effects have been widely studied and an extensive review has been given by Trahar (1981). Mineral flotation has typically been divided into 3 regions (Trahar, 1981); Fine, intermediate and coarse particle fractions. The intermediate fraction does not receive much attention as it floats well. It is fine and coarse fractions that have decreased flotation rate and recovery as illustrated in Figure 1.3.2 taken from Pease et al. (2006) who constructed this diagram as a solution for floating different particle sizes at different stages at Mt. Isa according to their floatability.

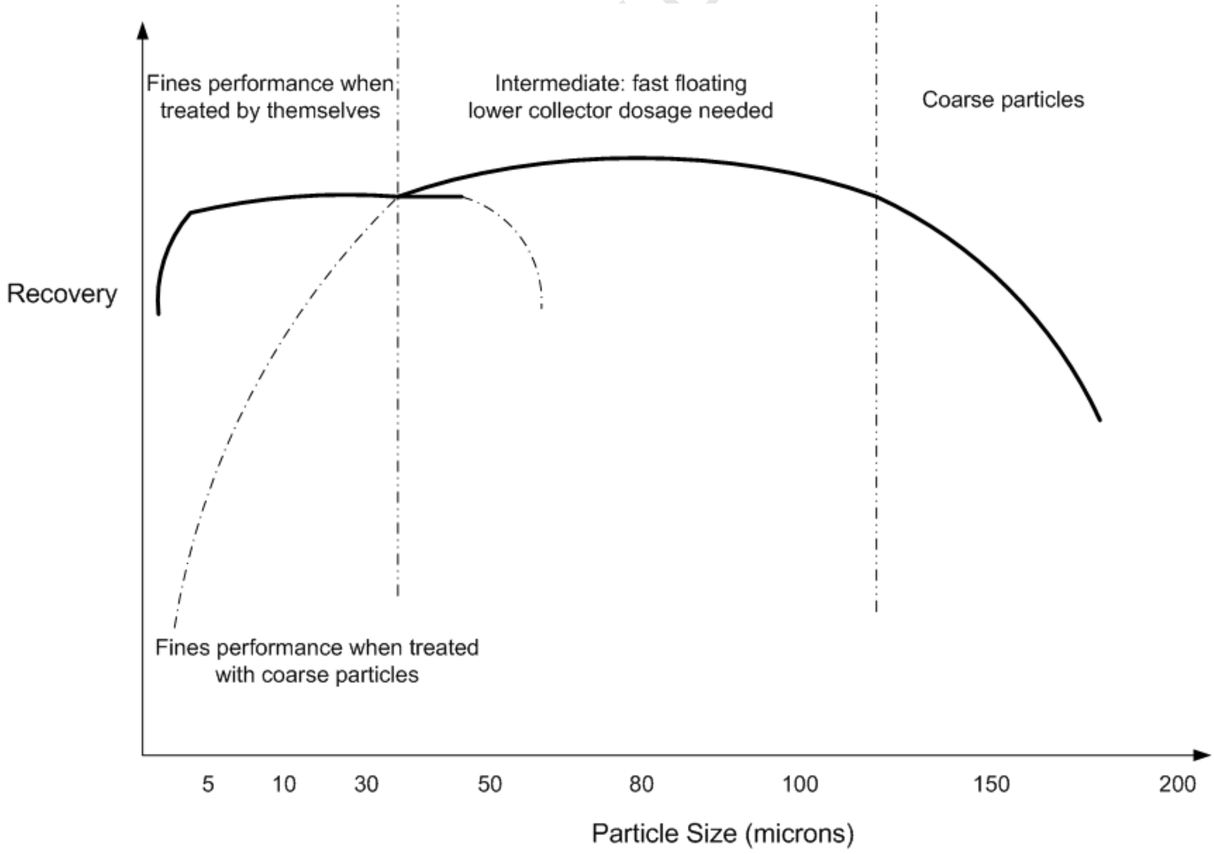


Figure 1.3.2: Variation of flotation recovery with particle size in industrial concentrators. Copied from Pease et al. (2006).

Trahar and Warren (1976) constructed a table in which they presented size ranges for which maximum recovery of numerous minerals under different conditions were observed. It was clear from the data that the intermediate size range (where maximum recovery was observed) varied greatly depending on the flotation condition.

1.3.3.1 Overall rate

The relationship between flotation rate and particle size is in theory thought to be linear (Reay and Ratcliff, 1973) and described by the following relationship:

$$k \propto d_p^n$$

where n is usually unity. It should be noted that this relationship is most probably only linear within certain particle size ranges, and not the full spectrum of particle sizes being floated in any given system. This relationship was shown to hold by Trahar (1981) for several minerals up to 50 μm. Where lower rates of flotation where attributed to the decreased probability of collision between particles and bubbles. Crawford and Ralston (1988) also found this to be true for hydrophobized quartz. It is clear from the various studies undertaken that interpretation of particle size and flotation rate is highly dependent on the methodology of the study. The range of most studies are either in the coarse or fine particle regions. Studies ranged from industrial scale to batch flotation or microflotation devices.

Care should be taken to distinguish between true flotation and recovery by entrainment for fine particles. Entrainment is a major factor in recovering fines (Trahar, 1981). Entrainment increases with decreasing particle size, as shown in a model proposed by Neethling and Cilliers (2009) to predict entrainment with particle size. Entrainment is also generally thought to be related directly to water recovery.

In summary, Sutherland (1948) considered the overall flotation rate (K) to be the sum of rates of recoveries (k_i) of the individual size fractions.

$$K = \sum_i k_i \tag{1.3.5}$$

1.3.3.2 Surface coverage and flotability

One of the first aspects of flotation research was to understand the effect of collector dosage on flotation rate and recovery. Gaudin et al. (1942) observed a reduction in flotation rate with collector dosage for galena particles coated with potassium ethyl xanthate. This was more evident for coarse particles. Trahar (1981) proposed a qualitative relationship in Figure 1.3.3.

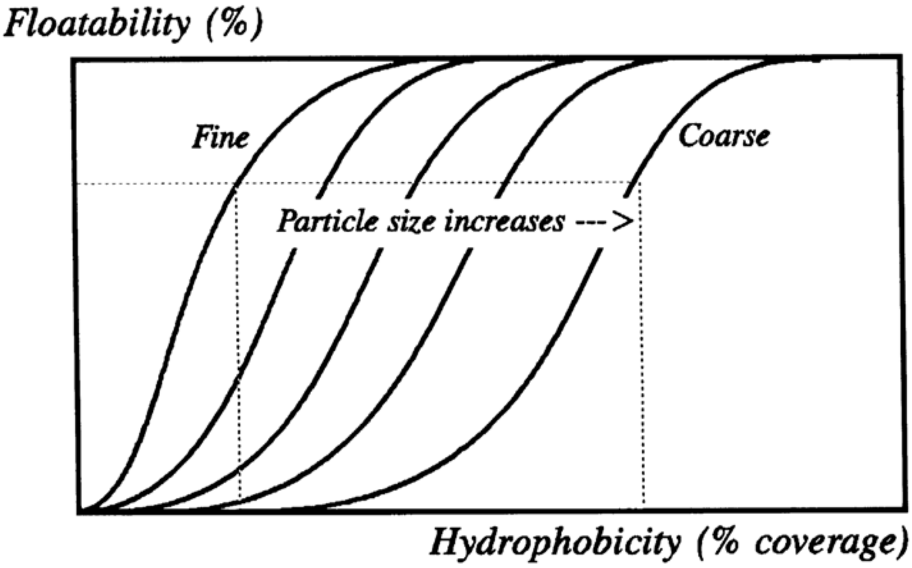


Figure 1.3.3: Qualitative representation of the influence of particle size on the relationship between flotability and hydrophobicity. Copied from Trahar (1981)

Crawford and Ralston (1988) suggested a similar relationship between particle size flotability and hydrophobicity. They floated different particle size classes of hydrophobized quartz. The degree of hydrophobicity was varied (contact angle) and they found that for a given size class there needed to be a critical contact angle for flotation to occur. The flotation domains are shown below in Figure 1.3.4 from Crawford and Ralston (1988).

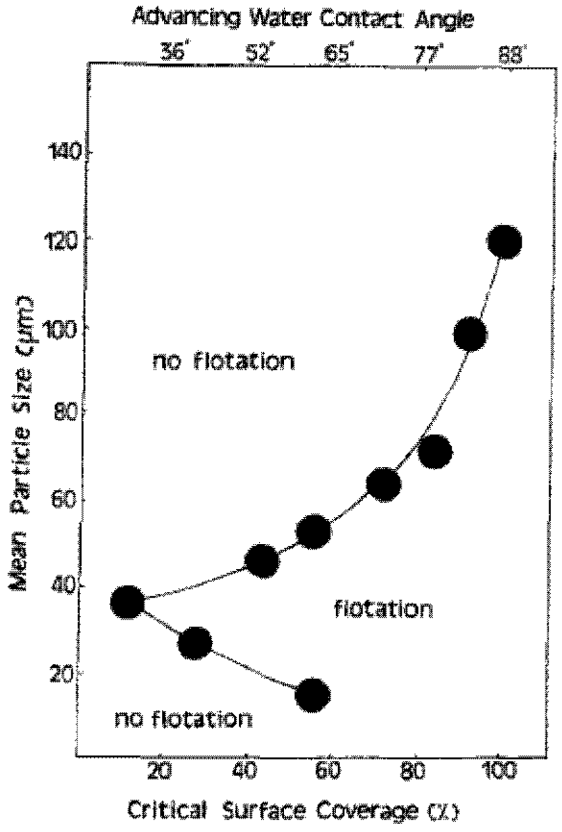


Figure 1.3.4: Flotation domains represented by the function of critical contact angle on particle size class flotability. Copied from Crawford and Ralston (1988).

In general coarser particles need to be more hydrophobic to float. Prestidge and Ralston (1996) investigated the relationship between increasing monolayer coverage of ethyl xanthate with three particle size regions of galena. Although not stated in their study, the three size classes investigated were thought to represent the fine (38-20μm) , intermediate (75-38μm) and coarse (150-75μm) particle size domains.

When a large size range of particles have to compete for the adsorption of collector, it is thought that the finer particles will consume most of it (Klimpel, 1999; King, 1982) because of their larger specific surface area (g/m^2). Collector mineral interactions are also more likely with finer particles because they are thought to have a higher specific surface free energy (j/m^2) than coarse particles. Trahar (1981) however strongly contested this view stating that surface area estimation techniques using the adsorption of gases would then also be subject to these differences in specific surface free energy. This would lead to different surface area estimation methods giving vastly different results.

A typical scenario could be as follows. Finer particles adsorb more collector and achieve their critical hydrophobicity faster than coarse particles due to the differences in available surface area. Increasing the collector dosage will eventually allow the coarse particles to achieve their required hydrophobicity for flotation. This increase in collector dosage will increase the recovery of the individual size classes. Rate of recovery for finer particles however starts to decrease because fine highly hydrophobic particles start to agglomerate and act as larger particles (Klimpel, 1999; Prestidge and Ralston, 1996; Gaudin et al., 1942). However no experimental evidence was presented for this postulate. Klimpel (1999) called this the R/K trade-off where a maximum rate can be achieved at a certain dosage and continued increase of dosage will start to decrease the flotation rate, while the recovery continues to increase. This is a most important aspect since in some systems the kinetics of flotation will be of critical importance (e.g. coal flotation) whereas in others final recovery is the key parameter (e.g. platinum group metal flotation). In addition, it has been shown that increasing collector dosage above a critical concentration can reduce rate and recovery due to a rearrangement of the collector molecules on the surface, creating a hydrophilic layer (Leja, 2004).

Particle size effects raise the following key points:

- When assessing flotation performance of fine particles, entrainment must be factored in as it accounts for the majority of fine particle recovery.
- Coarse particles are the best indicator of collector performance (Trahar, 1981). Any change in particle hydrophobicity will first be observed in coarse particle recovery as they have larger critical contact angles.
- Flotation rate of individual size classes is an important parameter in assessing how efficient flotation under certain conditions is.
- Loss of coarse particle recovery is mainly due to detachment and loss of fine particle recovery is mainly due to the low probability of bubble-particle collision (Tao, 2005).

1.3.4 Bubble size

The role of bubble size in flotation can be seen from two different, but equally important viewpoints. The first and more fundamental point relates to how bubble size affects the subprocesses of flotation as described in Section 1.2 and ultimately the rate of collection. The second point is an operational and design parameter for industrial flotation cells which relates the bubble surface area flux to a first order rate constant of flotation.

The bubble surface are flux S_b in a flotation cell is related to the superficial gas velocity J_g (m/s) and Sauter mean bubble diameter d_b (m) by Equation 1.3.7.

$$S_b = \frac{6J_g}{d_b} \tag{1.3.6}$$

This shows that the smaller the mean bubble size is, the greater the bubble surface area flux S_b will be, which is an intuitive relationship.

The first order rate constant (K) in a number of industrial flotation cells was shown to be related to feed ore flotability (P), bubble surface are flux (S_b) and recovery across the froth phase (R_f) in a series of investigations by Gorain et al. (1995, 1997).

$$K = P \cdot S_b \cdot R_f \tag{1.3.7}$$

The relationship shows that as bubble surface area flux increases with decreasing bubble size, the first order rate constant of particle floatability will increase, *ceteris paribus*.

There are however limits on how small the bubble size can be and a fundamental analysis and review of the literature on bubble size and flotation efficiency by Tao (2005) showed that smaller bubbles could increase the collection of coarse and fine particles. The trade off is however that small bubbles have difficulty in handling the load of coarse and dense particles (Tao, 2005).

1.3.5 Microflotation

Microflotation cells have been used to asses the suitability of a range of collectors and the affect of pH when floating a mineral (Wills and Napier-Munn, 2006).

The three types of microflotation cells are listed here:

1. The Hallimond Tube (and modified) used in numerous studies for fundamental research on bubble-particle interaction studies.
2. The Partridge and Smith (1971) cell, which has been used in numerous studies relating contact angle to the efficiency of bubble-particle collisions.
3. The UCT microflotation cell (Bradshaw and O'Connor, 1994).

Crozier (1991) has summarised the two-sided nature of using microflotation in research:

> "*The Hallimond tube* has been very popular in research laboratories because it eliminates the cost of assaying head, tailings and concentrate. The need to assay is avoided by studying artificial ores made by mixing pure minerals... As frothers normally sequester collectors and interfere with the operation of Hallimond tubes, they are usually omitted. Thus we have the anachronism that a device without a controllable froth is used to simulate froth flotation."

Microflotation is a useful tool to study the degree of bubble-particle recovery in the pulp. Because the froth phase is eliminated. The literature surveyed so far has revealed that the degree of this recovery gives us insight into the degree of hydrophobicity of the particle, keeping all else equal (bubble size, pH, particle size distribution etc.). It should also be pointed out that these systems are non-turbulent and there is no external energy added to the system by means of an impeller as in a batch flotation cell.

1.4 Chemical effects on flotation

1.4.1 Flotation reagents

Flotation reagents are typically placed into three major classes: Frothers, Regulators/Modifiers and Collectors, with some degree in overlap of function between them.

1.4.1.1 Modifiers/activators

This class of reagents includes depressants, pH modifiers and activators. As their name suggests their purpose is to modify the action of the collector (Wills and Napier-Munn, 2006). A common activator is $CuSO_4$, used in the activation of sphalerite. The $CuSO_4$ transforms the relatively inactive sphalerite surface into a relatively active copper ion surface. The action of the salt is basically to promote mineral and collector interaction. Depressants are the opposite of collectors, they are intended to act on the gangue in the ore by decreasing their hydrophobicity. Depressants are commonly used in sulphide flotation to reduce the recovery of gangue minerals. They include carboxy methyl cellulose and guar gum. Modifying the pH will also either enhance or decrease the flotability of a mineral by altering its surface characteristics.

1.4.1.2 Frothers

The froth phase of the flotation process is critical in collecting the bubbles loaded with value bearing minerals and allowing the entrained gangue to drain out simultaneously. Frothers are added to stabilise the froth phase. They are usually hetero polar organic compounds and are chemically similar to ionic collectors (Wills and Napier-Munn, 2006). They stabilise the froth by decreasing the surface tension of the air-water interface of bubbles formed in the pulp. This is possible because of their hetero polar nature, whereby the non-polar part of the molecule tends to force the frother into the air phase and the polar head remains in the water part of the interface. Frother types usually marketed are alcohols, polypropylene glycol and poly glycol ethers. An example of a common frother used in industry is methyl-isobutyl-carbinol (MIBC), which is thought to be relatively weak, but has the least collecting power (Mular et al., 2002).

Cho and Laskowski (2002) showed that frothers maintain a constant bubble size by controlling bubble coalescence. This is true at concentrations of frother above the critical coalescence concentration (CCC) of that frother. CCC is the frother concentration at which no further reduction in bubble size will be observed with increasing frother concentration.

Wiese et al. (2010, 2005) related froth activity (and thereby stability) to the water recovery within batch flotation systems. Whereby increased water recovery has been attributed to the presence of a stabilised froth and decrease in the rate and recovery of water is attributed to a destabilised froth.

1.4.1.3 Collectors

Collectors are typically made up of an inorganic group and a hydrocarbon tail. The inorganic portion will interact with the mineral surface via a chemical reaction. The hydrocarbon chain being orientated towards the bulk gives the mineral a certain amount of hydrophobicity. Collectors are classified as either ionising or non ionising when in solution (Fuerstenau, 1982c). This general scheme is shown in Figure 1.4.1.

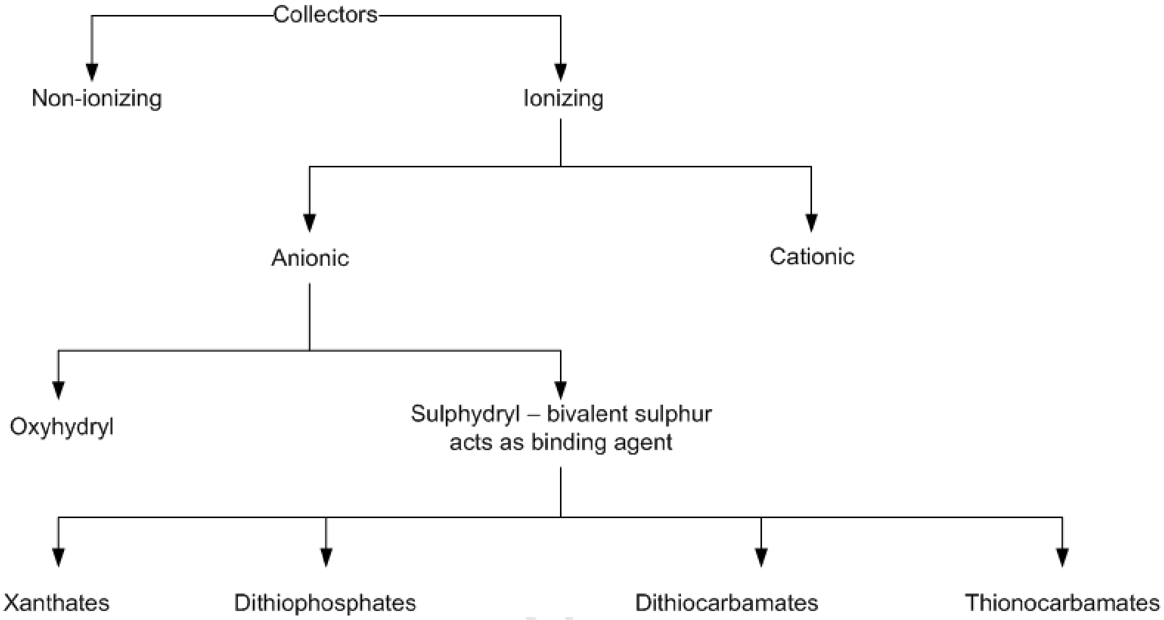


Figure 1.4.1: Classes of collectors commonly found in flotation

Collectors of interest in sulphide mineral flotation are anionic in nature and are known as thiol compounds. Each of these thiols has varying degrees of hydrophobicity and selective adsorption towards minerals. Choosing the right collector or suite of reagents needs to be done carefully to the address the metallurgical requirements of any plant (Nagaraj, 2005).

1.4.1.3.1 Xanthates (X) are the workhorse of sulphide mineral flotation and the most common thiol collector in use (Adkins and Pearse, 1992; Harris, 1988), accounting for 57.1% of all thiol collector consumption in the US (1985) alone (Crozier, 1991). Xanthates shown in Figure 1.4.2 are synthesised by reacting an alcohol, carbon disulphide and an alkali (Aplan and Chander, 1988) according to the following reaction:

$$R-OH+CS_2+NaOH \rightleftharpoons RO-(CS_2)Na+HOH \tag{1.4.1}$$

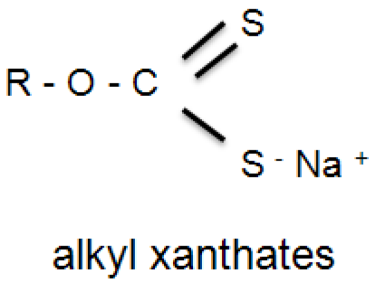


Figure 1.4.2: Molecular structure of an alkyl xanthate

The alkyl group of the alcohol will usually range from C_2 to C_8 depending on the application. The most common form of xanthates are sodium ethyl, sodium isopropyl, sodium isobutyl and potassium amyl xanthate (Adkins and Pearse, 1992; Harris, 1988), with the latter being the most common (Aplan and Chander, 1988). Xanthates are the cheapest of the thiol collectors and popular due to their strong collecting ability in bulk sulphide flotation (Klimpel, 1999). The disadvantage of using xanthates is their lack of selectivity towards the more value bearing sulphides, because of this they are sometimes used in the scavenging section of a flotation circuit, with a more selective collector being used first.

1.4.1.3.2 Dithiophosphates (DTP) accounted for about 21.2% of total thiol collector consumption in 1985 (Crozier, 1991) and 15% worldwide (Aplan and Chander, 1988). This class of collectors is the second largest used in sulphide flotation in terms of consumption and although more expensive than xanthates, they are cheaper than other options of thiol collectors (Klimpel, 1999). DTP shown in Figure 1.4.3 is reported to reach the same mineral recovery at lower dosages than its xanthate counterpart (Float-Ore Ltd.). They are prepared in a similar manner to xanthates.

$$4R-OH+P_2S_5+2NaOH \longrightarrow 2(RO)_2PSSNa+H_2S+2HOH \qquad (1.4.2)$$

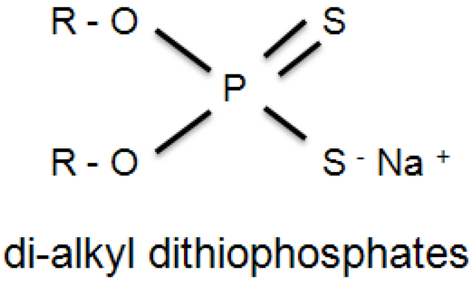


Figure 1.4.3: Molecular structure of a di-alkyl dithiophosphate

Dithiophosphates have been reported to display frothing properties along with collecting ability (Wiese et al., 2005; Adkins and Pearse, 1992; Mingione, 1984). Manufacturers sell low frothing versions of DTP when a high degree of froth control is needed (Cyanamid, 1986). This frothing property of DTP only becomes significant at chain lengths of C_4 or higher (Mingione, 1984). The collecting power of DTP is reported to be less than that of xanthates along with slower flotation kinetics, but show more selectivity and pyrite rejecting ability (Klimpel, 1999; Adkins and Pearse, 1992; Aplan and Chander, 1988). Mingione (1984) however disagrees with this view and stated that DTP had replaced xanthates at certain plants. Nagaraj (2005) also urged that a more holistic view of the flotation system should be taken when assessing a collectors performance. Dithiophosphates are often used together with other collectors such as xanthates (Adkins and Pearse, 1992; Cyanamid, 1986; Mingione, 1984).

1.4.1.3.3 Dithiocarbamates DTC are a lesser class of thiol collectors used in industry (Aplan and Chander, 1988) showing strong collecting power comparable to xanthates (Adkins and Pearse, 1992; Finkelstein and Poling, 1977). DTC has found application in industries outside mining, including fungicides and their metal (non alkaline) salts are known to be water insoluble. Dithiocarbamates shown in Figure 1.4.4 are formed by reacting either a primary or secondary amine with an alkali metal hydroxide, forming the thiol salt (Leja, 2004).

Synthesis using a primary amine:

$$RNH_2 + CS_2 + NaOH \longrightarrow RNHCSSNa + H_2O \tag{1.4.3}$$

or using a secondary amine:

$$R_1R_2NH + CS_2 + NaOH \longrightarrow R_1R_2NCSSNa + H_2O \tag{1.4.4}$$

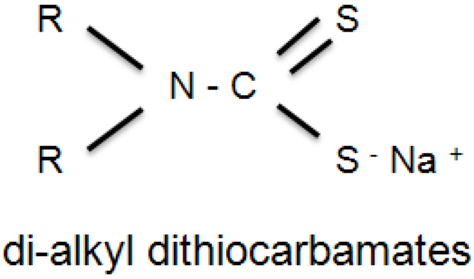


Figure 1.4.4: Molecular structure of a di-alkyl dithiocarbamate

DTC's are more expensive than most thiol collectors (Leja, 2004) and thus are less common in the mining industry.

1.4.2 Collector and mineral interaction

Interaction between various thiol collectors and mineral surfaces have been widely studied. The most fundamental ways in which collectors interact with a mineral surface where amongst the first questions that were addressed in flotation theory. Major ideas postulated are the chemical theory by Taggart et al. (1934), ion exchange (Cox and Wark, 1932) and electrochemical theory also called the 'mixed potential theory' proposed by Nixon (1957). Each of these is briefly outlined.

The presence of oxygen has been recognised as a requisite for flotation to occur (Ahlberg and Broo, 1996; Finkelstein, 1970; Plaskin and Bessonov, 1957), with much controversy over its actual role (Fuerstenau, 1982d). Poling and Leja (1963) argued that oxygen will have a negative effect on xanthate adsorption at mono-layer coverage.

There are three processes now accepted to be involved in thiol - sulphide mineral interactions (Buckley and Woods, 1997; Yoon and Basilio, 1993), chemisorption of the thiol, formation of the metal-thiol compound and physisorption of a dithiolate. This gives two main adsorption processes by which a mineral can be rendered hydrophobic. The first is a chemical interaction viz. chemisorption of the collector onto the mineral or precipitation of a metal-thiol salt onto the mineral. The second is physisoprtion of dithiolates onto the mineral surface, which will then be weakly held by van der Waal's forces.

1.4.2.1 The chemical interaction theory - Metathetical substitution

Chemical theory described many years ago by Taggart et al. (1934) is that an insoluble compound comprised of the metal and collector would form. It was proposed that thiol collectors reacted with minerals according to well recognised reactions. The interaction can best be described by an electrochemical mechanism - even though strictly there is no charge transfer occurring between the metal cation in the sulphide and the collector anion.

$$M^{z+}S^{z-} + zX^{-} \rightleftharpoons MX_z + S^{z-} \tag{1.4.5}$$

where z is the valence of the metal cation

X^- is the thiol anion

MX_z is the metal thiol salt

S^{z-} is the anion

The metal-thiol salt has a solubility product is given by the following equation:

$$K_{sp} = [M^{z+}]\,[X^{-}]^{z} \tag{1.4.6}$$

Taggart et al. (1934) proposed that the magnitude of this solubility product would determine the extent to which the reaction would proceed. The problem with this theory arose with flotation occurring at collector concentrations lower than those predicted by the solubility product of the metal-thiol salt (Woods, 1994).

1.4.2.2 Ion exchange

Ion exchange theory was proposed by Cox and Wark (1932). They proposed that the solubility of the mineral coated with the adsorbed layer of metal-xanthate was different from that of the metal-xanthate alone in solution. They disregarded the surface oxidation of the mineral by which sulphur was replaced by the collector anion. An alternative theory proposed was one of ion exchange (Gaudin, 1927; Cox and Wark, 1932) suggesting direct adsorption:

$$MS \mid OH^{-} + X^{-}(aq) \longrightarrow MS \mid X^{-} + OH^{-} \tag{1.4.7}$$

Another theory put forward by Cook and Nixon (1950) suggested that the acid form of the thiol underwent adsorption. This was discounted as the resultant mineral surface would be too charged to be hydrophobic (Woods, 1994).

1.4.2.3 The mixed potential theory

The type of reactions covered by this theory are reactions where charge is transferred from one element to another. Reactions consist of an anodic oxidation of the collector and cathodic reduction of oxygen at the mineral surface. Mixed potential theory was developed by Nixon (1957). There are many complex reactions that can occur within the process of flotation. The electrochemical potential (E_h) of the system will determine to which extent the electrochemical mechanism (EC) will occur. Several descriptions of the mixed potential theory are given in literature (Leja, 2004; Chander, 1999; Woods, 1994; Aplan and Chander, 1988). E_h will determine the availability of metal ions in the system and the stability constant (pK) of the metal-thiol compound will determine whether it can form at the said E_h (Yoon and Basilio, 1993).

Woods (1994) stated that the EC mechanism is now commonly accepted as the interaction between minerals and thiol collectors. There are three mechanisms which should be considered:

Oxidation of the mineral known as the electrochemical step (controlled by E_h):

$$MS \rightleftharpoons M^{2+} + S^0 + 2e^- \tag{1.4.8}$$

It should be noted that Equation 1.4.8 does not represent sulphur present after the interaction but rather a metal deficient sulphide (Woods, 1994).

The possible cathodic oxidation of the thiol to its dimer with the semi conducting sulphide mineral acting as a catalyst for the electron transfer:

$$2X^- \rightleftharpoons X_2 + 2e^- \tag{1.4.9}$$

Chemical reaction of the metal and collector

$$M^{2+} + 2X^- \longrightarrow MX_2 \tag{1.4.10}$$

The role of oxygen as the acceptor of the electrons and thus anodic reduction (also determined by E_h):

$$O_2 + 2H_2O + 4e^- \rightleftharpoons 2OH^- \tag{1.4.11}$$

It should be noted that galena was found to be a poor catalyst for the reduction of oxygen. The opposite was observed for pyrite. Ahlberg and Broo (1996) determined this by assessing the amount of hydrogen peroxide formed, which is an intermediate in the mechanism for oxygen reduction shown in Equation 1.4.11.

The mechanism of adsorption for each collector and mineral is different due to the varying oxidation/reduction potentials of minerals and collectors. The implication is that a more readily oxidised mineral is more likely to form a metal thiol compound (Nicholson and Shain, 1964). The oxidation of sulphur in the sulphide mineral lattice by oxygen is also crucial in this mechanistic scheme. This confirms the role of oxygen in collector-mineral interactions (Woods, 1994).

The difference between this theory and what would have happened were the collector bonded to a metal in the bulk is illustrated by example of a galena xanthate system (Woods, 1994). In the EC mechanism one xanthate molecule will be bonded to the lead atom in the sulphide lattice. Lead xanthate in the bulk however requires two xanthate radicals to be bonded to the lead atom which has been transferred out of the mineral. This was confirmed by Kartio et al. (1999) who found the dominant surface species to be chemisorbed xanthate molecules rather than a lead ethyl xanthate molecules by use of SR-XPS.

1.4.3 Dithiolates

The role of dithiolates in flotation has been extensively reviewed by Finkelstein and Poling (1977) and discussed by several other authors. Finkelstein and Poling (1977) stated:

> “The formation of dithiolates at the surface is not essential to the collecting action of thiols, although it does give increased flotability”

Improved flotability of a pyrite system was also proposed due to the co-adsorption of dixanthogen and dithiocarbamate (Bradshaw, 1997). The oxidation of thiol collectors to their dimers is strongly dependent on the potential of the pulp or mineral surface which acts as a catalyst to the reaction. Sulphide minerals are semi-conductors and as such are able to aid in electron transfer. A simple representation of the anodic oxidation of a thiol collector X^- to its dimer X_2 (Chander, 1999) is shown below:

$$2X^- \rightleftharpoons X_2 + 2e^-$$

Formation of a dithiolate can be predicted by comparing the thiol collector’s redox potential with the rest potential of the mineral surface it is to be in contact with (Finkelstein and Goold, 1972). It should be noted that the standard reduction potential of the thiol collector is dependent on the alkyl chain length as is shown by Finkelstein and Poling (1977).

For these measurements to be meaningful, they must be made relative to a collector in solution with a mineral. This was done by Finkelstein and Goold (1972), revealing that only pyrite was capable of oxidising all three thiol collectors viz. DTP, DTC and xanthate. Interaction between dithiolates and mineral surfaces is usually in the van der Waal's region (> 40 kJ/mole) resulting in a weak physical bond being formed (Aplan and Chander, 1988). The extent to which these dithiolates are formed is not stated.

1.4.4 Collector selectivity

Selectivity of collectors towards different minerals is crucial in flotation. Rejection of iron sulphide ores such as pyrite when floating copper ores is essential to maintain a reasonable grade of the concentrate. Selectivity of collectors is reported in literature according to the following order (Bagci et al., 2007; Bradshaw, 1997; Nagaraj, 1988).

$$\text{DTP} > \text{X} > \text{DTC}$$

with their strength as collectors being the reverse of the selectivity

$$\text{DTC} > \text{X} > \text{DTP}$$

Leja (2004) suggested that DTC has equal selectivity to xanthate. An example of this selectivity could be that a collector is able to discriminate between two sulphide minerals.

Selectivity can be based on the chemical nature of the collectors and specifically the reactive centre's electron-withdrawing or donating capabilities. The higher the electronegativity the more able the collector centre is to accept electrons. The lower the electronegativity, the more able it is to donate electrons (inductive effect). This electron withdrawing or donating ability of the collector determines how well it will interact with water and the mineral surface. Electronegativity of the atoms of interest are shown below for reference.

$$\text{O } (3.5) > \text{N } (3.07) > \text{S } (2.44) > \text{P } (2.06)$$

Oxygen is the most electron withdrawing element in this series and as such will tend to draw electrons towards it when compared to nitrogen. Oxygen has a lone pair of electrons and will be the most polarised when compared to the other three elements.

Fairthorne et al. (1997) stated that collector selectivity towards a specific metal ion was dependent on the nature of the functional group on the collector, the pK_a which indicates the donor atoms tendency to donate electrons to the metal cation or acceptor, and the nature of the donor atoms. The lower the pK_a the more electron withdrawing the substituent is.

The pK_a of each collector is given below.

Table 1.4.1: pK_a of selected thiol collectors

Collector	pK_a	reference
DTP	~ 0	Leja (2004)
Xanthatic acid	2.0 - 3.0	Harris (1988)
DTC	7.5	Raju and Forsling (1991)

Evaluating each collector's functional group we can infer the same order of electron withdrawing or donating capabilities as we would using pK$_a$. DTP has two O-R groups and thus is expected to have the greatest electron withdrawing effect and, therefore, the least electron density around its binding centre. The phosphate on the DTP is also more electronegative than the carbon in xanthate, adding to the electron withdrawing effect and further lowering the electron density around the reactive centre. DTC differs from xanthate in that it has one more alkyl group and nitrogen bonded to the CS_2 instead of oxygen. Oxygen is strongly electron withdrawing and nitrogen tends to be an electron donor (Fairthorne et al., 1997; Nagaraj, 1988). This causes a positive inductive effect towards the DTC binding centre and makes DTC the most electron dense collector at the binding centre. The collector's binding centres are shown in Table 1.4.2 for reference.

Table 1.4.2: Collector binding centres given in descending order of most electron donating according to literature pK$_a$ values.

Collector	Binding centre
Dithiocarbamate	OCS_2
Xanthate	$NHCS_2$
Dithiophosphate	O_2PS_2

1.4.5 Effect of chain length and branching

In general it has been though that the longer the alkyl chain length of a collector the better/stronger it will float a sulphide mineral (Harris, 1988; Ackerman et al., 1987). This observation came about from early contact studies done by Wark and Wark (1932) who showed for xanthates, dithiocarbamates and dithiophosphates that higher chain lengths had larger contact angles. A general result was also that amongst other sulphide minerals, galena and pyrite had the same contact angles when coated with the same collector.

Ackerman et al. (1987) compared microflotation results of different chain lengths of xanthates with pyrite (and copper sulphides). They found that ethyl xanthate was a poorer collector than amyl xanthate. The branched (iso) propyl (C_3) xanthate also showed greater recoveries for pyrite than its straight chain counter part. The opposite was however true for the C_5 and C_8 xanthate chain lengths (Ackerman et al., 1987). They attribute steric hindrance of the branched isomer to be the cause of the loss of performance.

With regards to the formation of dithiolates, Chander (1999) showed that as xanthate chain length increases the standard reduction potential for a dithiolate/thiol couple decreases. Which in essence means that longer chain lengths are oxidised more easily to their dimer. this is intuitively correct since, the longer the carbon chain length, the more positively inductive it is and the electron density gathers around the reactive centre. This increases the ease of oxidation.

1.4.6 pH effects on flotation

Pulp pH plays an important role in flotation as it determines the state of the mineral surface and reagent stability and activity, for e.g. xanthates are most stable in alkaline solutions (Wills and Napier-Munn, 2006). Lime and soda ash are commonly used as pH regulators and also fall into the reagent class of modifiers as discussed previously. The varying degree of natural flotability of minerals in different pH's can in theory also lead to their effective separation; at a pH chosen to float one and depress the other. The specific effects on flotation of pyrite and galena, the two minerals chosen for this study, will be discussed in more detail later on in this thesis. pH and dissolved oxygen content play an important role in determining the E_h (electrochemical potential) of the solution.

1.5 Minerals/Ores

1.5.1 Collector-less flotation and mineral oxidation

Sulphide minerals have different reactivities due to the variable oxidation state of sulphur (Leja, 2004). Mild oxidation of the surface which leads to metal deficient sulphides or poly-sulphides (Rumbold and Richmond, 1996) being formed is thought to cause the observed natural hydrophobicity of sulfide minerals. The formation of either a sulphur, metal deficient or poly-sulphide layer is strongly pH dependent (Hampton et al., 2011). The degree of natural flotability varies depending on how easily a mineral is oxidised. Poly-sulphides are most common at pH > 8; whereas at pH < 6 elemental sulphur is the dominant species (Chen and Morris, 1972). Extensive oxidation of minerals however is detrimental to flotatation as it inhibits collector adsorption and decreases hydrophobicity of the sulphide surface.

For comparison of the relative collectorless flotability of galena and pyrite Table 1.5.1 gives literature values of their rest potentials.

Table 1.5.1: sulphide mineral rest potentials in water at pH 4, adapted from Ralston (1991)

Mineral	**Rest Potential (V vs. SHE)**
Pyrite	0.66
Galena	0.40

From the data it is evident that pyrite is more readily oxidised than galena. Galena is ranked as a having a higher relative collectorless flotability than pyrite (Ralston, 1991).

Buckley et al. (2003) who investigated collector adsorption on pre-oxidised surfaces of selected sulphide minerals concluded:

> "In each case, the products of interaction of the mineral with the collector were the same for freshly exposed and pre-oxidised surfaces. Chemisorption at pre-oxidised surfaces occurs by ion exchange followed by reorganisation of the metal thiolate in the surface layer rather than by a dissolution/adsorption mechanism."

This means an ultra clean mineral surface is not crucial to ensure collector adsorption.

Ralston (1991) summarised collectorless flotation and mineral oxidation as follows:

> "All else being equal... the less easily oxidised the sulphide the more readily it floats without a collector... Conversely... rapid oxidation may cause a mineral such as galena to become non-flotable."

1.5.2 Collector surface species on minerals

Identification of the collector species responsible for hydrophobicity on the mineral surface has been the cause of much research. There has been a lot of disagreement on the validity of the methods used. Nagaraj and Brinen (2001) continued to be confident in SIMS studies identifying different collector surface species. Chander (1999) remained cautious of the SIMS study results due to varying oxidation products possibly being misinterpreted.

The minerals of concern for this project and their proposed collector surface species are discussed in more detail in the proceeding paragraphs. Nagaraj and Brinen (2001) summarised observations on adsorbed collector species quite aptly:

> "A simplistic view of collector adsorption on natural sulphide minerals involving one distinct species is probably far-fetched and often misleading."

1.5.3 Galena

Galena is major source of commercial lead and often associated with other sulphide ores such as sphalerite which is one of the primary sources of zinc. There are however exceptions where either zinc or lead are found as the only significant primary sulphide (Wills and Napier-Munn, 2006). Its crystal structure is cubic and is rarely found in any other crystalline shape. Galena feed grades range from 1-5% Pb (Wills and Napier-Munn, 2006). Galena deposits are also known to contain significant amounts of silver.

Flotation of galena (and separation from its associated sulphide - sphalerite) is effective and considered to be well established in industry. Galena is more naturally flotable than sphalerite and so is usually floated first. Sphalerite is depressed using $ZnSO_4$. Galena flotation occurs at a neutral or slightly elevated pH, the use of cyanide is common to help depress pyrite (usually the most abundant gaunge mineral). Optimum recoveries of galena are usually achieved using a combination of xanthates and dithiophosphate collectors (cf. Section 1.4.1.3.2). Weaker frothers such as MIBC are used in lead flotation, due to galena's inherent natural flotability.

Fundamentals of galena flotation have been studied extensively, this is mainly due to its availability in its natural form and the fact that lead does not change oxidation states readily, like copper (Fuerstenau, 1982b). Collectorless hydrophobicity of galena is similar to that of most sulphide ores. Natural hydrophobicity of galena is commonly attributed to the formation of a lead deficient sulphur rich or elemental sulphur species (Leja, 2004).

Surface speciation diagrams are a thermodynamic method of determining which surface species are present on a mineral as a function of pH. Kelebek and Yoruk (2002) constructed such an equilibrium distribution for a Pb-S-Carbonate system as shown below in Figure 1.5.1 which has been directly copied from their work.

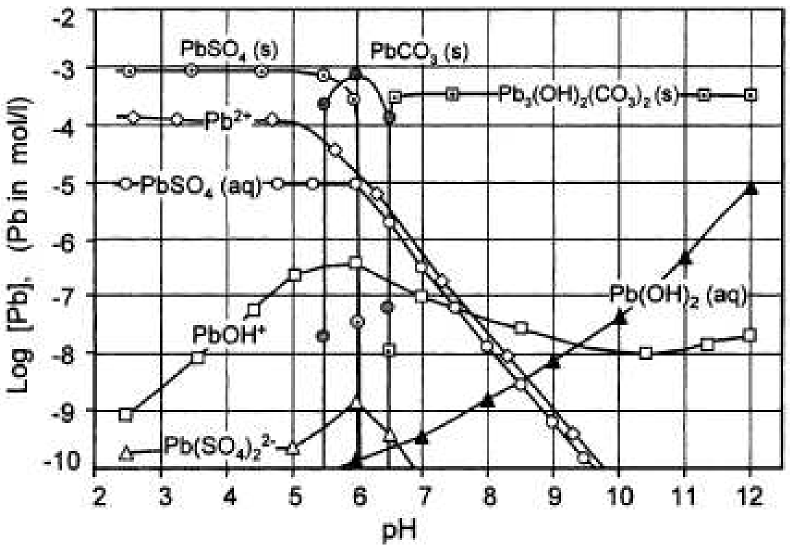
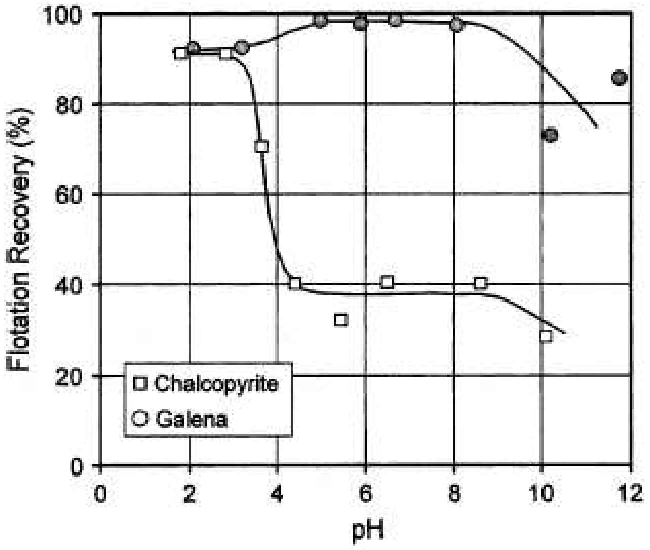
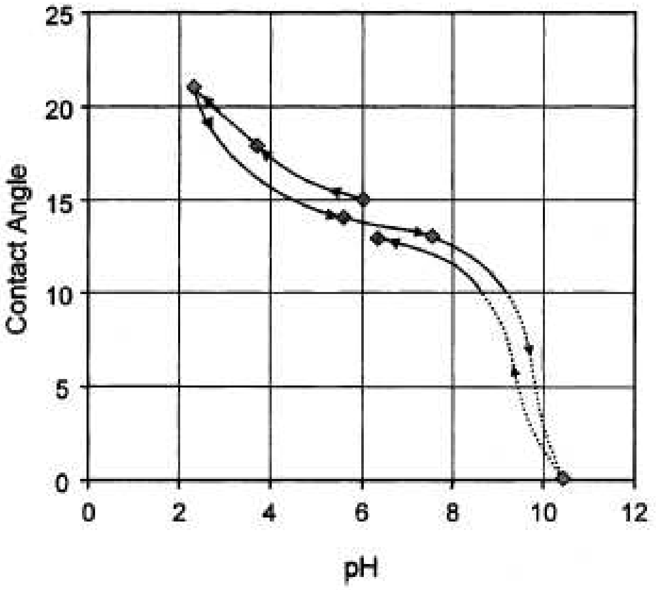


Figure 1.5.1: Equilibrium distribution of Pb species in Pb–S–carbonate– water system at 10—3 M and 300 mV (SHE) as a function of pH. Copied from Kelebek and Yoruk (2002).

It is clear that from pH 6.5 upwards hydrophilic species $Pb(OH)_2(aq)$ and insoluble $Pb(OH)_2(CO_3)_2(s)$ become dominant in the system, with $Pb(OH)_2$ steadily increasing as the system becomes more alkaline making galena less flotable. This was also evident from the flotation recovery and contact angle measured by Kelebek and Yoruk (2002) given below in Figure 1.5.2.



(a) Microflotation recovery of galena (with no collector) in distilled water as a function of pH



(b) Bubble-particle contact angles of galena (with no collector) in distilled water as a function of pH

Figure 1.5.2: Flotation recovery and contact angle results for galena. Copied from Kelebek and Yoruk (2002).

Galena flotation in the presence of xanthate is shown by Figure 1.5.3, where galena flotation is only inhibited at pH's below 2 and above 11, but fully recovered between these two pH values.

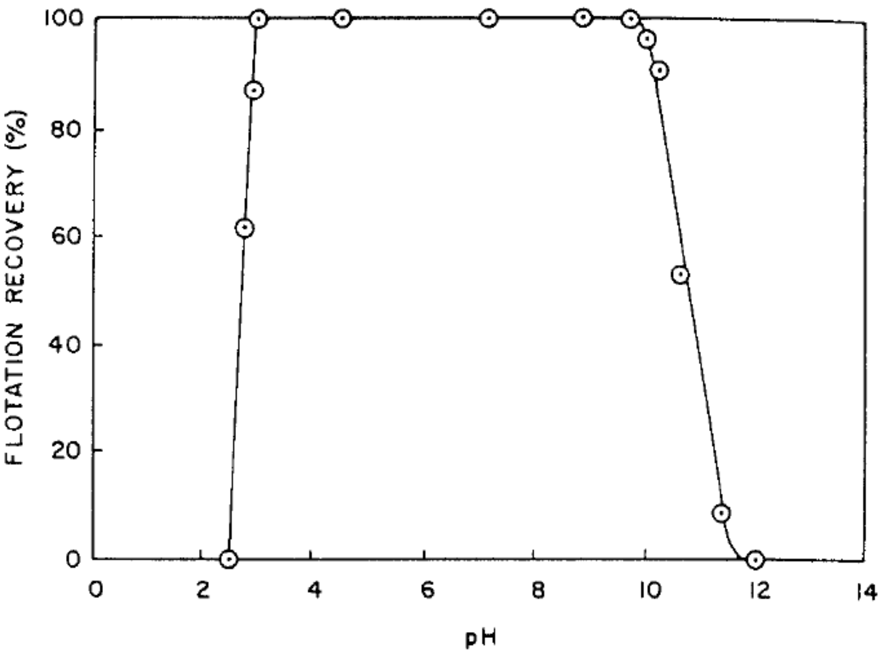


Figure 1.5.3: Flotation recovery of galena as a function of pH with 1 x 10^{-5}mol/l ethyl xanthate. Copied from Fuerstenau (1982b).

Finkelstein and Poling (1977) extensively reviewed the literature on the xanthate surface species responsible for rendering galena flotable and found it to be the metal xanthate. Fuerstenau (1982d) stated that on galena the metal xanthate is the only surface product formed in any significant quantities and Yoon and Basilio (1993) found no evidence of dixanthogen formation using *in situ* FTIR. As stated previously the dominant xanthate surface species has been found to be the chemisorbed xanthate radical (Kartio et al., 1999; Woods, 1994).

Stowe et al. (1995) found DTP to be the dominant species on the galena surface by time of flight secondary ion mass spectroscopy (ToF-SIMS) mapping of the surface. An interesting result of their work is that they stated that collector adsorption on the sulphide mineral was found to be localised and non-uniform. The dithiocarbamate surface product on galena is uncertain. However, the reduction potentials for a galena-DTC (Finkelstein and Goold, 1972) system (cf. Table 1.5.2) also suggest that the oxidation of both DTC and DTP is not probable on galena.

1.5.4 Pyrite

Pyrite also known as fool's gold is the most common sulphide mineral in the earth's crust. Its crystal structure can vary from cubic to octahedral. It is for the most part considered as gaunge in all base metal operations, but can also have associated gold. Pyrite is the feed stock used in production of elemental sulphur and subsequently sulphuric acid, one of the world's most consumed industrial chemicals.

A study by Ekmekci and Demirel (1997) on pyrite showed it to have collectorless flotability in mildly acidic solutions. This was thought to be a result of elemental or metal deficient sulphide being formed at the pyrite surface under acidic conditions. In alkaline solutions a collector was needed to float pyrite. Raichur et al. (2000) showed by measuring the rate of change in contact angle, that pyrite oxidises fastest at pH 9.

Xanthate species responsible for hydrophobicity on pyrite up to pH 11 is commonly thought to be dixanthogen (Buckley, 1994; Leppinen et al., 1989; Fuerstenau, 1982b; Finkelstein and Poling, 1977). This view was contested by Nagaraj and Brinen (2001) who by using secondary ion mass spectroscopy (SIMS) found it to be a possible combination of both the dimer and iron-xanthate complex. They found similar results for dithiophosphate and dithiocarbamate. Finkelstein and Goold (1972) using infrared spectrophotometry found the existence of only the DTC and DTP dimers. This was in line with their prediction using measured rest potentials of the mineral and thiol as seen in Table 1.5.2. The dithiolate is formed when the redox potential of the mineral in solution with the thiol exceeds the redox potential to form the thiols dimer (cf. Section 1.4.3).

Table 1.5.2: Standard reduction potential of pyrite in solution with 100 ppm thiol collectors (relative to S.H.E). Adapted from Finkelstein and Poling (1977).

	DTC	**DTP**
Reduction potential of 100 ppm solution of	+0.081 (volts)	+0.448 (volts)
Pyrite rest potential in 100 ppm solution of	+0.475 (volts)	+0.545 (volts)
Galena rest potential in 100 ppm solution of	-0.035 (volts)	+0.238 (volts)

However DTP is harder to oxidise to its dimer and so is not found experimentally above pH 6 in the presence of pyrite (Fuerstenau, 1982b). Its ability to interact with pyrite is reduced at higher pH's (Finkelstein and Goold, 1972). Nagaraj and Brinen (2001) found evidence of both the DTC dimer and a metal-thiol complex being present on the pyrite surface using SIMS, their findings were however inconclusive.

Pyrite is seen to go through two recovery maxim, one at pH 3-4 and the second at pH 7-8 with addition of ethyl xanthate at different concentrations (Fuerstenau, 1982b). Pyrite flotation with ethyl xanthate shows a clear minimum at pH 6 and after pH 11 no flotation occurs. At very high additions of ethyl xanthate complete recovery is achieved from pH 3 -9 as seen in Figure 1.5.4.

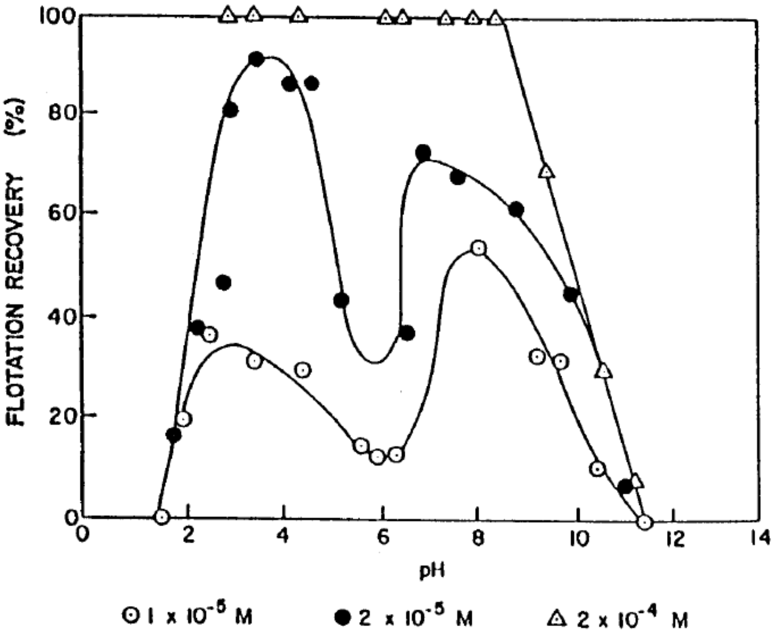


Figure 1.5.4: Recovery of pyrite as a function of flotation pH various additions of potassium ethyl xanthate. Copied from Fuerstenau (1982b).

1.6 Mixtures of collectors

Increased flotation performance when using a thiol collector mixture over their pure components is well known in sulphide flotation. The term synergy is understood by the performance of a mixture being greater than the sum of the individual parts. However little fundamental work has been done in understanding these improvements on flotation performance. This view is further confirmed by a review on thiol collector mixtures by Lotter and Bradshaw (2010), who summarised the benefits of using mixtures as follows:

- Improved flotation rate (Adkins and Pearse, 1992).
- Improvement of coarse particle recovery (Plaskin and Bessonov, 1957).
- Reduction in dosage requirement (Bradshaw, 1997).
- An distinct ratio of the mixtures constituents existed where flotation performance was at an optimum (Bradshaw, 1997; Valdiviezo and Oliveira, 1993; Mingione, 1984).

A summary of literature findings that indicate increased flotation performance when using thiol mixtures is given by Bradshaw and O'Connor (2000) and outlined in Table 1.6.1.

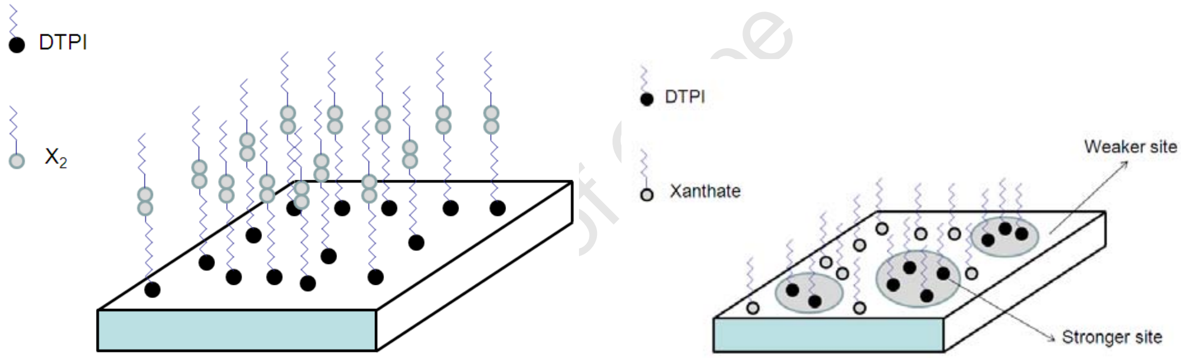
Table 1.6.1: The effects of mixing reagents in flotation, adapted from Bradshaw and O'Connor (2000)

Observation	Techniques	Reference
Preferential DTP adsorption from mixture	Adsorption and bubble pick-up	Wakamatsu and Numata (1979)
Batch flotation recovery of PGM ore increased significantly	Batch flotation	Mingione (1984)
Xanthate : Di-alkyl dithiophosphate mixtures		
Improved recovery and rate of flotation of galena.	Batch flotation	Plaskin et al. (1954)
More even coverage of collector on mineral (galena) surface	Radiographic adsorption	Plaskin and Zaitseva (1960)
Enhanced flotation rate and recovery of Cu in mixed sulphide/oxide copper ore	Batch flotation	Adkins and Pearse (1992)
Xanthate : Di-alkyl dithiocarbamate mixtures		
Better flotation performance in treatment of chalcopyrite than pure DTC	Batch flotation	Falvey (1969)
Very slight increase in batch flotation recovery of chalcopyrite/pyrite ore	Batch flotation	Jiwu et al. (1984)
Increased recovery of pyrite ore	Batch flotation	Bradshaw (1997)
Increased bubble loading and heat of adsorption on pyrite	Bubble loading and thermochemical measurements	Bradshaw et al. (1995)
Lowered surface tension, increased microflotation recovery and extent of adsorption at a 33:66 ratio of ethyl X: di-ethyl DTC	Adsorption, surface- tension and microflotation	Critchley and Riaz (1991)

1.6.1 Mechanisms of synergy

There are three main theories by which synergy is thought to occur. The first two are based on there being strong and weak adsorption sites available on the mineral. Strong sites are proposed to be less oxidised and thus more likely to form surface complexes with thiol collectors than weak sites. It is assumed that this type of oxidation is the kind that inhibits collector adsorption (cf. Quote 1.5.1).

The second theory is that more evenly chemisorbed species (Woods, 1994) would provide a more uniform surface on which dimers could adsorb. Dimers are thought to adsorb unevenly on mineral surfaces. This is though to increase the overall flotability (Lotter and Bradshaw, 2010). Bagci et al. (2007) investigated sequences of addition of dithiophosphinate and xanthate to test this hypothesis. It was not made clear which one of the two theories (cf. Figure 1.6.1) was prevalent or if it was a combination of both when increased adsorption of collector was observed in a mixture.



(a) Anchor site **(b)** Strong site weak site

Figure 1.6.1: Anchor ideas proposed by Bradshaw (1997), diagrams adapted from Bagci et al. (2007).

The third theory put forward is that DTC catalyses the formation of the xanthate dimer (Lotter and Bradshaw, 2010) and thereby causes one of the previous mechanisms to occur. No direct evidence was however available to support this hypothesis.

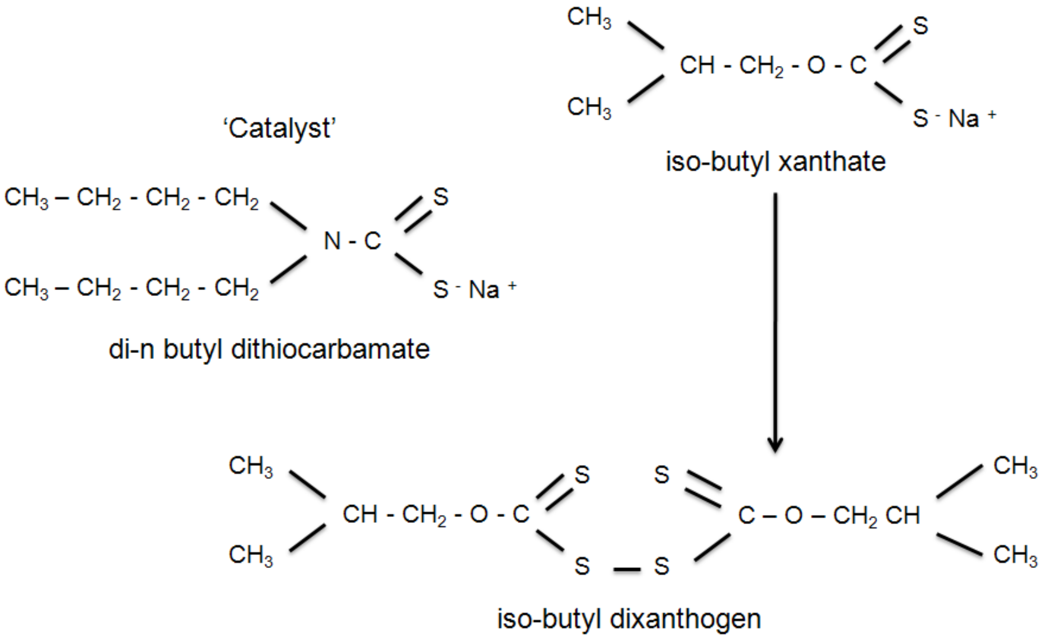


Figure 1.6.2: The proposed reaction pathway for the catalysed formation of a xanthate dimer, with the di-alkyl dithiocarbamate acting as the catalyst. Diagram adapted from Lotter and Bradshaw (2010).

When studying the literature is becomes evident that there is no clear understanding of how these mixtures may result in the observed increases in flotability of sulphide minerals. Mechanisms of synergy proposed are frequently speculative. The available literature is basically a continuous summary of the same findings (Lotter and Bradshaw, 2010; Hangone et al., 2005; Bradshaw and O'Connor, 2000; Bradshaw et al., 1998; Bradshaw, 1997), with little fundamental research being conducted to build a more concise picture of collector mixture behaviour. The points that stand out are that there is a change in observed froth behaviour (Hangone et al., 2005; Wiese et al., 2005), increased collector adsorption (Bagci et al., 2007) and particle hydrophobicity (Bradshaw, 1997; Valdiviezo and Oliveira, 1993). In fact it is arguable that in some instances where synergism is proposed as an explanation of an experimental observation it is also feasible that the observation may simply be the result of two parallel actions by each collector.

1.7 Scope of work

The South African platinum and base metal industry often makes use of collector mixtures because of enhanced performance over single collectors. The variability and simplicity by which collectors are often dosed and/or chosen in a plant environment requires a fundamental understanding of the action of each collector in the mixture. The purpose of this thesis is to observe changes in mineral flotability when using mixtures of xanthate:dithiocarbamate and xanthate:dithiophosphate. These collectors were chosen because they are among the most widely used collectors used in flotation.

Determining the mineral's hydrophobicity after contact with the collector is of critical importance in terms of the pulp phase behaviour. Mineral hydrophobicity may also be different for different size classes. Hydrophobicity can be measured using a variety of techniques. Classically contact angles are proposed as an indication of hydrophobicity. However a microflotation cell is also a useful practical device to determine the extent to which a particle-collector aggregate will attach to a bubble and successfully rise to the lip of the cell. The recovery of the particles will hence be an indicator of their hydrophobicity. Flotation response of the different size classes with mixtures would also provide a greater insight into the behaviour of particles. All this is however limited by the fact that such an investigation is restricted to the pulp phase whereas it is widely known that the behaviour of particles in the froth phase is arguably the most important sub-process in flotation. Hence the present work largely focuses on the effect of pure collectors and mixtures of collectors on the hydrophobicity of the particles.

In this investigation pure samples of pyrite and galena were used. The former was chosen because of its widespread occurrence in sulphide ores being floated throughout the world. The latter has a unique regular cubic morphology and is frequently used in fundamental studies due to this particular morphological property.

Collector mixtures were not investigated for a metallurgically optimum performance (Bradshaw, 1997). But rather to understand how a small amount of one collector effected the behaviour of the other. Ethyl and isobutyl alkyl chain lengths had to be investigated to see if synergy was limited to weaker or stronger collectors. Sequence of addition was investigated for the binary mixture. The initial pH was kept at 9 as this is the natural pH found on most platinum and base metal operations in southern Africa.

This thesis did not aim to investigate fundamental causes for observed changes in flotation behaviour when using mixtures of collectors. The scope was rather to observe whether there would be any observable changes (when using mixtures of collectors) in the pulp phase flotability of pure minerals. The investigation of fundamental causes using techniques such as enthalpies of reactions when adding collectors to the mineral surface would have been beyond the time available and the scale of this thesis. Possible investigations into the fundamental mechanisms involved in observed changes in flotation behaviour of a mineral with different collector conditions are given in the concluding remarks of this thesis.

1.8 Objectives of research

1. To determine the recovery of galena and pyrite when using individual thiol collectors having different alkyl chain lengths.

2. To determine the recovery of galena and pyrite when using different thiol collector types having the same alkyl chain length.
3. To determine the effect of using various mixtures of different thiol collectors having different alkyl chain lengths.
4. To carry out preliminary tests to evaluate the extent to which any results obtained in the pulp-only system were sustained in a system in which a froth phase was present.

The objectives described in points 1 to 3 were carried out using a microflotation cell. Objective number 4 was carried out in a batch flotation cell (modified 3L Leeds cell). The methodologies used are fully described in the Experimental chapter of this thesis.

1.9 Key questions

- Do differences in alkyl chain lengths of the thiol collectors have any effect on recoveries or rates of flotation as observed in a microflotation cell?
- Do collector mixtures have any effect on recoveries or rates of flotation compared to the constituent single collectors?
- Do different size classes respond differently in the above regard?
- Do differences observed in rates or recoveries during microflotation carry through to batch flotation?

1.10 Hypothesis

The central hypothesis of this thesis is summarised below:

> Pulp phase flotability of a sulphide mineral is enhanced synergistically by the use of mixtures of both X:DTC and X:DTP. The reason for this is that each collector will have different characteristics of adsorption onto the mineral surface. This will result in a more extensive adsorption of collectors onto the surface which consists of a wide distribution of sites of different energies. This will cause a more evenly distributed collector coating which in turn will lead to increased particle hydrophobicity.

1.11 Thesis structure

The scope of the thesis is to investigate the effect collector mixtures of xanthate:dithiophosphate and xanthate:dithiocarbamate might have on the pulp phase flotability of galena and pyrite at pH 9. It is with this in mind that chemical and physical effects of flotation are reviewed in the following chapter. This includes looking at factors such as particle size, pH, thiol-mineral interactions and a review of available literature on collector mixtures. Research objectives, key questions and a hypothesis are proposed to outline the central theme of this thesis.

The experimental chapter justifies the approach taken to address and test the hypothesis and address key questions and research objectives. Experimental procedures and preliminary experiments are given. Results are divided into single collector and collector mixture results. The results are then discussed in relation to literature and the validity of the hypothesis. Conclusions and recommendations are given to consolidate the central theme of the thesis and future work that could help further understanding of collector mixtures in sulphide flotation.

Chapter 2

Experimental

2.1 Introduction

This chapter described how the pulp phase flotability of galena and pyrite under different collector conditions was investigated using microflotation. The aim of this thesis was to assess whether mixtures of xanthate with either dithiophosphate or dithiocarbamate had a synergistic effect on the recovery of either galena or pyrite. Two different minerals were tested to observe if there were any commonalities in their flotation behaviour. Collector mixtures were investigated at both the ethyl and isobutyl alkyl chain length in order to test the effect of alkyl chain length on pulp phase mineral floatability.

A size-by-size analysis of the microflotation tests was conducted. Size classes were divided into -105 +75 μm, -75 +38 μm and -38 μm (equivalent sphere diameter). Theses represented the three regions discussed in chapter 1.3.3. The flotation response of different size classes would give in-depth indications of where changes in flotation behaviour occurred. The objective was to observe how a primary collector's performance would be affected by the addition of a secondary collector. Molar ratios assessed were 10:90 and 90:10 of the total collector dosage. Sequence of collector addition was assessed, but found to influence only a few of the results with mixtures of collectors. A selected set of tests were done using a batch flotation cell to see whether or not microflotation flotation results with a collector mixture were sustained when a froth phase was present. A synthetic ore was prepared to simulate a sulphide ore more realistically.

This chapter starts by giving an overview of the test work done. The mineral preparation route and reagents used for all microflotation experiments are described. The microflotation procedure including particle size analysis and data processing are outlined. This provides a clear understanding of the results that each experimental run gave. A brief overview of the batch flotation procedure is given and the reagent conditions that were tested in the batch flotation cell. Preliminary experiments characterised the pyrite and galena quantitatively (using ICP) and qualitatively (using microscopy, XRD and particle shape analysis). Collector dosage and use of laser diffraction (by means of a *Malvern Mastersizer*) to assess size class flotability were justified by experimental investigation. The conclusion of the chapter is an outline of the experimental program.

2.2 Overview of test work

The test work was carried out in the following order:

- Samples of pyrite and galena were received in boxes from Wards Natural Science Establishment Rochester NY, each box contained an approximately 1 kg chunk of up to 150 mm diameter. Each mineral was separately hammered and ground down using a laboratory disk mill (*Siebtechnik*) to 100% passing -106 μm sieve size. To minimise oxidation of the samples they were stored in air tight bags at -30°C.
- Mineralogical analysis on both minerals was done on a quantitative and qualitative basis to asses if they were suitable for this study.
- Individual and combined size classes were floated to validate the use of Malvern data to determine size class flotation behaviour within a mixed size class feed.
- Scoping tests were done to determine an appropriate total collector dosage to be used for each mineral.
- Microflotation tests were done in duplicate for each collector condition. The experimental program was aimed at addressing the objectives and key questions of this study.
- Batch flotation was carried out on selected reagent conditions using a synthetic ore consisting of (by mass) 5% sulfide (galena), 47.5% pyroxene rich ore and 47.5% plagioclase rich ore.

2.3 Mineral preparation

Minerals were obtained from Ward's Natural Science Establishment Rochester NY. Each sample was received in chunks of particles of up to 150 mm diameter. The mineral was hammered down to 100% passing -1000 μm sieve. The hammered sample was then pulverised using a laboratory disk mill (*Siebtechnik*) in manageable batches for 15 seconds at a time. Each batch was dry sieved through -250 μm and -106 μm consecutively. The oversize particles were milled again until all material was 100% passing -106 μm sieve. The final product was divided using a rotary splitter into 10 samples and stored in air tight bags. The bags were pressed down to remove as much air as possible. The split samples were stored in a -30 °C freezer to minimise mineral oxidation.

2.3.1 Particle size distribution analysis

Microflotation experiments were performed with the 100% passing -106 μm (sieve size) galena or pyrite feed. The particle size distribution (PSD) of all materials were determined by laser diffraction using the Malvern Mastersizer 2000. The details of the method are given in Appendix B.

The PSD determined by laser diffraction is given in equivalent sphere diameter (esd) (Malvern (2005) and cf. Appendix B). Percentage passing values for the feed material of both galena and pyrite are given in Table 2.3.1.

Table 2.3.1: Percentage of the galena and pyrite feed material reporting to the three size classes, -150 +75 μm, -75 +38 μm and -38 μm. All sizes are in reported in equivalent sphere diameter.

Particle size region (μm - esd)	**Galena (PbS) volume %**	**Pyrite (FeS_2) volume %**
-150 +75	24.5	19.6
-75 +38	27.8	26.1
-38	47.7	54.3
Total	100	100

Particle size distributions of the galena and pyrite feed materials were similar, this is described further in the Results chapter of this thesis.

2.4 Reagents

2.4.1 Collectors

Collectors used in this study were supplied by Senmin (Pty) Ltd. South Africa. Xanthates were received in powder form; Dithiocarbamates and dithiophosphates were received as a high pH solution, which stabilises these types of collectors. Purity is given in weight %. Reagents were prepared on a daily basis using deionised water at pH 9. Table 2.4.1 lists the names, abbreviations and molecular weights of these collectors.

Table 2.4.1: Characteristics of the collectors used in this thesis.

Name		**Molecular weight (g/mole)**	**Purity [wt. %]**
chain length	abbreviation	sodium (S) or potassium (P) xanthates	
ethyl	SEX	144	99
isobutyl	SIBX	172	97
normal butyl	PNBX	188	90
normal pentyl (amyl)	PAX	202	90
sodium di-alkyl dithiophosphates			
di-ethyl	SEDTP	208	50
di-isobutyl	SIBDTP	264	51
sodium di-alkyl dithiocarbamates			
di-ethyl	SEDTC	171	41
di-isobutyl	SIBDTC	227	31

2.4.2 Frother

Frother was used to maintain a constant bubble size (Cho and Laskowski, 2002) throughout the investigation. DOW 200 (which is a polypropylene glycol ether) was used at 15 ppm which a previous investigation has shown to be above the critical coalescence concentration (CCC) for this frother. The CCC is the point at which an increase in the frother concentration does not cause a further decrease in bubble size.

2.4.3 Water and pH

Deionised *Milli-Q* water was used throughout this investigation. Use of deionised water would remove any possible observed effects that ions would have on collector-mineral flotation behaviour. The deionised water was brought to pH 9 using a 0.1 M solution of NaOH. pH 9 was used as it is the naturally occurring pH found on most base metal and platinum concentrators in South Africa. This would make the findings of this thesis more industrially relevant. The water was then dosed to a 15ppm concentration of DOW 200 frother. Frother was present in all mineral conditioning, microflotation and wash water to avoid frother dilution as the experiment proceeded.

2.5 Microflotation experiments

2.5.1 Experimental procedure

Figure 2.5.1 shows the microflotation rig used in this thesis (Bradshaw and O'Connor, 1994).

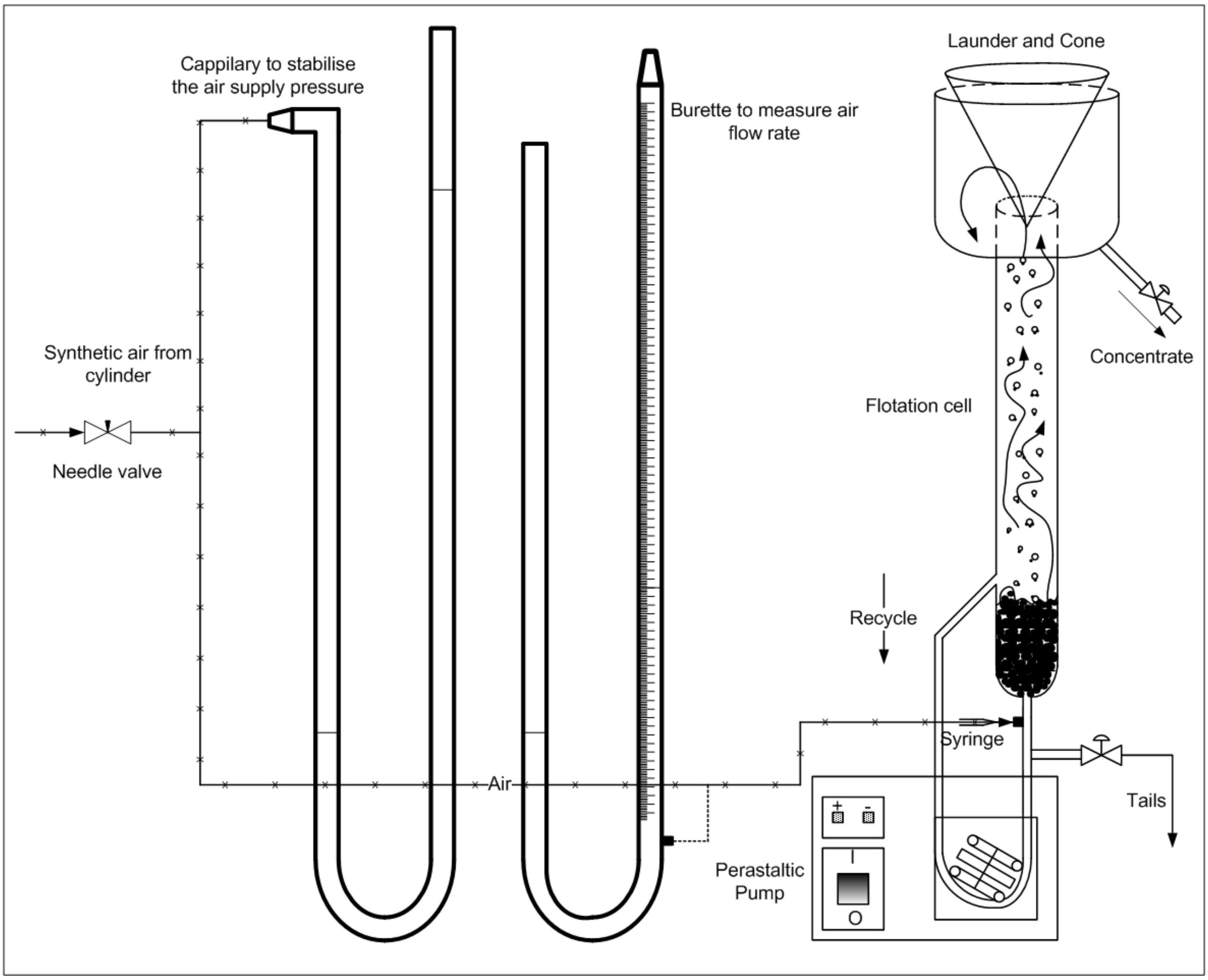


Figure 2.5.1: Schematic diagram of microflotation cell used in this investigation

For each experimental run 3 grams of either -106 μm pyrite or galena was weighed out. The feed sample was added to 50 ml water and placed in an ultrasonic bath for 5 minutes. This was done to de-slime the larger particles of ultra fines and break up particle aggregates. All water used was deionised, at pH 9 (pH adjusted using NaOH) and contained 15 ppm frother (cf. Section 2.4.3). The cell was filled with water up to the recycle point. The peristaltic pump was set at 33% of maximum speed, this condition allowed a stable fluidised bed to form when the pulp was added, with minimal solids entering the recycle stream. Before adding the pulp, the recycle line was purged of air by circulating the pump at maximum speed. The ultrasonicated pulp was then transferred to the cell and topped up with water. The cone was place on the launder. This ensures that bubbles that reach the surface release their collected particles into the launder and not back into the cell.

Collector solution (cf. Section 2.6.1.1) was added by means of a 1 ml syringe at the air supply point. Introduction of the reagent at the air supply point allowed for maximum contact between mineral particles and collector. Collector conditioning time was 6 minutes. In the case of sequential addition of collector mixtures, the mineral was conditioned with the first collector for 6 minutes and there after the second collector was introduced and allowed to condition for a further 6 minutes. After conditioning the air supply was turned on. Air flow rate was kept at 7 ml/min. Synthetic air was supplied from a pressurised cylinder. Air flow rate was measured before each experimental run by means of volume displacement in the adjacent burette and timed with a stop watch.

Concentrates were collected consecutively at 2, 6, 12 and 20 minute intervals. The air supply was turned off at each time interval. Concentrates were washed and collected from the launder in a beaker. Tailings were removed from the bottom of the cell after the last concentrate had been collected. Concentrates and tailing were separately filtered onto pre-weighed *Whatmann qualitative* filter papers and dried in an oven at 110 °C overnight. The four concentrates and one tailings mass for each experimental run were recorded. Concentrates were then analysed for particle size distribution (PSD) using Malvern.

2.5.2 Data processing

Data obtained from the microflotation cell consisted of 4 concentrate masses collected consecutively over 20 minutes as outlined in Table 2.5.1. Volume percent of each size class (cf. Section 2.3.1) within each concentrate and the feed was also determined by laser diffraction.

Table 2.5.1: Microflotation data for an experimental run

Concentrate mass	Collected at (minutes)
C1	2
C2	6
C3	12
C4	20
Tails	at conclusion of experiment

The recovery of each size class was determined as follows:

$$C_{j,i} = S_{j,i} \cdot C_i \tag{2.5.1}$$

$$R_{j,final} = \sum_i \frac{C_{j,i}}{F_j} \tag{2.5.2}$$

where:

i - time step at which the concentrate is collected - 2, 6, 12 or 20 minutes

j - size class - fine, middling or coarse

C_i - concentrate mass at each time step i [g]

$\mathrm{S}_{j,i}$ - volume percentage of the size class within the concentrate at time step i [volume %]

$\mathrm{C}_{j,i}$ - concentrate mass of size class j at each time step i [g]

F_j - mass of feed material of size class j used in the experimental run [g]

$\mathrm{R}_{j,final}$ - total mineral recovery after 20 minutes of microflotation of size class j [%]

This gave the cumulative time based recovery of the overall (-106 μm - sieve size), coarse (-150 +75 μm), intermediate (-75 +38 μm) and fine (-38 μm) size classes. The overall size class volume percentage was 100%. Cumulative recovery at each time step was fitted to the first order rate model:

$$R = R_\infty \left(1 - e^{-k\tau}\right) \tag{2.5.3}$$

Model parameters are described below:

where:

R - recovery of the mineral (recorded variable)

R_∞ - infinite (equilibrium) recovery - maximum possible recovery of mineral (parameter 1)

k - first-order rate constant [1/min] (parameter 2)

τ - flotation time [min] (independent variable)

The two parameters R_∞ and k were obtained by using a nonlinear curve-fitting routine in the least-squares sense. The first order model applies in non turbulent conditions, this being the case for microflotation (cf. Section 1.3.5) .

2.6 Preliminary experiments

Preliminary experiments carried out determined:

- Total collector dosage to be used for each mineral.
- Validity of using the *Malvern Mastersizer 2000* particle size distribution data to determine the flotation response of size classes within the feed.

2.6.1 Collector dosage

Total collector dosage to be used for each mineral was an important parameter to establish. If the dosage was too high there may be no observable effects between the different collector conditions. If the dosage was too low there may be no increase in recovery beyond collectorless flotation. Dosage was determined on a pseudo monolayer coverage basis, i.e. how many molecules would be required to cover the available surface area of the microflotation feed material. It was assumed that a xanthate, dithiocarbamate and dithiophosphate molecule occupied approximately the same surface area when attached to the mineral surface.

Table 2.6.1 lists two references for a calculated area that one molecule of a collector would occupy.

Table 2.6.1: Surface area occupied by one molecule of a collector on a mineral surface. These authors do not elaborate on the basis of their calculations.

Collector	Surface area occupied by one molecule ($\AA^2$)	Reference
ethyl xanthate	28.8	Grano et al. (1997)
di-ethyl dithiocarbamate	37	Raju and Forsling (1991)

The following calculations are based on the di-ethyl dithiocarbamate sulfhydryl head occupying a surface area of 37 ($\AA^2$). A sample calculation to determine the amount of collector required to cover an equivalent 50% of the pyrite specific surface area is shown in Table 2.6.1.

Table 2.6.2: Sample calculation of collector dosage equivalent to 50% pyrite monolayer coverage

Parameter	**value**
Pyrite surface area	1.073 m^2/g
Feed mass	3 g
Available surface area (ASA)	3.22 m^2
50% monolayer coverage (50% of ASA)	1.61 m^2
one molecule head	$3.7x10^{-19}$ m^2
molecules required to cover 50% ASA	$4.4x10^{18}$
total collector dosage for 3 grams of pyrite	$7.2x10^{-6}$(moles)

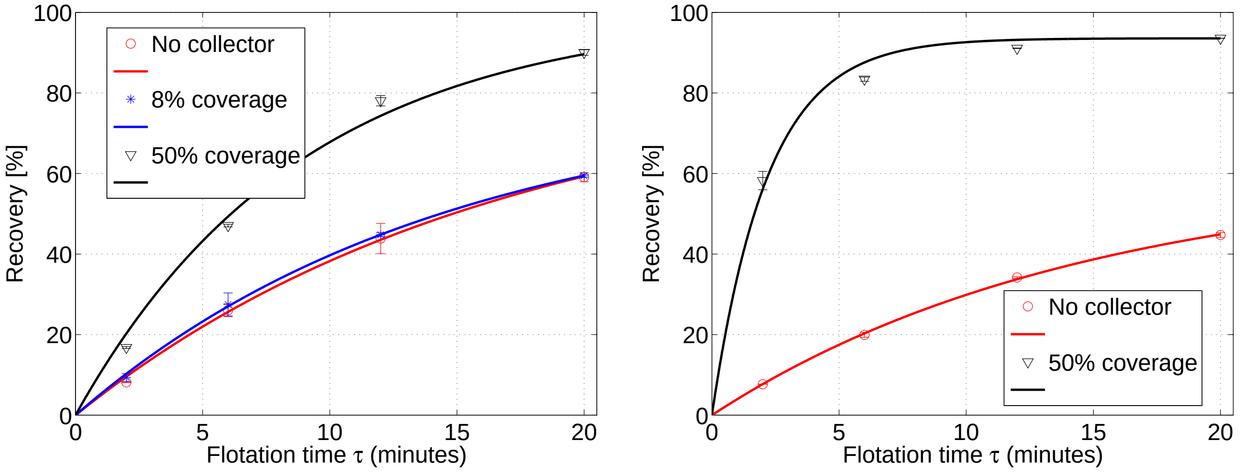
There was initial uncertainty over whether to maintain a constant collector dosage for pyrite and galena even though their specific BET surface areas were different. The collector dosage required to cover 50% of the total galena surface area covers only 8% of the pyrite surface area. Total surface area was calculated by multiplying the feed mass used for an experimental run (3 grams regardless of the mineral) by the specific surface area of the mineral. Specific surface area for each mineral was found by BET gas adsorption using a *Micromeritics ASAP 2020.*

Collector dosages, surface areas and monolayer coverages are shown below in Table 2.6.3.

Table 2.6.3: BET specific surface area for galena and pyrite 100% -106μm (sieve size) microflotation feed material. Dosage is given as moles of collector per gram of pure mineral.

Mineral	**BET surface area (m^2/g)**	**8% pseudo monolayer coverage (moles / g)**	**50% pseudo monolayer coverage (moles / g)**
Galena	0.169	-	$3.8x10^{-7}$
Pyrite	1.073	$3.8x10^{-7}$	$2.4x10^{-6}$

Figure 2.6.1 is a comparison of microflotation tests using 8% and 50% pseudo monolayer coverage of pyrite and galena, respectively, with potassium amyl xanthate. The collectorless flotation result has been shown for reference.



(a) Pyrite with potassium amyl xanthate and collectorless

(b) Galena with potassium amyl xanthate and collectorless

Figure 2.6.1: Mass recovery of of pyrite and galena with amyl xanthate at different coverages and collectorless conditions. [pH = 9]

Figure 2.6.1b shows that a 50% surface coverage of potassium amyl xanthate recovered 93% of the galena. In Figure 2.6.1a the same collector dosage on pyrite (which amounts to 8% monolayer coverage) did not increase the recovery beyond that of using no collector. Only when the dosage on pyrite was increased to an equivalent surface coverage (but not total molar dosage) was pyrite flotation observed to be similar to that of galena.

Thus, all future experiments were performed at 50% monolayer coverage for that specific mineral. This includes binary mixtures of collectors where the cumulative coverage was still only 50%. This collector dosage was not deemed to be too high because there was not full recovery for either mineral at 50% coverage even though amyl xanthate is known to be a relatively strong collector (Harris, 1988).

2.6.1.1 Collector preparation

For each experimental condition a fresh batch of collector solution was prepared daily. Total molar concentration of the collector solution used (cf. Section2.5) for each mineral is given in Table 2.6.4. As mentioned previously 1 ml of this solution was added to the pulp to condition the 3 grams of mineral to have an approximately 50% collector pseudo monolayer coverage.

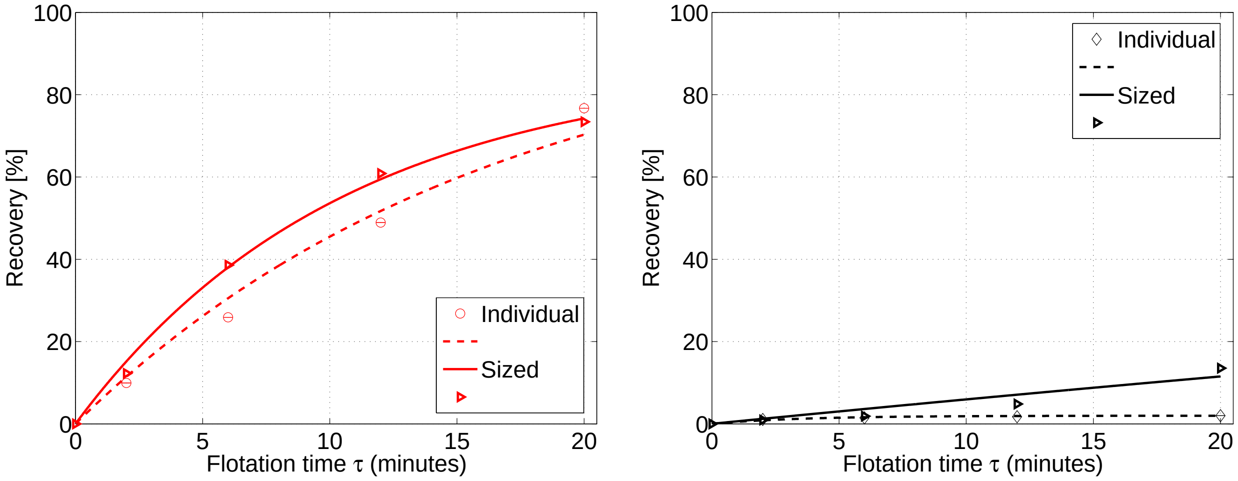
Table 2.6.4: Total molar concentration of collector solution used (single collector or mixture of collectors) to attain 50% monolayer coverage of the mineral surface.

Mineral	Total collector solution concentration (moles/dm^3)
Galena	1.14x10^{-3}
Pyrite	7.20x10^{-3}

2.6.2 Individual and combined size class flotation

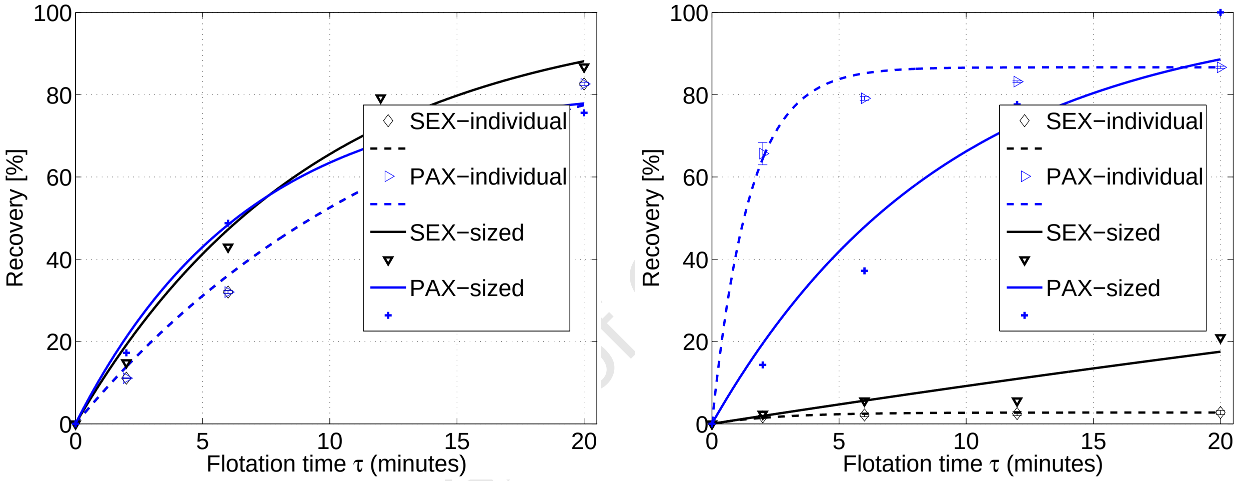
The use of the laser diffraction data obtained from the Malvern Mastersizer 2000 was validated by floating the two extreme size classes (coarse and fine) individually. PSD results obtained from mixed sized class flotation (cf. Equation 2.5.1) were reconciled with the flotation behaviour of the individual size class floated on its own. It has been previously shown that different size classes do not affect each others flotation behaviour (Trahar, 1981), and that this phenomenon is independent of the material being floated (Trahar, 1981). Therefore, this validation was applied to pyrite and extended to galena as well.

Figure 2.6.2 is a summary of the comparative flotation results between the sized and individual size classes. In the following text, “sized” refers to the entire 100% -106 μm (sieve size) sample being floated. Thereafter, each concentrate was separated into coarse, medium and fine size classes using the Malvern. “Individual size classes” means that the coarse or fine size class was floated on its own with no other size class material present.



(a) Collectorless condition [-38μ**m**]

(b) Collectorless condition [-150+75μ**m**]



(c) Ethyl and amyl xanthate [-38μ**m**]

(d) Ethyl and amyl xanthate [-150+75μ**m**]

Figure 2.6.2: Time based mass recoveries of sized and individual pyrite size classes at pH = 9.

Coarse (-150+75 μ**m** - esd) and fine (-38 μ**m** - esd) size fractions of pyrite were floated individually. The intermediate (-75 +38 μ**m** - esd) fraction was not investigated as it was assumed that it would give similar observations as the two extreme sizes. Individual size fractions were obtained by wet sieving with 106, 75 μ**m** and 38μ**m** sieves respectively. Sieved products were then dried at 35 °C. Individual size classes were floated using a 50% monolayer surface coverage of collector molecules based on their individual (BET) specific surface areas.

Rates and recoveries of individual and sized collectorless flotation showed good correlation as seen in Figures 2.6.2a and 2.6.2b. With respect to Figure 2.6.2c, flotation of the -38μ**m** fraction with xanthates gave similar results for both sized and individual size class flotation.

However as observed in Figure 2.6.2d, individual size class flotation of the coarse fraction with xanthates resulted in lower rates and recoveries than the sized results. This highlighted that there were differences in mixed and individual size class flotation when collector was present.

The same observation was not made for collectorless and xanthate conditions with the -38μ**m** fraction, which meant that it did not respond to different experimental conditions, such as floating size classes individually or adding collector (as was the case for the coarse fraction). This indicated that there was probably a high amount of fines entrained in the microflotation cell.

2.7 Mineralogical analysis of feed materials

It was important to investigate the characteristics of the feed materials used in this investigation. The minerals needed to be as pure as possible to avoid complex interactions between impurities, collectors and the bulk mineral. Mineral impurities were identified qualitatively using X-ray diffraction (XRD). Quantitative studies were done using inductively coupled plasma optical - emission spectroscopy (ICP-OES). This was done to determine elemental purities within the minerals.

Crystalline purity of both galena and pyrite (using the Rietveld analysis route) is 100% as shown in Table 2.7.1.

Table 2.7.1: X-ray diffraction results (using the Rietveld analysis route) for -106 μm (sieve size) microflotation feed of galena and pyrite

Mineral	**Purity [%]**	**Chemical formula**	**Source**
Galena	100.0	PbS	Morocco
Pyrite	100.0	FeS_2	Zacatecas, Mexico

ICP results for both the galena and pyrite 100% -106 μm feed material is shown in Table 2.7.2. This further confirmed that only trace amounts of elemental impurities were present in both feed materials. Both minerals showed to have trace amounts of aluminium and tin present, pyrite also had a trace amount of a copper present.

Table 2.7.2: Minor elemental impurities of the galena and pyrite -106 μm feed material analysed by ICP-OES.

Impurity (given in ppm)	**Galena (PbS)**	**Pyrite (FeS_2)**
Al	79.77 $\pm^*$ 0.33	96.50 ± 0.72
Co	-	0.94 ± 0.01
Cu	-	2.76 ± 0.03
Mg	-	0.20 ± 0.00
Ti	0.75 ± 0.01	0.89 ± 0.00

*standard deviation

2.8 Limitations of using a microflotation cell

There is some advantage to using bubble particle attachment as seen in a microflotation cell above thermodynamic measurements such as contact angle. Nagaraj and Ravishankar (2007) aptly summarised this:

> “Questions such as: ’What contact angle (or hydrophobicity) is required for flotation in a real ore system?’ will not elicit meaningful answers. Kinetic approach is fundamental in understanding the flotation process taking place under long term non-equilibrium conditions.”

However it is recognised that microflotation measurements provide an indication of the relative hydrophobicity of the treated minerals, since a microflotation cell only provides information on the efficiency of bubble particle contact and the extent to which the bubble-particle aggregate reaches the launder. It is recognised in this thesis that microflotation cells do not simulate in any way the real flotation process (as meant by Nagaraj and Ravishankar (2007)) because of the absence of the froth phase and totally different hydrodynamics.

2.9 Experimental program

The experimental program is outlined in Figure 2.9.1. It was designed to address the key questions of this investigation (cf. Section 1.9). The reasoning behind this structure was to have a ’from the ground up’ approach. This meant first establishing baseline cases from which to asses the microflotation performance of collector mixtures. Collectorless flotation of the mineral was determined as the first baseline. The second step was to understand how each individual collector and chain length would increase the flotability of the mineral and relate this to accepted findings in literature. Performance of each collector mixture against its constituent single collectors could now be assessed on an overall and size class basis. The whole program incorporated two different minerals, pyrite and galena.

The molar ratio is always expressed to give the xanthate fraction first. For example a 10:90 mixture of X and DTP denotes 10% xanthate and 90% dithiophosphate of the total collector dosage.

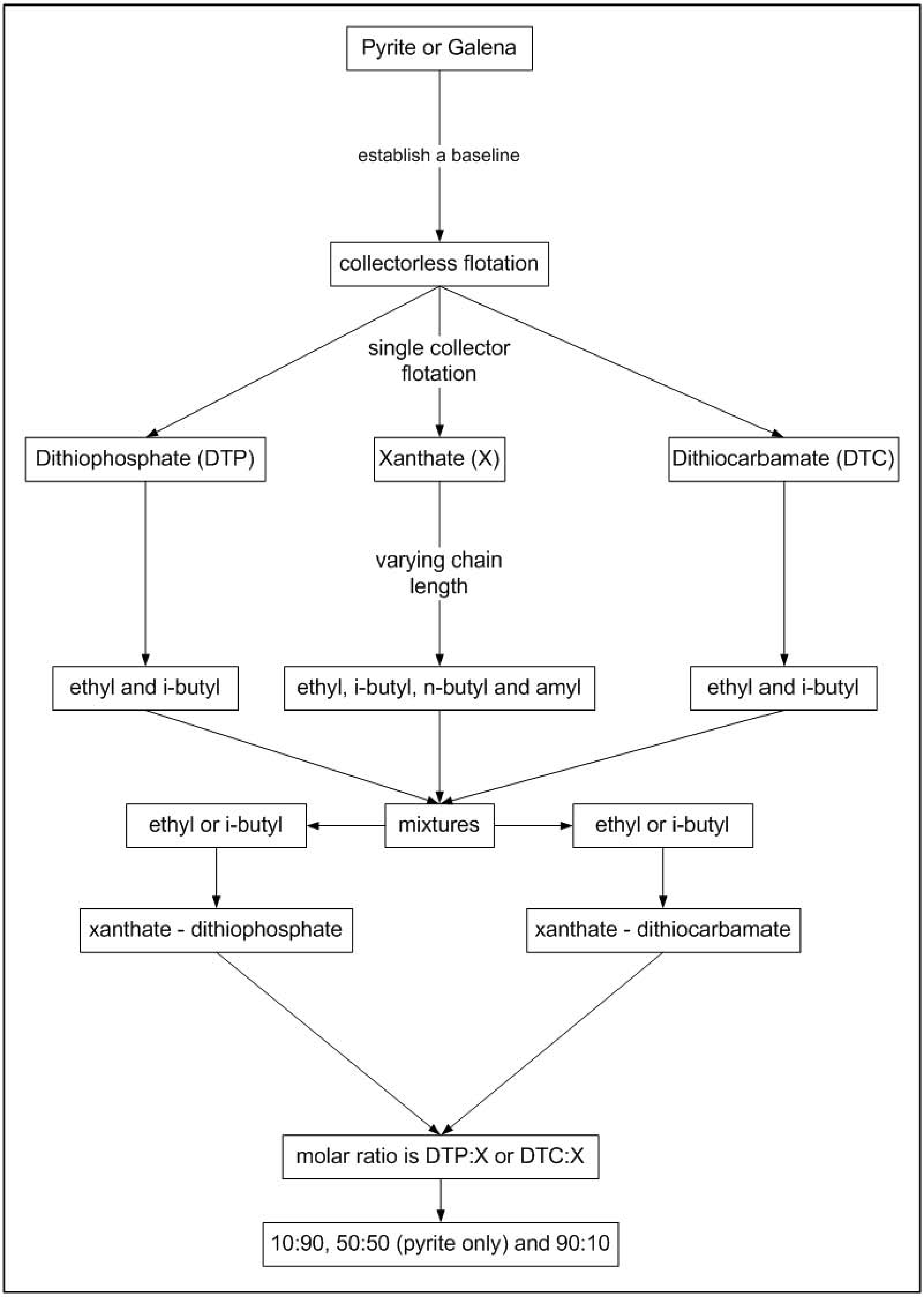


Figure 2.9.1: Flow diagram representing the scheme of experimental work to be done with both pyrite and galena.

2.10 Batch flotation

Batch flotation studies were carried out to address the research objective stated in the introduction and literature review chapter of this thesis. The objective is stated below for convenience.

- To carry out preliminary tests to evaluate the extent to which any results obtained in the pulp only system were sustained in a system in which a froth phase was present.

Batch flotation was carried out using a synthetic ore made up of galena (the same galena as in Table 2.7.1), a plagioclase-rich ore and a pyroxene-rich ore. The minerals which made up the ore used in the batch flotation studies are shown in Table 2.10.1.

Table 2.10.1: Mineral composition of the synthetic ore by mass used in batch flotation tests.

Mineral	Total mass
Galena (PbS)	5%
Plagioclase (a series of tectosilicate minerals)	47.5%
Pyroxene (a group of inosilicate minerals)	47.5%

The galena, plagioclase and pyroxene were prepared in the same manner as the microflotation feed materials (cf. Section 2.3) and were blended in the proportions shown in Table 2.10.1 to make up 1 kg batches which were all 100% -106 μm (sieve size).

2.10.1 Batch flotation procedure

Batch flotation was carried out in a modified 3L Leeds cell and deionised water was used to make up the cell to 35% solids. All experimental conditions were done in duplicate. As with microflotation experiments the water was conditioned to pH 9 using NaOH (cf. Section 2.4.3). All experiments were caried out at room temperature which was 25 °C. DOW 200 (polypropylene glycol ether) was used throughout the batch flotation tests and kept at a constant dosage of 15 ppm. The order of reagent conditioning and concentrate collection is given in Table 2.10.2.

Table 2.10.2: Chronological order of reagent conditioning and concentrate collection in a batch flotation experiment.

Time (minutes)	Collected at (minutes)
0	Add collector
3	Add frother
4	Air supply on
6	Concentrate 1
10	Concentrate 2
16	Concentrate 3
24	Concentrate 4 and two tailings samples

The froth was scraped manually every 15 seconds. The impeller speed was 1200 rpm and the air supply flow rate to the cell was kept constant at 7 l/min. The flotation concentrates were analysed for Pb using standardless X-ray fluorescence (XRF). The standardless results for a pure galena compared to a calculated mass % is shown in Table 2.10.3.

Table 2.10.3: Reagent conditions tested in batch flotation of a synthetic sulfide ore made up of 5% galena, 47.5% pyroxene-rich ore and 47.5% plagioclase-rich ore.

Method	Pb mass % in pure galena (PbS)
calculated by molar mass	87%
XRF result	93.6%

The XRF result was used to calculate the Pb mass recovery in each concentrate. An example is shown in Table 2.10.4.

Table 2.10.4: Sample calculation for Pb mass recovery in a batch flotation concentrate

Parameter	value
Feed mass of galena in 1 kg ore	50 g
XRF Pb % in feed galena	93.6 %
Feed Pb	46.9 g
Total concentrate 1 mass (after 2 minutes)	3.09 g
XRF Pb % in concentrate 1	66.6 %
Pb in concentrate 1	2.06 g
Pb recovery after 2 minutes	4.4 %

The set of reagent conditions that were tested in the batch flotation cell are shown in Table 2.10.5.

Table 2.10.5: Reagent conditions tested in batch flotation of a synthetic sulfide ore made up of 5% galena, 47.5% pyroxene rich ore and 47.5% plagioclase rich ore.

Reagent condition	**Sequence of addition**
Collectorless	-
ethyl xanthate only	-
di-ethyl DTC only	-
90:10 - ethyl xanthate:di-ethyl DTC	ethyl xanthate first

These specific set of conditions were chosen because the 90:10 ethyl xanthate: di-ethyl DTC reagent condition showed the greatest increase in microflotation performance of galena beyond using either single constituent collector. The collectorless and pure collector conditions were also carried out to give a baseline from which to asses changes in flotation performance when using the collector mixture.

2.10.1.1 Batch flotation collector dosage

The collector dosage used in the batch flotation tests was also set to ensure an equivalent 50% pseudo monolayer coverage of the sulfide mineral surface (galena) in the synthetic ore (cf. Section 2.10.1). As shown in Table 2.10.1, 5% of the 1 kg of synthetic ore was made up of galena. The BET surface area and collector dosage of this sample is shown in Table 2.10.6.

Table 2.10.6: BET specific surface area of galena -106μm (sieve size) batch flotation feed material. Dosage is given as moles of collector per gram of galena.

Mineral	**BET surface area (m^2/g)**	**50% pseudo monolayer coverage (moles / g)**
Galena	0.2632	$5.9\text{x}10^{-7}$

Chapter 3

Results

3.1 Introduction

The results chapter of this thesis outlines the microflotation studies carried out with galena and pyrite when using:

- Single collectors. These experiments served as a benchmark for assessing changes in flotation performance when compared to collector mixtures.
- Binary mixtures of xanthate with either dithiophosphate (DTP) or dithiocarbamate (DTC). Binary mixtures were either ethyl or isobutyl alkyl chain lengths. Results presented in this chapter are when xanthate was allowed to contact with the mineral first, then the secondary collector was added.
- Sequence of collector addition (viz. simultaneously, xanthate first, DTC or DTP first) was investigated for all mixtures and is presented only for cases where increased flotability was observed.
- The flotation behaviour of the individual size classes was assessed by use of Malvern analysis of the flotation concentrates.

A selected set of collector conditions was also tested by means of batch flotation using a synthetic ore made up of galena, plagioclase-rich ore and a pyroxene-rich ore (cf. Table 2.10.1). These were done to determine the extent to which observations made in a microflotation cell were sustained in a system which included a froth phase.

This chapter begins by discussing the reproducibility of overall and individual size class data obtained for each microflotation experimental run. Pure collector results for all collectors used are presented for both minerals. Flotation results consist of overall (100% -106 μm, sieve size), coarse (-150 +75μm) , intermediate (-75+38μm) and fine (-38μm) size fraction mass recoveries as a function of time, for each experimental condition. The solids (measured by mass) recovery is equivalent to the mineral recovery, since pure minerals were used. The results for the xanthate:dithiophosphate and xanthate:dithiocarbamate mixtures are presented for each mineral. Batch flotation (of a synthetic ore) results of selected collector conditions are given to address the final research objective (cf. Section 1.8).

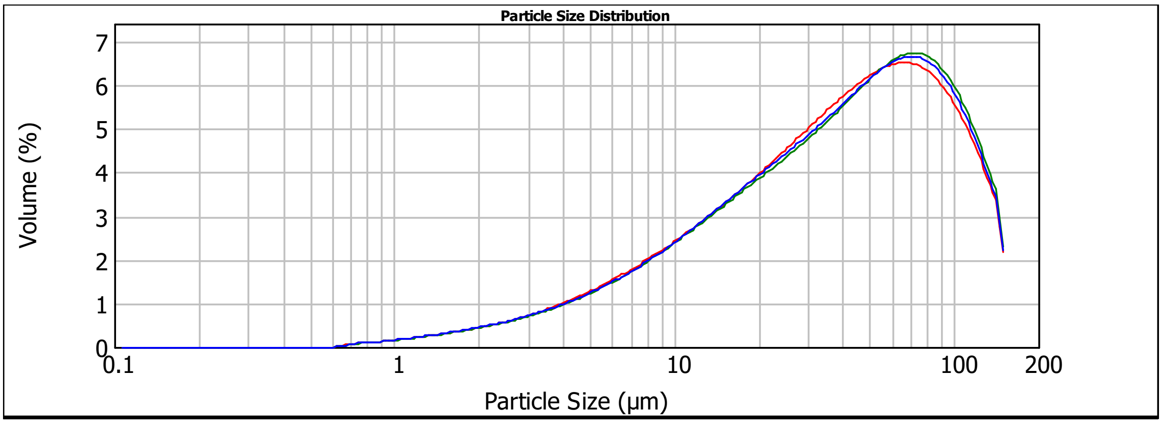
Each microflotation test was done using 3 grams of 100% passing -106 μm of pyrite or galena. Total collector dosage for single and mixed collector conditions was always equivalent to 50% pseudo-monolayer coverage based on the individual surface area (determined by BET gas adsorption) of each mineral. It was assumed that the collector cation (sodium or potassium) did not affect the collector's performance. All water used was deionised, conditioned to pH 9 using NaOH and contained 15ppm of DOW 200 frother (polypropylene glycol ether). The detailed procedure and conditions for an experimental run are given in the experimental chapter of this thesis (cf. Section 2.5). Abbreviations of the collectors used in this section are given in Table 2.4.1.

3.2 Reproducibility of microflotation results

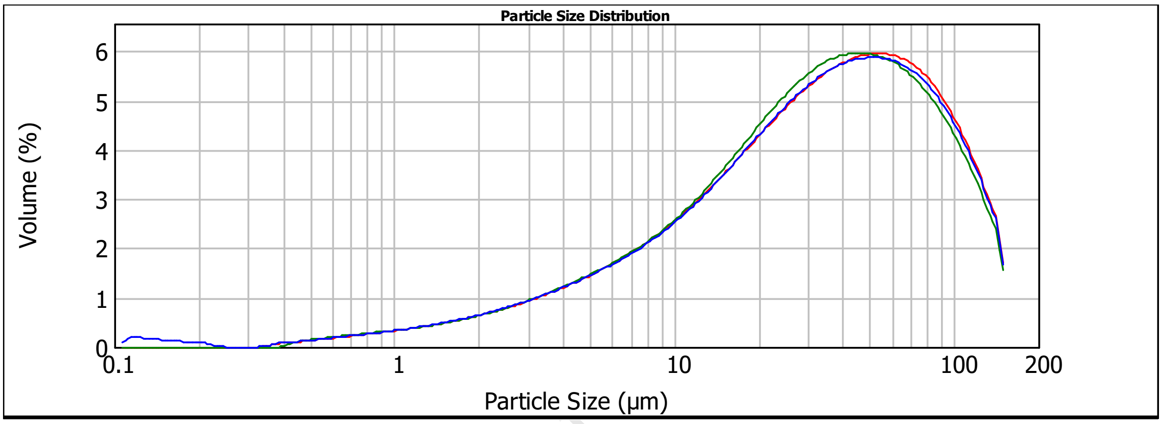
Particle size distribution (PSD) of the feed material used in each experimental run had to be reasonably constant for a comparison between different collector conditions to be meaningful. For each mineral three random samples from separate feed bags (cf. Section 2.3) were analysed for particle size distribution using Malvern, the results are given in Figure 3.2.1. All particle sizes are given in equivalent sphere diameter (Malvern, 2005). It should be noted that the three randomly chosen samples for each mineral had very similar particle size distributions, as indicated by the similar d_{90} and d_{50} values shown in Table 3.2.1.

Table 3.2.1: d_{90} and d_{50} Malvern results of galena and pyrite microflotation feed material.

	Galena	Pyrite
d_{90}	106.4μm	98.8μm
d_{50}	40.1μm	33.6μm



(a) Galena particle size distribution. [d90 = 106.4μm, d50 = 40.1μm]



(b) Pyrite particle size distribution. [d90 = 98.8μm, d50 = 33.6μm]

Figure 3.2.1: Particle size distribution of three randomly chosen microflotation feed samples to illustrate reproducibility.

Results for a triplicate experimental condition using ethyl xanthate with galena and a duplicate with pyrite under the standard microflotation conditions is shown below in Tables 3.2.2 and 3.2.3 respectively. These show the reproducibility criteria for microflotation data obtained in this thesis. All microflotation experiments were done in duplicate. Duplicates ensured that a standard deviation and standard error of the mean were obtained.

Table 3.2.2: Reproducibility of ethyl xanthate with galena microflotation experiments. [pH = 9; collector dosage = 55 g/t equivalent to 50% monolayer coverage]

	cumulative mass recovery [%]				
flotation time	run 1	run 2	run 3	average	std. dev. [%]
2 minutes	10.8	9.6	9.7	10.0	0.7
6 minutes	26.2	26.7	26.4	26.4	0.3
12 minutes	40.5	41.8	42.3	41.5	0.9
20 minutes	50.9	51.7	54.8	52.5	2.0

Table 3.2.3: Reproducibility of ethyl xanthate with pyrite microflotation experiments. [pH = 9; collector dosage = 347 g/t equivalent to 50% monolayer coverage]

	cumulative mass recovery [%]			
flotation time	run 1	run 2	average	std. dev. [%]
2 minutes	11.0	11.0	11.0	0.04
6 minutes	30.2	34.1	32.1	2.8
12 minutes	50.0	53.7	51.9	2.6
20 minutes	64.0	66.1	65.0	1.5

These results showed that the microflotation cell mass recovery results had a high level of reproducibility. When comparing different collectors the standard error of the mean was used to asses whether two results had a significant difference.

Standard error of the mean is defined as:

$$SD = \frac{\sigma}{\sqrt{n}} \tag{3.2.1}$$

where:

σ is the standard deviation of the population

n is the population size, e.g. for a duplicate $n = 2$.

All error bars shown on graphs are the SD value for that test or data point. If the standard error of two results overlapped, their difference was not deemed significant. Use of confidence levels was avoided as duplicates do not represent a significant statistical population (Neter et al., 1988).

Individual concentrate masses were of insufficient sample size to be accurately analysed by Malvern. This meant duplicate concentrate masses had to be combined to achieve a sufficient sample size for Malvern analysis. Figure 3.2.2 shows the reproducibility of duplicate particle size analysis for a microflotation concentrate. This particular experiment had sufficient sample mass from one concentrate to be analysed in duplicate for PSD. The results in Table 3.2.1 indicate that there was excellent reproducibility for size class data obtained with Malvern for a microflotation concentrate. This is shown by the small standard deviation between the coarse, intermediate and fine volume percentages for the concentrate duplicate.

Table 3.2.4: Reproducibility of particle size distributions obtained from a duplicate microflotation concentrate. [Galena; pH = 9; SEX:SEDTC, 90:10]

size class	Volume % of concentrate			
	run 1	run 2	average	std. dev. [%]
-150 +75 (μm)	37.4	37.2	37.3	0.098
-75 +38 (μm)	39.3	37.9	38.6	0.98
-38 (μm)	22.4	24.3	23.4	1.3

It is assumed that this reproducibility is not a function of mineral type as pyrite and galena had similar feed particle size distributions. Unless stated otherwise, the standard deviation between recoveries of sized concentrates is taken to be less than 1.5%.

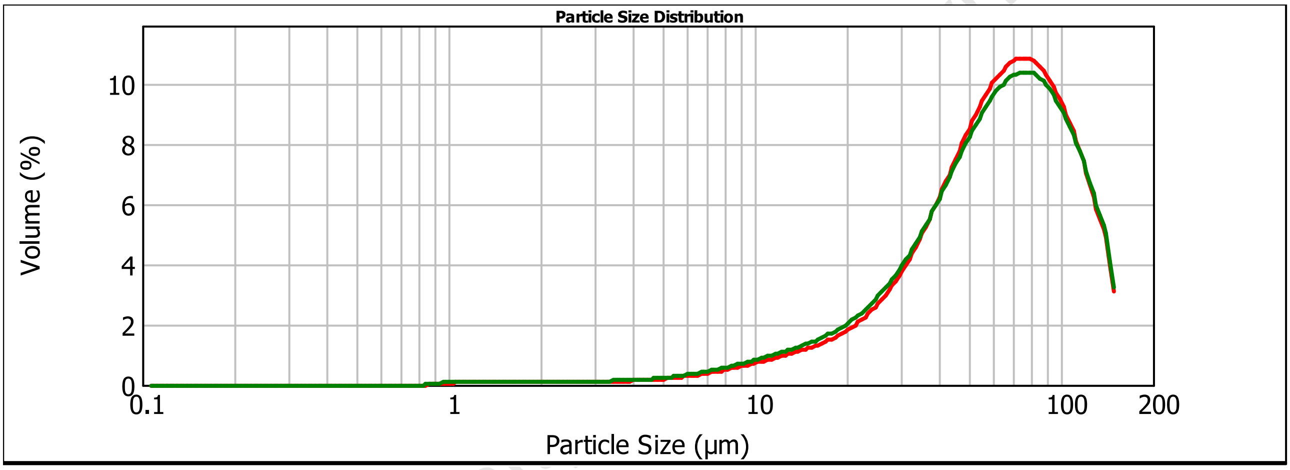


Figure 3.2.2: Reproducibility of duplicate concentrate particle size distributions. The concentrate was obtained after 2 minutes of flotation. [Galena; pH = 9; SEX:SEDTC, 90:10]

A mass balance was done to reconcile the cumulative mass recoveries of the individual size classes (obtained from Malvern) to the final mass recovery recorded from the microflotation experiment. The calculation of mass balance error is outlined below:

$$MB = \left| \left(\frac{\sum R_i - R}{F} \right) \right| \tag{3.2.2}$$

where:

MB	is the difference between the calculated and the actual mass recovery
i	is the size class - coarse, intermediate or fine.
R$_i$	is the calculated final mass recovery [g] (after 20 minutes) of each size class.

R	is the overall final mass recovery [g] (after 20 minutes) obtained from the microflotation experiment.
F	is the feed mass - which is 3 grams for both galena and pyrite

An example is outlined below for the collectorless flotation of galena.

$$R = \text{final mass recovery} = 1.3396\text{g}$$

$$R_{-150+75\mu m} = \text{final coarse mass recovery} = 0.0634\text{g}$$

$$R_{-75+38\mu m} = \text{final intermediate mass recovery} = 0.3431\text{g}$$

$$R_{-38\mu m} = \text{final fine mass recovery} = 0.3925\text{g}$$

$$\sum R_i = 1.3391\text{g}$$

$$MB = |\left(\frac{1.3391\text{g} - 1.3396\text{g}}{2.9943\text{g}}\right)| * 100 = 0.07\%$$

Mass balance reconciliations for each test are shown in Appendix A. In all experiments the value of MB was less than 10% unless otherwise indicated. Excellent reconciliation of the Malvern data with recorded mass recoveries of tests highlights the reliability of the size class flotation results. In cases where the calculated recovery of a size class was over 100% due to experimental error, this size class recovery was assumed to be 100%.

3.3 Particle shape analysis of galena and pyrite samples

Flotation feed samples (100% -106 μm, sieve size) were analysed using scanning electron microscopy (SEM) and software for particle shape analysis (Cotton, 2011). The particles were analysed for the following particle shape factors:

Particle Roundness (R) – measures how closely the particle resembles a circle. This value varies from *one* which is a perfect circle, to *zero* which represents a fibrous particle and is calculated as follows:

$$R = \frac{4\,A}{\pi\, d_{max}^2} \tag{3.3.1}$$

where A is the area of the particle and d_{max} is the maximum particle diameter.

Form factor (FF) - similar to particle roundness, but based on the perimeter (p) of the particle rather than the diameter. The form factor is more sensitive to variations in roughness of the particle perimeter.

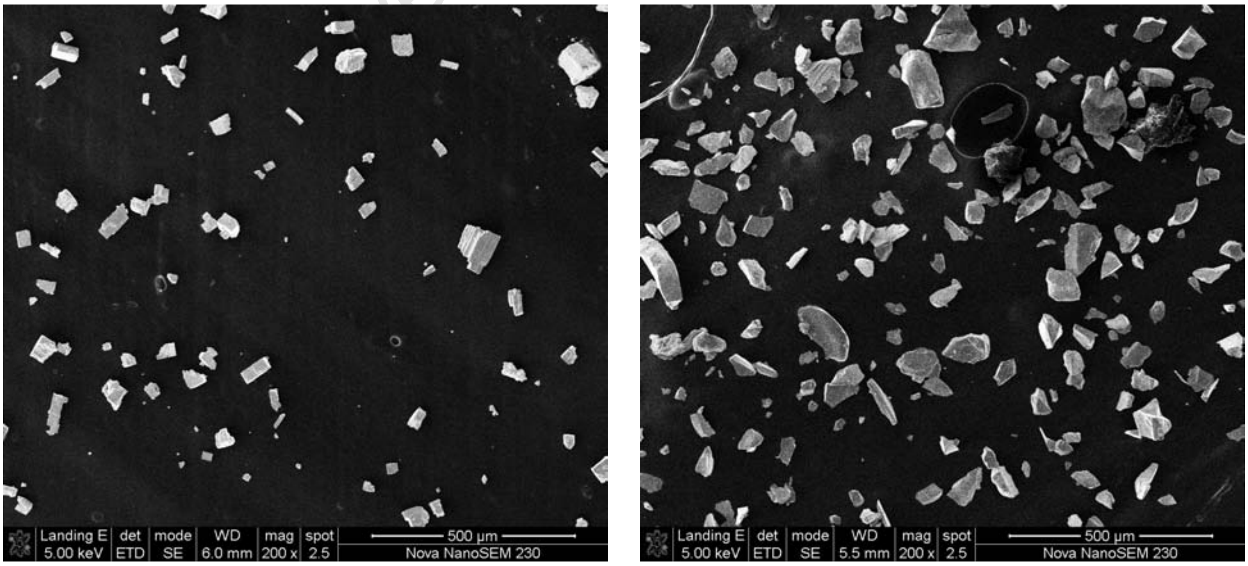
$$FF = \frac{4\pi A}{p^2} \tag{3.3.2}$$

Statistical averages of the two shape parameters investigated (for particles above 41 μm) are shown in Table 3.3.1. Roundness of both galena and pyrite particles are similar. Form factor (FF) however is significantly different. This means that the pyrite surface is more irregular as the form factor is based on particle perimeter. This finding coincides with the fact that the BET surface area of pyrite was approximately 8 times higher than that of galena (cf. Table 2.6.3).

Table 3.3.1: Average of each particle parameter (above 41 μm) measured in the flotation feed of each mineral.

Mineral	Roundness	Form Factor
Galena	0.640	0.590
Pyrite	0.546	0.320

It is also evident from Figure 3.3.1 which represents scanning electron microscope (SEM) images (courtesy of Cotton (2011)) that galena particles are cubic, whereas pyrite is more irregular in shape.



(a) Galena particles above 41 μm **(b)** Pyrite particles above 41 μm

Figure 3.3.1: Scanning Electron Microscope (SEM) images of galena and pyrite flotation feed (100% passing -106 μm, sieve size) samples.

3.4 Microflotation tests with pure collectors

The purpose of these experiments was to asses the pulp phase hydrophobicity of a galena and pyrite sample, respectively, with single collectors. Single collector performance served as a benchmark for assessing any improvements when using a co-collector. Collectors used were xanthate (X), dithiophosphate (DTP) and dithiocarbamate (DTC). Each collector was tested using at least two alkyl chain lengths, viz. ethyl and isobutyl. Xanthates were further investigated at the normal butyl and amyl chain lengths. Details of each collector and method of preparation are given in Section 2.4.1. All particle sizes are given in equivalent sphere diameter (Malvern, 2005) unless indicated otherwise.

This section has two representations of the single collector results. The first is a graphical representation of the time based mass recoveries fitted to a first order rate equation (cf. Section 2.5.2 and equation 2.5.3). The second is the tabulated results of overall and sized final (after 20 minutes) mass recoveries and first order flotation rates to highlight the observations made in the time based mass recovery graphs.

3.4.1 Galena

3.4.1.1 Collector dosages

Table 3.4.1 lists the collector dosages used equivalent to a 50% pseudo monolayer coverage of the galena surface area (cf. Section 2.6.1). Dosage is converted to *grams* of collector per *ton* of pure mineral. It was assumed that the collector cation (e.g. Potassium or Sodium) did not affect the collectors performance, even though its molecular weight was included in the calculation of the dosage requirement.

Table 3.4.1: Single collector dosages for galena equivalent to a 50% pseudo monolayer surface coverage. [grams of collector per ton of pure mineral]

Collector	Dosage (g/t)
SEX	55
SIBX	65
PNBX	71
PAX	77
SEDTP	79
SIBDTP	100
SEDTC	65
SIBDTC	86

3.4.1.2 Collectorless flotability

Table 3.4.2 shows the overall and sized recovery of galena at pH 9. No collector was used in this experiment. As previously discussed in Section 2.9.

Table 3.4.2: First order rate constant, overall final (after 20 minutes) recovery and recovery by size class. [Galena; pH = 9; no collector]

Galena (PbS)	**Final Mass Recovery [%] (after 20 minutes)**	**First order rate constant (min^{-1}) x10^{-2}**
Overall	44.7	6.9
-150 +75 (μm)	8.8	3.8
-75 +38 (μm)	41.1	2.5
-38 (μm)	65.2	9.5

Collectorless microflotation mass recovery of galena at pH 9 is 44.7%. The fines fraction (-38 μm) makes up 69.6% of the overall 44.7% mass recovery, indicating that a high amount of fines was probably recovered by entrainment.

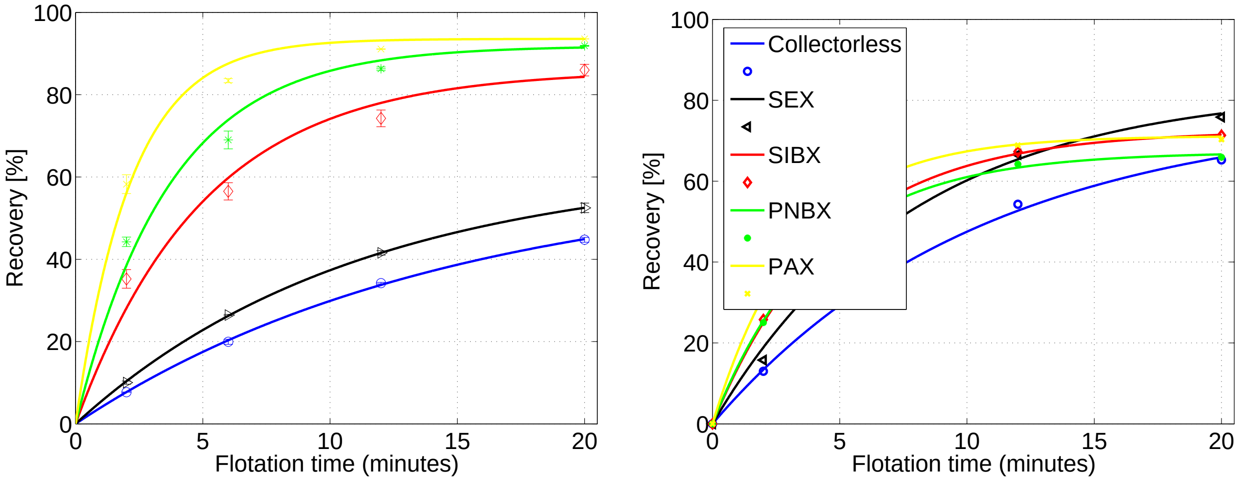
3.4.1.3 Xanthates

Figure 3.4.1 and Table 3.4.3 show that the flotation rate and recovery of galena for all size classes increased with increasing alkyl chain length. With respect to xanthates of equivalent alkyl chain lengths, normal butyl had an increased rate and recovery to that of the isobutyl. As stated previously, it is assumed in these studies that the cation present has no effect on the collector's performance. It was also noted that there was very little difference between the performance using SEX and the performance in the absence of collector.

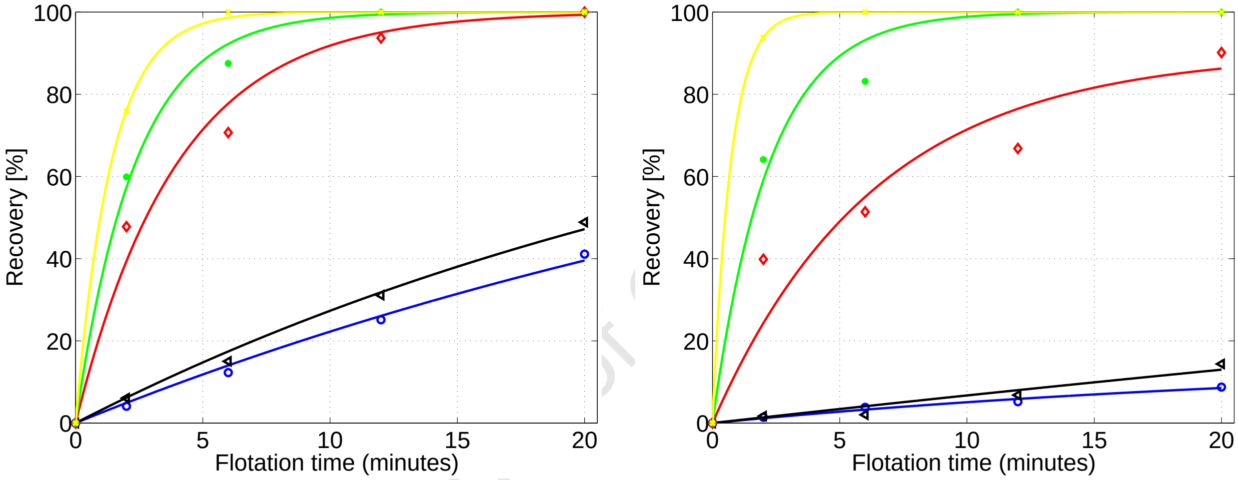
Figure 3.4.1b shows that with regards to the -38 μm fraction there is essentially no difference in the performance of the different collectors. This observation supports the proposal that in the microflotation cell this fraction is probably recovered mostly as a result of entrainment.

Figures 3.4.1c and 3.4.1d show that SEX had little effect on the intermediate and coarse recovery from that of collectorless flotation and that as expected from the overall result, PAX produced the highest rates and recoveries at the intermediate and coarse fractions. Notably, the higher alkyl chain lengths (PAX and PNBX) fully (i.e. 100% final mineral recovery) recovered the coarse and intermediate fractions, with SIBX recovering almost all of the coarse at 90.1%.

When comparing the flotation response of galena with SIBX at the intermediate and coarse fractions, it is clear that the intermediate fraction was more easily floated, this is also evident from the individual size class rates of recovery shown Table 3.4.3.



(a) Overall recovery **(b)** -38 μm recovery



(c) -75+38 μm recovery **(d)** -150+75 μm recovery

Figure 3.4.1: Overall and mass recovery by size with xanthates of different chain lengths. [Galena; pH = 9; 3.8x10^{-7}moles/g]

The final recoveries using PNBX and PAX are similar and essentially 100%. The discriminant in these cases is the rate of flotation. The effect of increasing chain length can be seen by the increasing rate constants (PNBX, 27.2x10^{-2} min^{-1} and PAX, 46.0x10^{-2} min^{-1}) as shown in Table 3.4.3.

Table 3.4.3: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of different chain lengths of xanthate. [Galena; pH = 9]

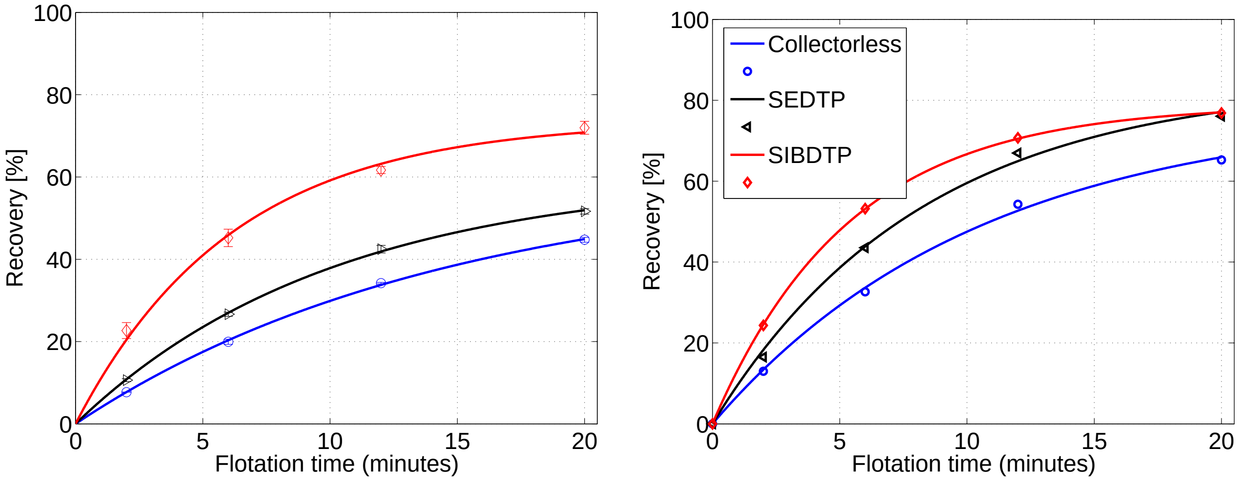
Collector	**Mass recovery [%]**			
	Overall	-150 +75 (μm)	-75 +38 (μm)	-38 (μm)
SEX	52.5	14.4	48.9	75.8
SIBX	86.0	90.1	100.0	71.3
PNBX	91.9	100.0	100.0	65.9
PAX	93.6	100.0	100.0	70.3
First order rate constant (min^{-1}) x10^{-2}				
SEX	9.0	0.7	3.2	12.9
SIBX	19.8	15.7	25.1	22.2
PNBX	27.2	44.7	42.6	23.9
PAX	46.0	139.3	71.5	29.2

3.4.1.4 Dithiophosphate

Figure 3.4.2a shows that galena recovery, when using dithiophosphates, increased with increasing alkyl chain length, as was the case for xanthates. The isobutyl chain length also recovered galena at a significantly higher overall rate compared to di-ethyl DTP (cf. Table 3.4.4).

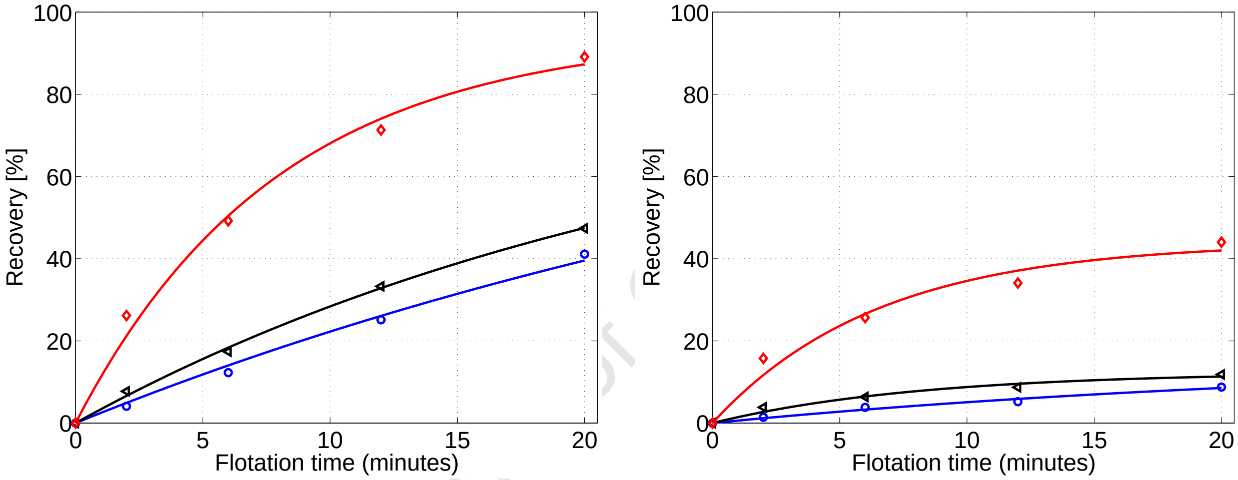
Figure 3.4.2b also shows that neither ethyl nor isobutyl alkyl chain lengths significantly improve the recovery the fine fraction, indicating that again entrainment of this fraction dominates and is probably an intrinsic feature of the microflotation cell. This becomes more evident when comparing the rates of the different size classes in Table 3.4.4, where only the -38 μm fraction does not change significantly from SEDTP to SIBDTP.

Figures 3.4.2c and 3.4.2d show a large difference between rate and recovery of SEDTP and SIBDTP for the coarse and intermediate size classes, with SIBDTP being a superior collector to its ethyl counterpart. SEDTP showed little improvement in the flotation of galena from the collectorless condition. This is most notable in Figure 3.4.2d (the coarse fraction). These results are similar to those observed for ethyl xanthate under the same conditions. Again coarse fraction flotation proved to be the best indicator of increased flotability as it was the most difficult to float and thus would be the first fraction to show increased hydrophobicity.



(a) Overall recovery

(b) -38 μm recovery



(c) -75+38 μm recovery

(d) -150+75 μm recovery

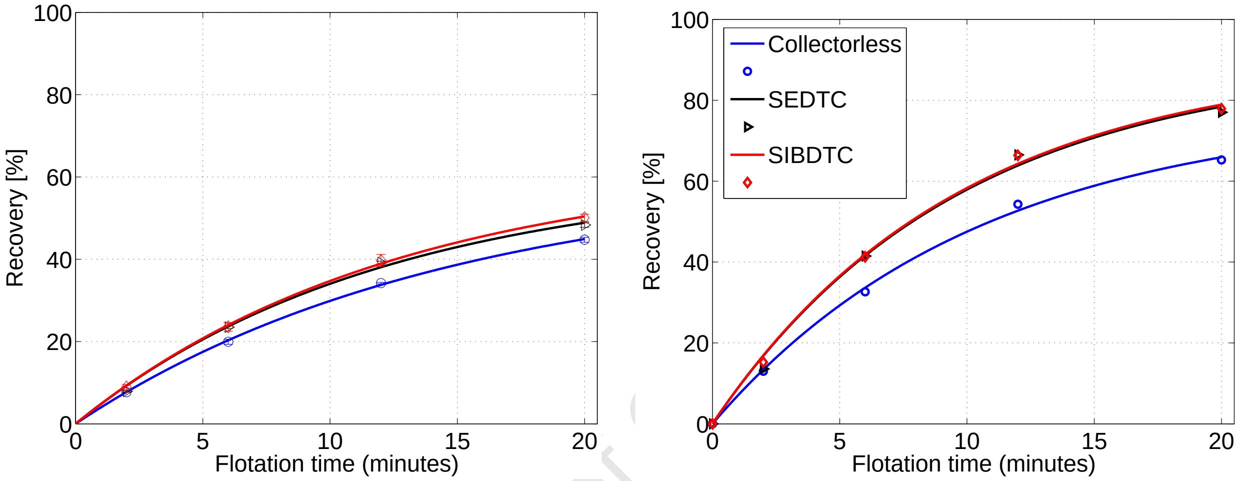
Figure 3.4.2: Overall and recovery (mass) by size of galena with ethyl and isobutyl dithiophosphate. [Galena; pH = 9; 3.8x10^{-7}moles/g]

Table 3.4.4: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of ethyl and isobutyl dithiophosphate. [Galena; pH = 9]

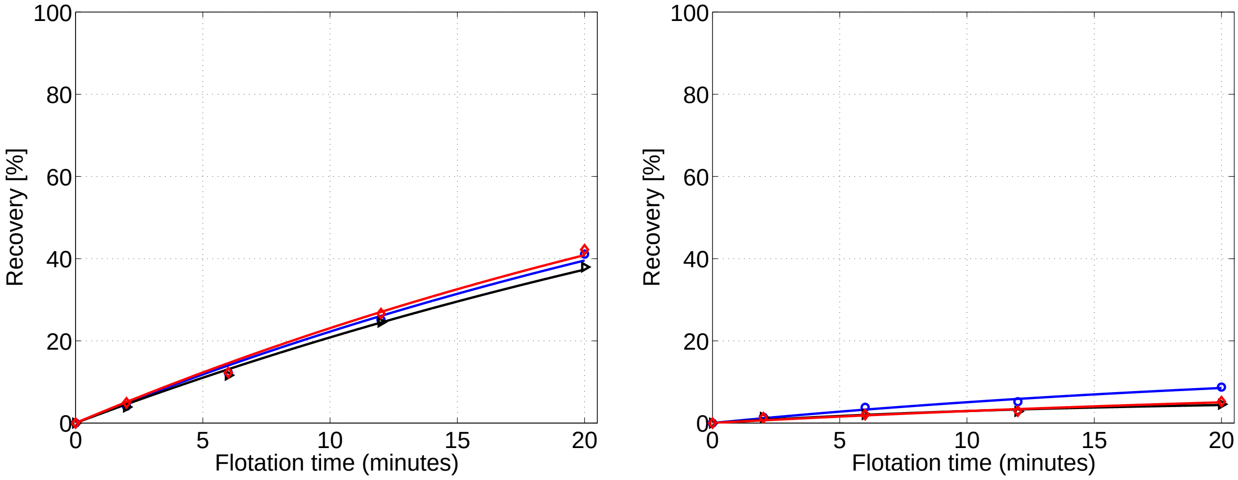
Collector	**Mass recovery [%]**			
	Overall	-150 +75 (μm)	-75 +38 (μm)	-38 (μm)
SEDTP	51.6	11.8	47.4	76.0
SIBDTP	72.0	44.0	89.1	77.0
First order rate constant (min^{-1}) x10^{-2}				
SEDTP	9.9	7.2	6.8	14.8
SIBDTP	16.2	15.4	12.6	18.6

3.4.1.5 Dithiocarbamate

Flotation of galena using dithiocarbamate (both isobutyl and ethyl alkyl chain lengths) did not have a significant effect on the rate or recovery of galena relative to results obtained in the absence of any collector under these conditions. This is most notable from Figures 3.4.3c and 3.4.3d which represent intermediate and coarse fraction flotation respectively, with the only increase in recovery for both SEDTC and SIBDTC being observed in Figure 3.4.3b at the fine fraction. The increase is however not significantly higher than that obtained with dithiophosphates and xanthates and has been suggested to be mostly due to entrainment.



(a) Overall recovery **(b)** -38 μm recovery



(c) -75+38 μm recovery **(d)** -150+75 μm recovery

Figure 3.4.3: Overall and recovery (mass) by size with ethyl and isobutyl dithiophosphate. [Galena; pH = 9; 3.8x10^{-7}moles/g]

Table 3.4.5 showed that DTC at both chain lengths did not significantly increase the rate of flotation of galena beyond the collectorless condition, supporting the proposition that in this system DTC did not appear to have strong collecting properties.

Table 3.4.5: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of ethyl and isobutyl dithiocarbamate. [Galena; pH = 9]

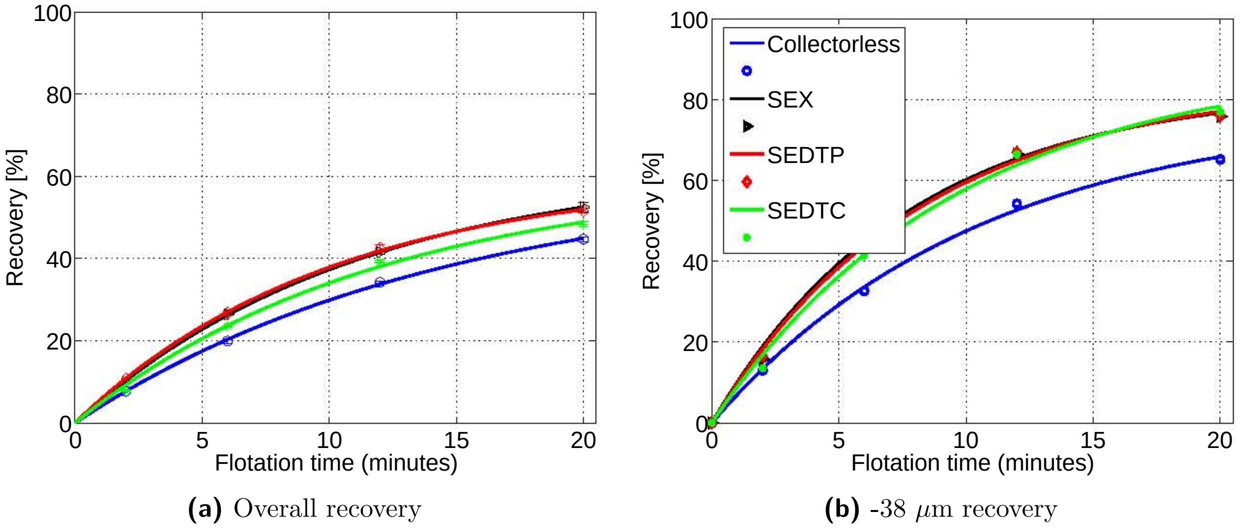
Collector	**Mass recovery [%]**			
	Overall	-150 +75 (μm)	-75 +38 (μm)	-38 (μm)
Collectorless	44.7	8.8	41.1	65.2
SEDTC	48.3	4.6	38.0	77.0
SIBDTC	50.1	5.2	42.2	77.9
First order rate constant (min^{-1}) x10^{-2}				
Collectorless	6.9	3.8	2.5	9.5
SEDTC	8.3	6.9	2.3	10.4
SIBDTC	7.9	3.1	2.6	10.4

3.4.2 Flotation of galena: The role of alkyl chain lengths

A comparison of collectors across both alkyl chain lengths would give an indication of the strength of the role of the alkyl chain length for different thiol collectors.

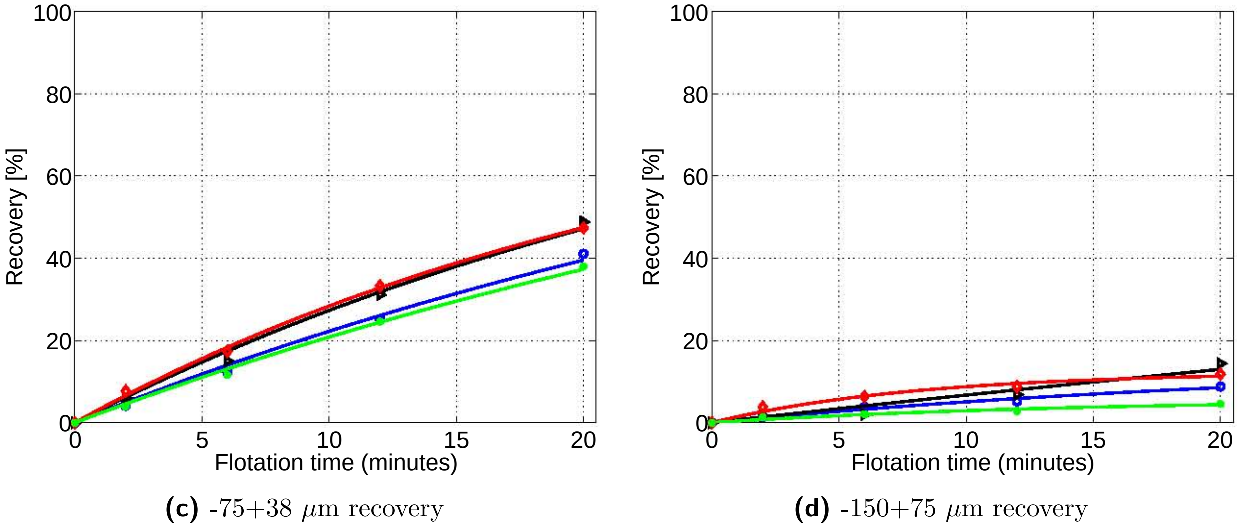
3.4.2.1 Ethyl collectors

From the overall, coarse and intermediate recoveries (cf. Figures 3.4.4a, 3.4.4c and 3.4.4d) it is evident that SEX and SEDTP exhibited very similar flotation performance. However as mentioned previously, their performance was only slightly better than that of the collectorless condition. The biggest increase in flotation performance for SEX and SEDTP is observed in Figure 3.4.4c the intermediate fraction. SEDTC had little effect on galena flotation under these conditions. This was evident for all size classes.



(a) Overall recovery

(b) -38 μm recovery



(c) -75+38 μm recovery

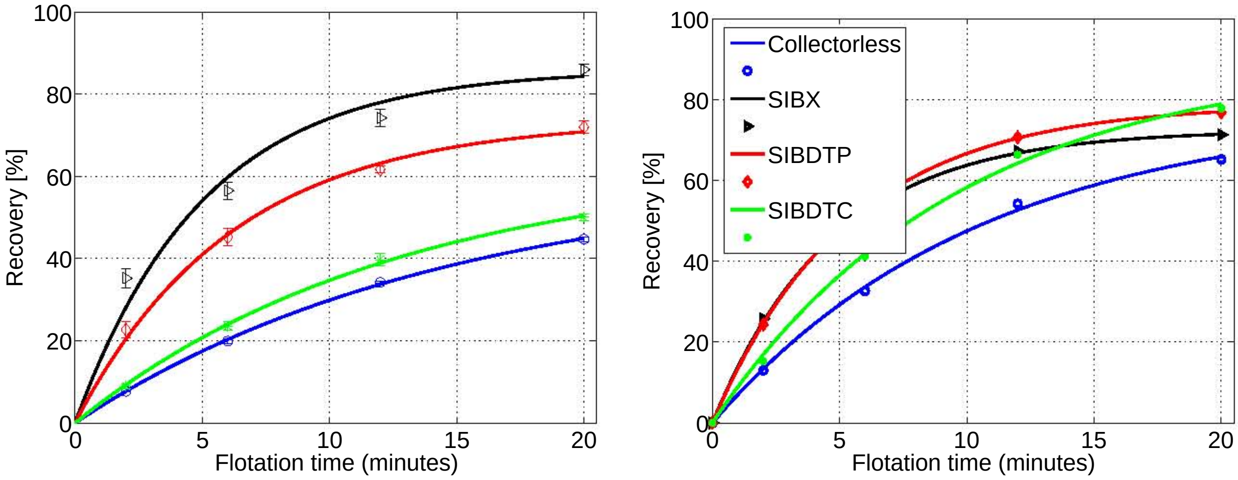
(d) -150+75 μm recovery

Figure 3.4.4: Overall and recovery (mass) by size with ethyl chain length xanthate, dithiophosphate and dithiocarbamate. [Galena; pH = 9; 3.8x10^{-7}moles/g]

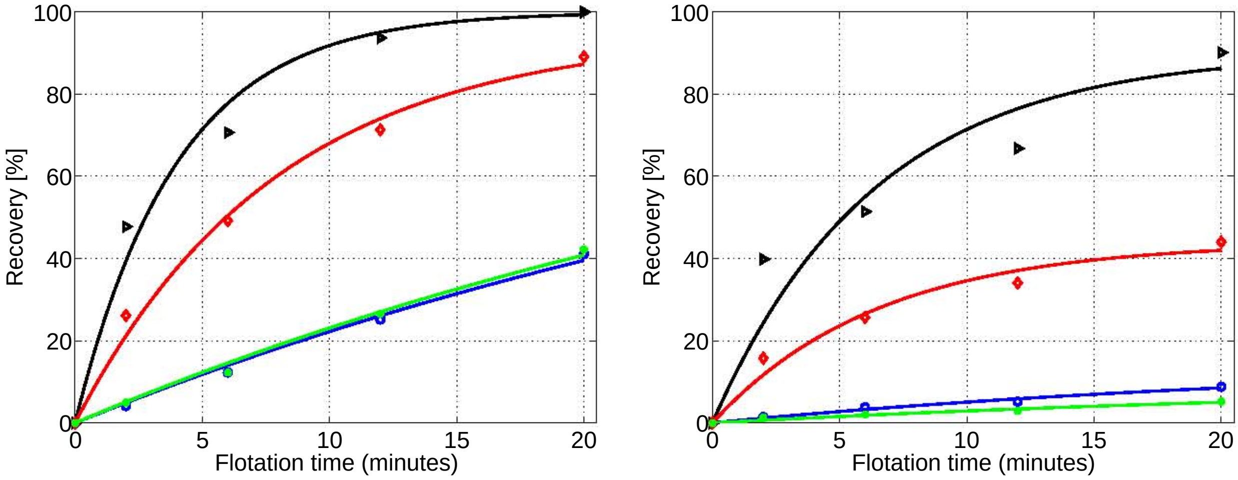
3.4.2.2 Isobutyl collectors

SIBX was the superior collector when compared to SIBDTP and SIBDTC for the -150 +75 μm and -75 +38 μm fractions. This is most notably observed in the coarse fraction (Figure 3.4.5d) where recovery using SIBX was 90.1% (cf. Table 3.4.3) compared to SIBDTP at 44.0% (cf. Table 3.4.4).

SIBDTC, as in the case of its ethyl equivalent, exhibited almost no collecting properties under these conditions. SIBDTC did not increase the rate or recovery for both the intermediate and coarse size fractions as shown in Figures 3.4.5c and 3.4.5d.



(a) Overall recovery **(b)** -38 μm recovery



(c) -75+38 μm recovery **(d)** -150+75 μm recovery

Figure 3.4.5: Overall and recovery (mass) by size with isobutyl chain length xanthate, dithiophosphate and dithiocarbamate. [Galena; pH = 9; 3.8x10^{-7}moles/g]

3.4.3 Pyrite

3.4.3.1 Collector dosages

Table 3.4.6 lists the collector dosages used equivalent to a a 50% pseudo-monolayer coverage of the pyrite surface area. Dosages are converted to *grams* of collector per *ton* of pure mineral. It is clear that these dosages are higher on a grams per ton basis than those for galena. This is due to the higher pyrite surface area, which requires a greater dosage to reach a 50% monolayer coverage. However this ensures that each mineral is exposed to the same amount of collector molecules per unit surface area, and this is of great importance for comparative purposes.

Table 3.4.6: Single collector dosages for pyrite equivalent to a 50% pseudo monolayer surface coverage. [grams of collector per ton of pure mineral]

Collector	Dosage (g/t)
SEX	347
SIBX	415
PNBX	453
PAX	487
SEDTP	501
SIBDTP	636
SEDTC	412
SIBDTC	547

3.4.3.2 Collectorless flotability

Table 3.4.7 shows the overall and sized recovery of pyrite at pH 9 in the case where no collector was added to the microfloat.

Table 3.4.7: First order rate constant, overall final (after 20 minutes) recovery and recovery by size class. [Pyrite; pH = 9; no collector].

Pyrite	Final Mass Recovery [%] (after 20 minutes)	First order rate constant (min^{-1}) x10^{-2}
Overall	59.1	6.0
-150 +75 (μm)	13.5	0.6
-75 +38 (μm)	63.0	4.2
-38 (μm)	73.4	9.6

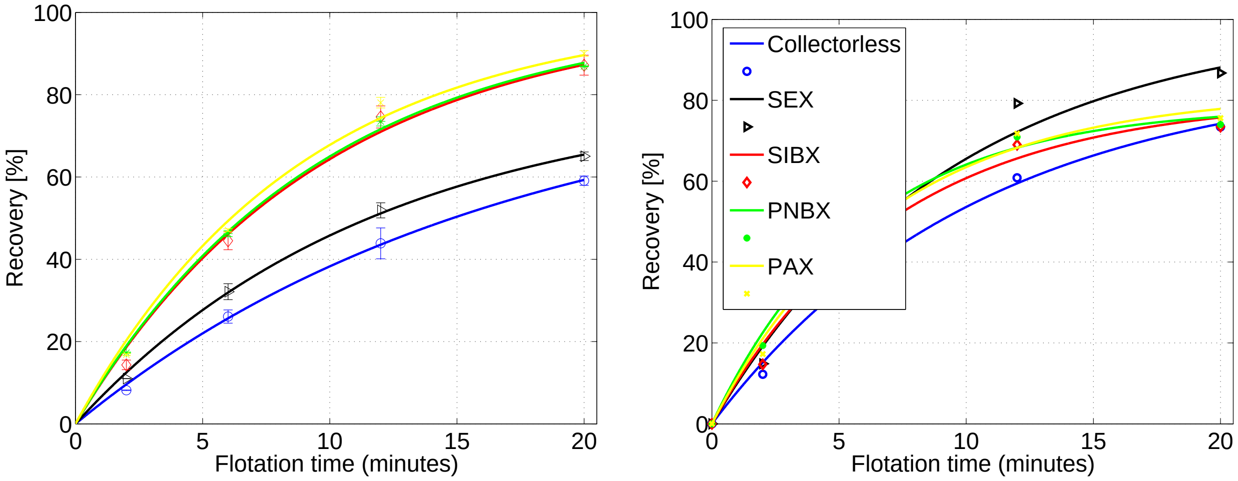
The fine fraction constituted 67.5% of the overall 59.1% mass recovery. As already mentioned, high amounts of collectorless recovery for both pyrite and galena in the fine fraction (cf. Section 3.4.1.2) indicated that a high degree of fines entrainment was occurring in the microflotation cell. When comparing galena and pyrite flotation, their overall rates and recoveries were similar (galena, 6.9x10^{-2} min^{-1} - 44.7% and pyrite, 6.0x10^{-2} min^{-1}- 59.1%). This was not the case for the intermediate and coarse fraction results (cf. Table 3.4.2), where Pyrite had greater recoveries and rates at the intermediate fraction. However the rate of recovery for galena was greater than that of pyrite at the coarse fraction.

3.4.3.3 Xanthates

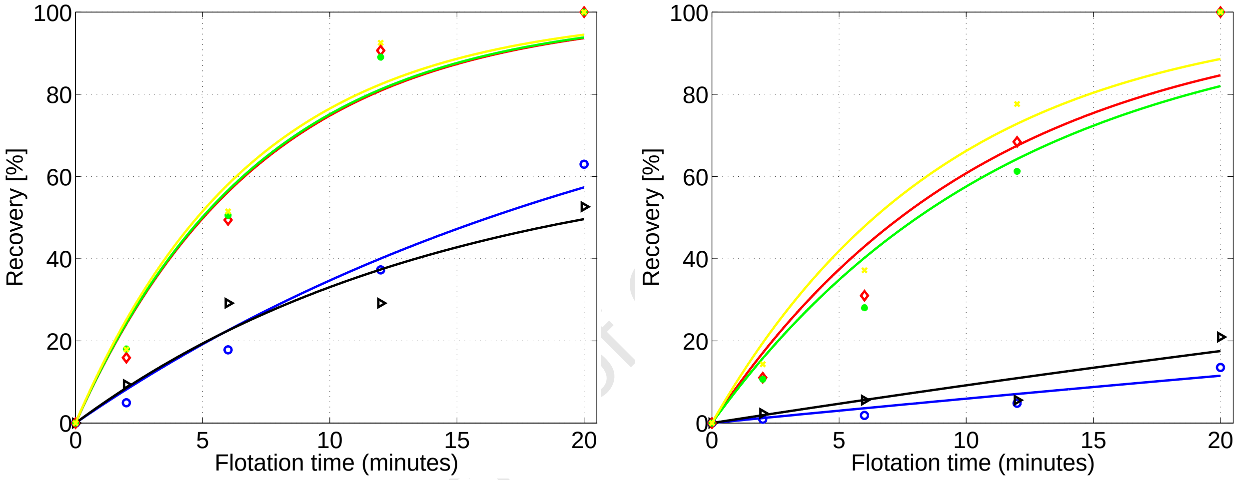
Figure 3.4.6a shows the overall flotation rate and recovery of pyrite increasing with an increase in xanthate chain length. PAX, PNBX and SIBX did not have significantly different rates or recoveries at either the overall, intermediate or coarse fractions (Figures 3.4.6a,3.4.6c and 3.4.6d respectively). No distinguishable differences in rate or recovery were observed between SIBX and PNBX with pyrite. This is in contrast to the result observed for galena (cf. Section 3.4.1.3) where the straight chain butyl (PNBX) out-performed the branched butyl (SIBX). This result indicates that the nature of the alkyl chain length and branching has a different influence on flotation.

SEX did not result in an increase in the rate or recovery of pyrite flotation compared to that of the collectorless condition. This is especially evident in the coarse and intermediate fractions (Figures 3.4.6c and3.4.6d). The 5% increase in overall recovery from collectorless flotation is mostly from the fine fraction as observed in Figure 3.4.6b. However this is not a significant result, and as in previous sections for galena flotation and collectorless pyrite flotation (cf. Section 3.4.3.2) the fines fraction is thought to be recovered mostly by entrainment.

Coarse and intermediate fraction final recoveries of SIBX were both 100% (it should be noted that there was a poor fit of the first order rate equation to these data sets, as the experimental data point is at 100% recovery and the R_{max} value is lower). An increase in floatability when using a secondary collector with SIBX would not be observable if judged by coarse fraction final recovery. In such cases the rate of recovery would have to be considered as well. As seen in Table 3.4.3 this is a justifiable approach as rate increases for overall, coarse and intermediate fraction as alkyl chain length increases, even though complete coarse and intermediate recovery had been reached for the longer alkyl chain length xanthates.



(a) Overall recovery **(b)** -38 μm recovery



(c) -75+38 μm recovery **(d)** -150+75 μm recovery

Figure 3.4.6: Overall and recovery (mass) by size with xanthates of different chain lengths. [Pyrite; pH = 9; 2.4x10^{-6}moles/g]

Table 3.4.8: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of different chain lengths of xanthate. [Pyrite; pH = 9]

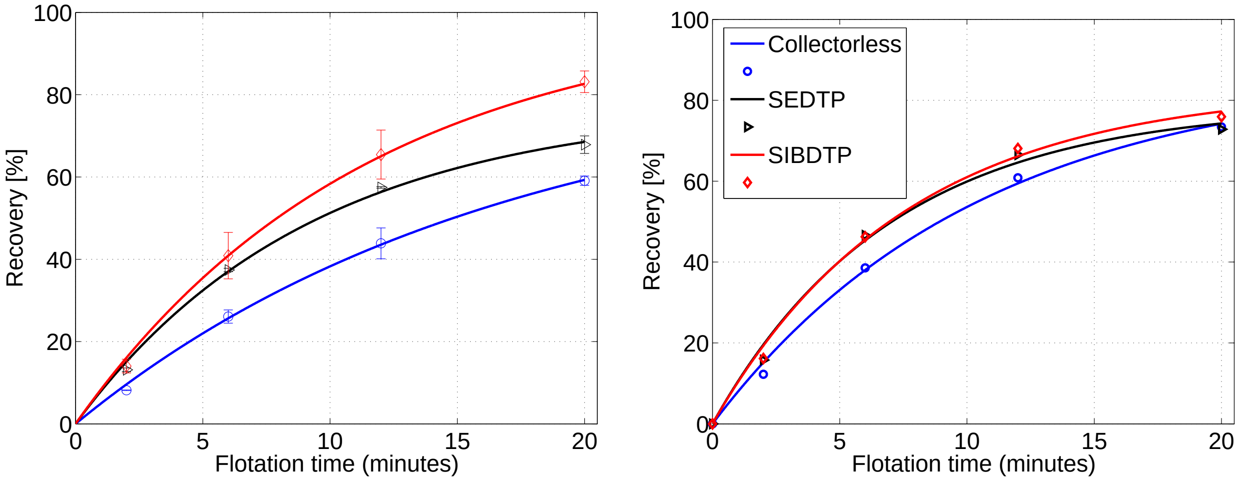
Collector	**Mass recovery [%]**			
	Overall	-150 +75 (μm)	-75 +38 (μm)	-38 (μm)
SEX	65.0	20.9	52.6	86.8
SIBX	87.2	100.0	100.0	73.5
PNBX	86.9	100.0	100.0	74
PAX	90	100.0	100.0	75.6
First order rate constant (min^{-1}) x10^{-2}				
SEX	8.4	1.0	6.9	10.7
SIBX	10.3	9.4	13.8	14.0
PNBX	10.5	8.6	13.9	17.0
PAX	11.3	10.9	15.0	14.8

3.4.3.4 Dithiophosphate

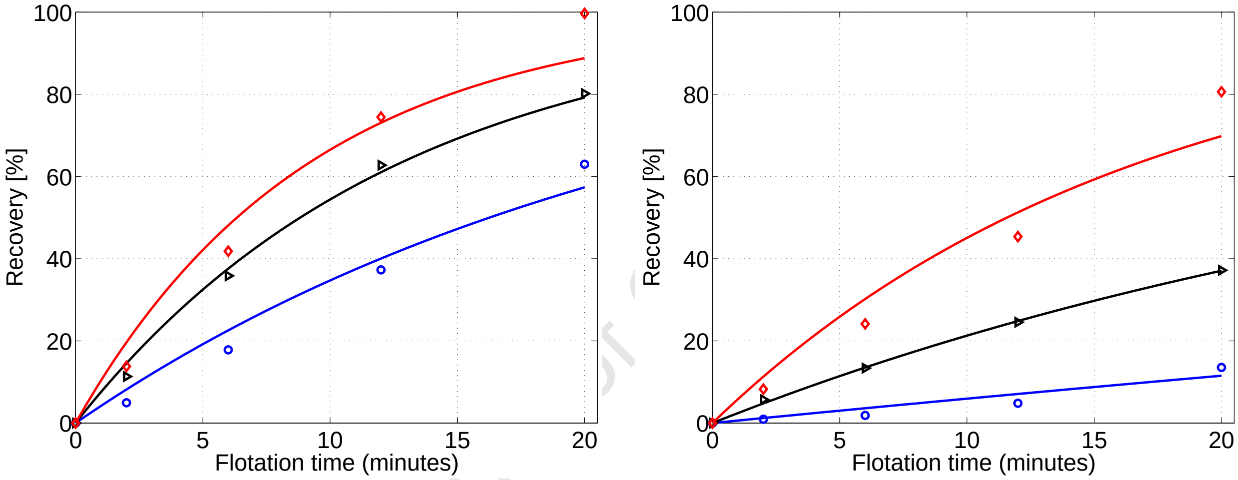
Figure 3.4.7a shows di-ethyl and di-isobutyl DTP displayed identical flotation behaviour up to 6 minutes, where-after the isobutyl chain length reached a higher final recovery.

Coarse and intermediate recoveries shown in Figures 3.4.7d and 3.4.7c indicate that SIBDTP was a more powerful collector than SEDTP under the same conditions. This observation is also clear when comparing the rate of recovery of SEDTP and SIBDTP, as the isobutyl chain length rate is double that of the ethyl. (cf. Table 3.4.9). This was consistent with previous findings with galena and dithiophosphates.

The fine fraction recovery and rate in Figure 3.4.7b and Table 3.4.9 did not increase from the collectorless condition at either chain length, further confirming that the microflotation cell recovered this fraction mainly by entrainment.



(a) Overall recovery **(b)** -38 μm recovery



(c) -75+38 μm recovery **(d)** -150+75 μm recovery

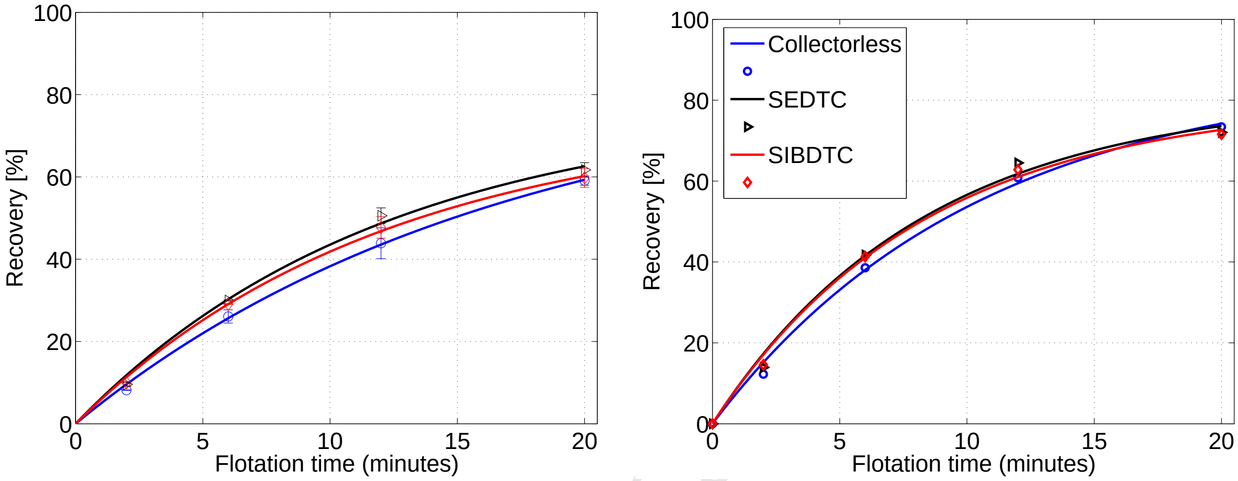
Figure 3.4.7: Overall and recovery (mass) by size of galena with di-ethyl and di-isobutyl dithiophosphate. [Pyrite; pH = 9; 2.4x10^{-6}moles/g]

Table 3.4.9: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of ethyl and isobutyl dithiophosphate. [Pyrite; pH = 9]

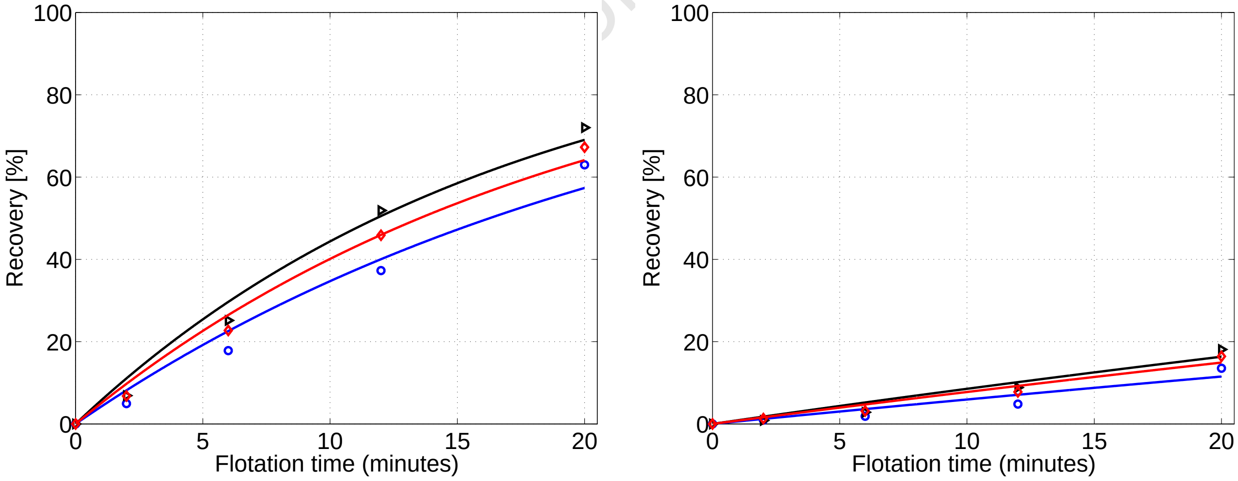
Collector	**Mass recovery [%]**			
	Overall	-150 +75 (μm)	-75 +38 (μm)	-38 (μm)
SEDTP	67.9	37.2	80.2	72.8
SIBDTP	83.1	80.6	99.7	75.9
First order rate constant (min^{-1}) x10^{-2}				
SEDTP	10.8	3.0	7.9	14.3
SIBDTP	8.9	6.0	10.9	13.2

3.4.3.5 Dithiocarbamate

The use of dithiocarbamate did not significantly affect flotation of pyrite compared to the case of collectorless flotation. This is the case for all size fractions although there were slight increases for the -75 +38 μm fraction (Figure 3.4.8 and Table 3.4.10). The weak collector properties of DTC are significant in the context of later results when DTC is used as a co-collector with xanthate. Galena showed a similar result (cf. Section 3.4.1.5).



(a) Overall recovery **(b)** -38 μm recovery



(c) -75+38 μm recovery **(d)** -150+75 μm recovery

Figure 3.4.8: Overall and recovery (mass) by size of galena with di-ethyl and di-isobutyl dithiocarbamate. [Pyrite; pH = 9; 2.4x10^{-6}moles/g]

Table 3.4.10: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of di-ethyl and di-isobutyl dithiocarbamate. [Pyrite; pH = 9]

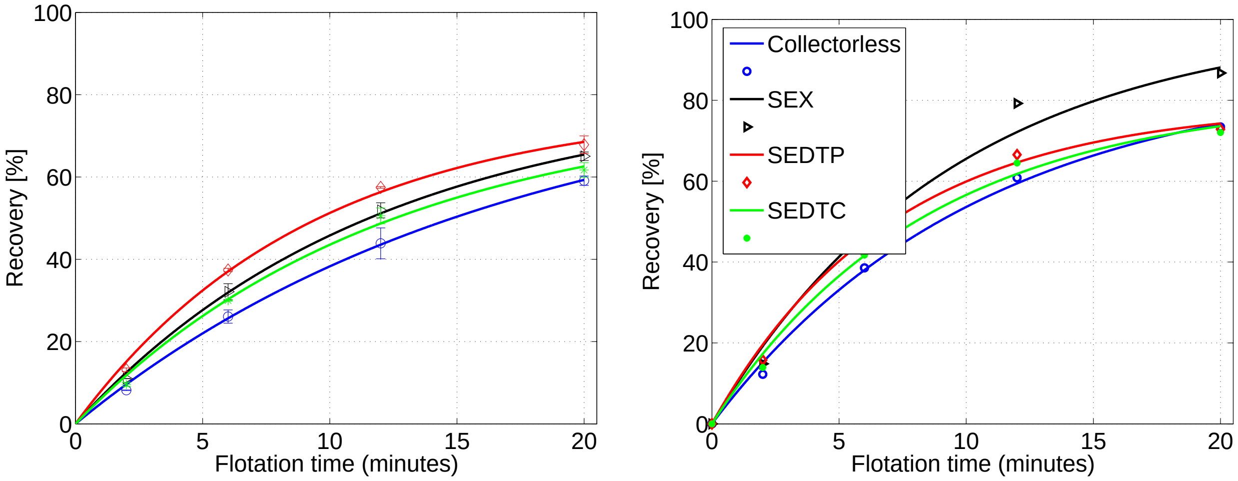
Collector	**Mass recovery [%]**			
	Overall	-150 +75 (μm)	-75 +38 (μm)	-38 (μm)
Collectorless	59.1	13.5	63.0	73.4
SEDTC	61.7	18.09	72.02	72.04
SIBDTC	59.7	16.4	67.3	71.6
First order rate constant (min^{-1}) x10^{-2}				
Collectorless	6.0	0.6	4.2	9.6
SEDTC	8.3	0.9	6.0	12.0
SIBDTC	8.3	0.8	5.1	12.0

3.4.4 Flotation of pyrite: The role of alkyl chain lengths

3.4.4.1 Ethyl collectors

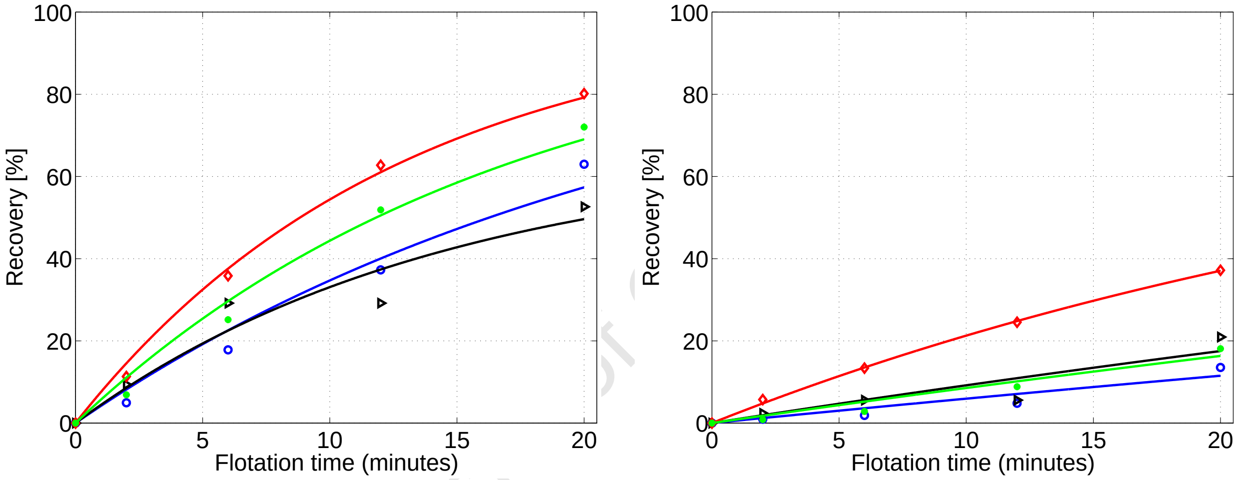
Figures 3.4.9a, 3.4.9c and 3.4.9d represent the overall, intermediate and coarse fraction recoveries when using the ethyl chain lengths of xanthate, DTP and DTC. This Figure shows SEDTP to be the superior collector for this chain length.

Figure 3.4.9c shows an interesting result in that SEDTC performs better than SEX at the intermediate faction. It should be noted though that this is still only a slight improvement compared to the case of using no collector.



(a) Overall recovery

(b) -38 μm recovery



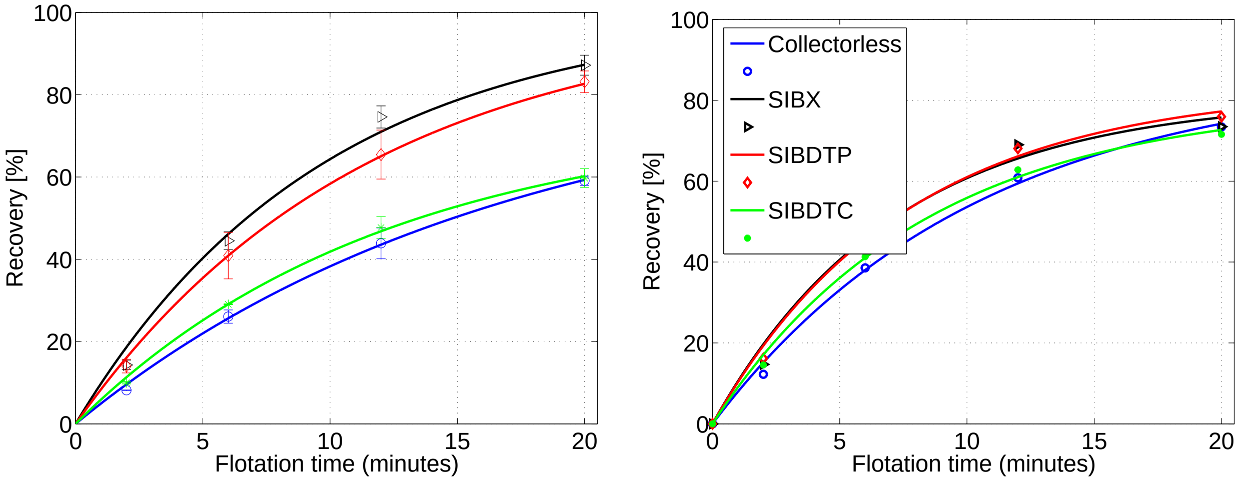
(c) -75+38 μm recovery

(d) -150+75 μm recovery

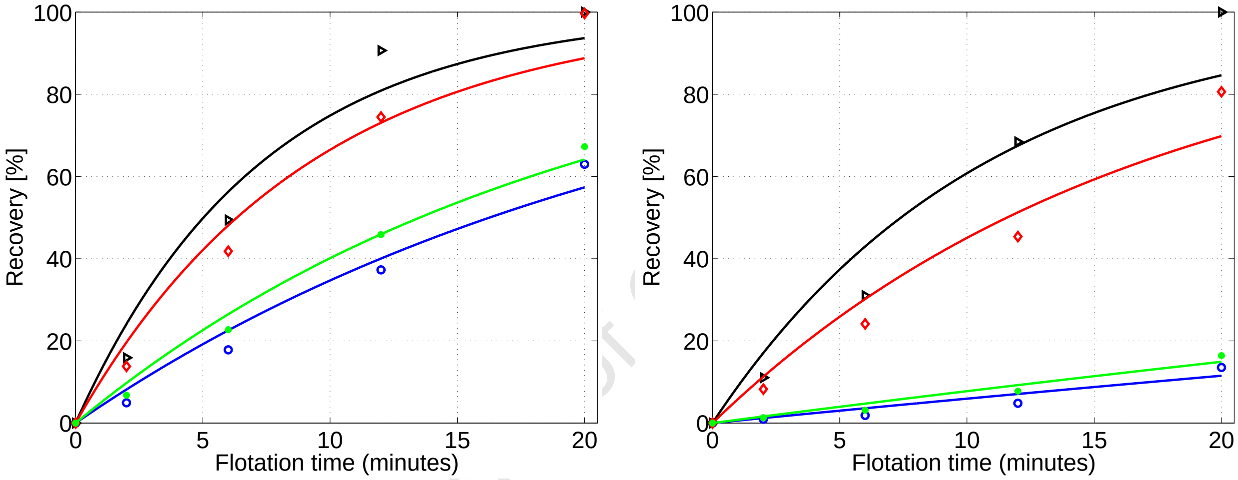
Figure 3.4.9: Overall and recovery (mass) by size with ethyl alkyl chain length xanthate, dithiophosphate and dithiocarbamate. [Pyrite; pH = 9; 2.4x10^{-6}moles/g]

3.4.4.2 Isobutyl collectors

Figure 3.4.10 shows that SIBX and SIBDTP have similar overall rates and recoveries of the intermediate fraction. Figure 3.4.10d however shows that SIBX is again the superior collector for the coarse fraction, as was the case for galena (cf. Figure3.4.5d). Again it is seen that DTC is a weak collector in all instances.



(a) Overall recovery **(b)** -38 μm recovery



(c) -75+38 μm recovery **(d)** -150+75 μm recovery

Figure 3.4.10: Overall and recovery (mass) by size with isobutyl alkyl chain length xanthate, dithiophosphate and dithiocarbamate. [Pyrite; pH = 9; 2.4x10^{-6}moles/g]

3.4.5 Summary

Table 3.4.11 compares the recoveries of galena and pyrite with different collectors. The purpose of this table is to investigate the differences and similarities in the use of different collectors for both minerals. For each mineral, overall collectorless recovery was subtracted from the results obtained with collectors to emphasise the effect of adding collector. Standard deviation for all results was less than 4%.

Table 3.4.11: Comparison of the final (after 20 minutes) mass recoveries of galena and pyrite with different collectors at pH =9. In this Table collectorless recovery was subtracted from observed recoveries to emphasise the effect of collector action.

Collector	**Galena (PbS)**		**Pyrite (FeS_2)**	
	mass recovery [%]	first order rate constant (min^{-1}) x10^{-2}	mass recovery [%]	first order rate constant (min^{-1}) x10^{-2}
SEX	7.7	9.0	5.9	8.4
SIBX	41.2	19.8	28.1	10.3
PNBX	47.1	27.2	27.8	10.5
PAX	48.8	46.0	30.9	11.3
SEDTP	6.9	9.9	8.8	10.8
SIBDTP	27.7	16.2	24.0	8.9
SEDTC	3.6	8.3	2.6	8.3
SIBDTC	5.3	7.9	0.6	8.3

An increase in alkyl chain length from ethyl to isobutyl increased both rate and recovery of galena and pyrite. This was particularly significant for dithiophosphates and xanthates. For dithiocarbamates increase in recovery was minimal. The strength of xanthate collector chain length for galena, as indicated by recovery, was in the order:

amyl > normal butyl > isobutyl > ethyl

Pyrite did not show any significant increase in recovery from the isobutyl to amyl chain length for xanthates. The strength of xanthate collector chain length for pyrite was observed to be:

amyl = normal butyl = isobutyl > ethyl

Isobutyl xanthate floated galena better than pyrite, recovering 13.1% more galena than pyrite under the same conditions.

Ethyl xanthate and di-ethyl DTP had very similar recoveries for both minerals. This meant that their performance as mixtures could be compared on the same basis across both minerals. Di-ethyl DTP however showed to have a slightly better ability to collect pyrite than did SEX. Di-ethyl DTP was also seen to recover the coarse fraction of both galena and pyrite at higher rates than SEX.

Di-isobutyl DTP was a weaker collector of galena when compared to isobutyl xanthate. However, their collecting action on pyrite was very similar.

Dithiocarbamate at both alkyl chain lengths only slightly improved the recovery of galena beyond the collectorless condition. Pyrite flotation had little response to the presence of DTC compared to the collectorless condition. This indicated that under these conditions and dosages, di-alkyl DTC did not display significant collecting properties on both minerals.

Size class flotation for both minerals showed that the fine fraction was probably recovered mostly by entrainment and did not show any significant response to the presence of any of the collectors. The recovery of the intermediate fraction of both minerals was 100% with di-isobutyl DTP and isobutyl xanthate. This meant the intermediate size class was not a suitable indicator of increased flotability with isobutyl mixtures containing either one of these collectors. This size class was also shown to be most easily recovered when compared to coarse fraction flotation. The coarse fraction was the size class most difficult to recover. This makes it a good indicator of the relative collecting abilities of each reagent. It is also interesting to note that in general when looking at the higher chain length xanthates and the isobutyl DTP, galena had higher flotation rates of recoveries, this may have indicated that it was more amenable to flotation that pyrite. This is most notable when comparing the overall rate of recovery of PAX between the two minerals (cf. Table 3.4.11).

Findings on alkyl chain length were consistent with general literature (cf. Section 1.4.5) and validated the methodology used in this thesis. Order of collector strength based on coarse fraction recovery for both minerals was observed to be the following (only collectors of interest to mixed collector flotation have been included):

Galena: SIBX > SIBDTP > SEX = SEDTP > SIBDTC = SEDTC

Pyrite: SIBX = SIBDTP > SEDTP > SEX > SIBDTC = SEDTC

3.5 Mixtures of collectors

The purpose of these experiments was to observe changes in pulp phase hydrophobicity when using mixtures of either xanthate and dithiophosphate or xanthate and dithiocarbamate. These results were compared to the use of pure collectors, as described in the previous section. All flotation conditions and total collector dosages i.e. the total molecules added per unit surface area, were the same as in the previous section. Ethyl and isobutyl alkyl chain lengths were investigated. The fraction of each collector within the binary mixture was varied, molar ratios chosen were 90:10, 10:90 and 50:50. The latter molar ratio was investigated only for pyrite. The fine fraction (-38 μm) results have been omitted from this section as they are believed to be recovered mostly by entrainment (cf. Section 3.4.5).

The naming convention for mole ratios is that the xanthate contribution is always the first number shown. For example 10:90 SIBX:SIBDTP denotes a 10% isobutyl xanthate and 90% di-isobutyl DTP mixture. An example for galena with a 10:90 mixture of SIBX:SIBDTP is given in Table 3.5.1.

Table 3.5.1: Collector dosage example for a 10:90, SIBX:SIBDTP mixture with galena.

Collector	**Moles added to 3 grams of galena**	**% of total dosage**	**fractional surface coverage**
SIBX	1.1x10^{-7}	10	5%
SIBDTP	1.0x10^{-6}	90	45%
Total	1.1x10^{-6}	100	50%

As stated previously (cf. experimental chapter, Section 2.9), the mineral was first conditioned with xanthate and then the secondary collector. The opposite sequence of addition was also investigated. The results for selected reagent conditions where a significant difference between sequence of collector addition for a reagent condition was observed are given in further on in this chapter. The results shown in the bar graphs and times based recoveries are shown again in Tables for convenience.

3.5.1 Microflotation with mixtures of xanthate and dithiophosphate

3.5.1.1 Galena

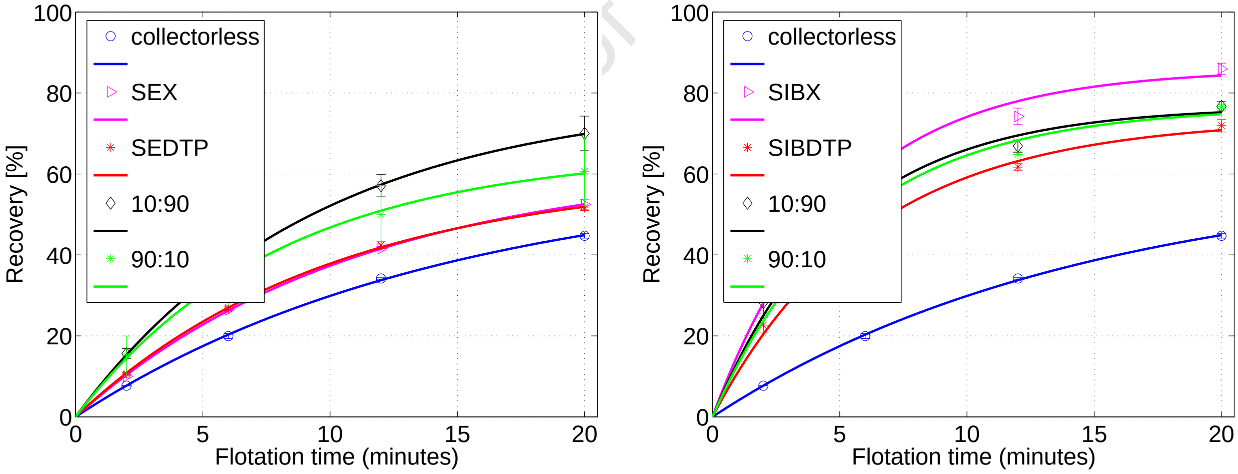
Figure 3.5.1 shows the microflotation recovery of galena as a function of time using xanthate and dithiophosphate mixtures. Figure 3.5.1a shows results for the ethyl chain lengths and

Figure 3.5.1b shows results for the isobutyl chain lengths. The most notable result in Figure 3.5.1a is that a 10:90 SEX:SEDTP mixture significantly increased the overall recovery of galena by 17% beyond that of using only SEX or SEDTP.

Figure 3.5.2 shows the coarse and intermediate fraction final mass recoveries (after 20 minutes) for both ethyl and isobutyl mixtures. Figure 3.5.2a shows that the coarse fraction final recovery improved by 49% and the intermediate fraction by 39% for the 10:90 SEX:SEDTP mixture. It should be pointed out that the coarse fraction had the largest improvement in flotation recovery. This is an interesting result as the intermediate fraction generally showed itself to be more amenable to flotation when pure collectors were used. The rate of flotation recovery of the 10:90 is also seen to be similar to that of using SEDTP in all size fractions (cf. Table 3.5.2).

Even though the overall recovery of the 90:10 ethyl mixture is lower than that of the 10:90 mixture, it is clear that the 90:10 mixture has a higher rate of recovery across all size fractions compared to the other three collector conditions (cf. Table 3.5.2).

The 90:10 SEX:SEDTP condition also showed increased flotation performance from using either single collector, but it was is difficult to draw any inferences due to the large experimental error associated with it.

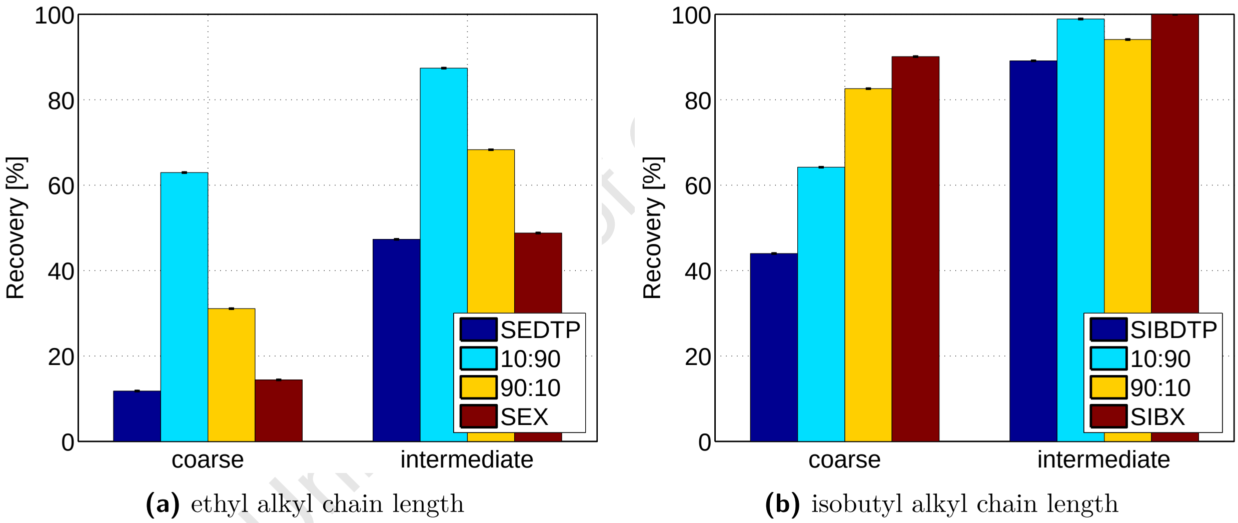


(a) ethyl alkyl chain length **(b)** isobutyl alkyl chain length

Figure 3.5.1: Overall recovery (mass) of xanthate and dithiophosphate mixtures. [Galena; pH = 9; total dosage = 3.8x10^{-7}moles/g]

With respect to the isobutyl chain lengths, no significant improvement in recovery beyond that of using SIBX only (the stronger collector in the mixture) was observed when using mixtures of SIBX and SIBDTP as seen in Figure 3.5.1b. This result is consistent in the sized recoveries as seen in Figure 3.5.2b. Adding a minor amount of SIBX to SIBDTP (10:90) only marginally improved the galena recovery from using SIBDTP only. The coarse fraction recovery follows a linear trend increasing as the fraction of SIBX in the mixture increases (cf. Table 3.5.3). This trend shows that a dilution effect of the collecting power of SIBX occurs when replacing the SIBX with the weaker SIBDTP. This is also seen in Table 3.5.3 where in general the rate of recovery across al size fraction is seen to increase with increasing the SIBX fraction in the mixture.

It should be noted that in Figure 3.5.1b both the 90:10 and 10:90 conditions had similar overall flotation behaviour. This result was unexpected because the 90:10 mixture should have performed better due to the larger amount of SIBX present, and mentioned previously, the coarse fraction recovery is seen to increase in this manner. The 10:90 mixture however had larger fine fraction recovery (10:90 = 70.7%; 90:10 = 63.5%), but as mentioned previously, this fraction was proposed to be recovered mostly by entrainment and so no conclusions would be drawn from its flotation response to different collector conditions. It is interesting to note that the rate of recovery increased for the coarse fraction when using mixtures of SIBX and SIBDTP (cf. Table 3.5.3).



(a) ethyl alkyl chain length

(b) isobutyl alkyl chain length

Figure 3.5.2: Sized final mass recoveries of xanthate and dithiophosphate mixtures. [Galena; pH = 9; total dosage = 3.8x10^{-7}moles/g]

Table 3.5.2: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of mixtures of ethyl xanthate and di-ethyl DTP. [Galena; pH = 9]

Collector	**Mass recovery** [%]		
	Overall	-150 +75 (μm)	-75 +38 (μm)
SEDTP	51.6	11.8	47.4
10:90	70.0	62.9	87.5
90:10	60.7	31.1	68.3
SEX	52.5	14.4	48.9
First order rate constant (min^{-1}) x10^{-2}			
SEDTP	9.9	7.2	6.8
10:90	10.7	7.2	9.7
90:10	12.5	16.1	8.4
SEX	9.0	0.69	3.2

Table 3.5.3: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of mixtures of isobutyl xanthate and di-isobutyl DTP. [Galena; pH = 9]

Collector	**Mass recovery** [%]		
	Overall	-150 +75 (μm)	-75 +38 (μm)
SIBDTP	72.0	44.0	89.1
10:90	76.7	64.2	98.9
90:10	76.6	82.6	94.1
SIBX	86.0	90.1	100.0
First order rate constant (min^{-1}) x10^{-2}			
SIBDTP	16.2	15.4	12.6
10:90	19.7	18.8	179
90:10	18.5	19.9	18.1
SIBX	19.8	15.7	25.1

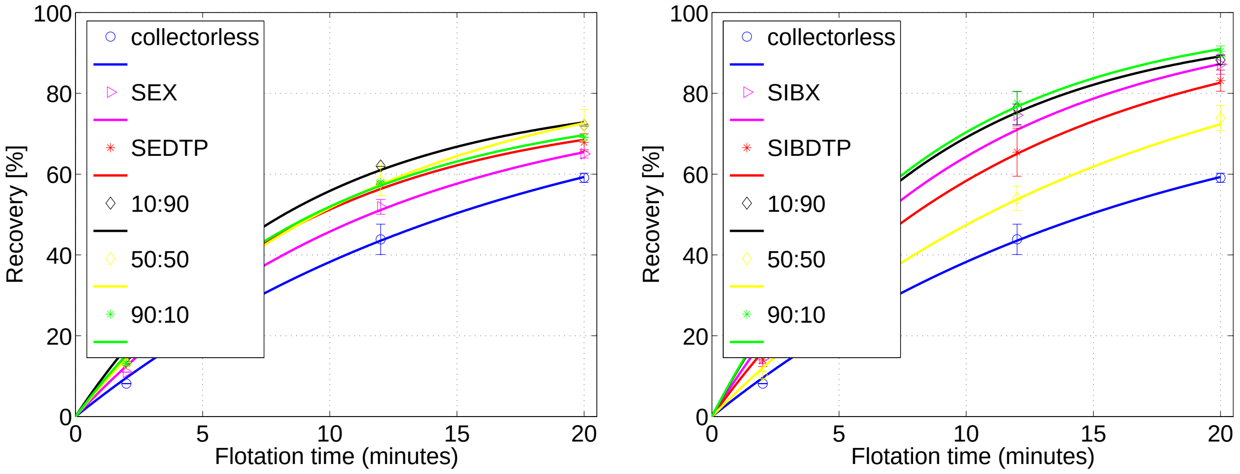
3.5.1.2 Pyrite

As mentioned previously, SEDTP performed slightly better than SEX with pyrite, however the difference was only slight (cf. Table 3.5.4). Figure 3.5.3a shows that both the 10:90 and 50:50 mixtures of SEX:SEDTP did increase the overall flotation response of pyrite above using either constituent single collector. This improvement in flotation is also seen in Figure 3.5.4a and Table 3.5.4 for the coarse and intermediate fraction final recoveries. The 50:50 ethyl mixture is seen to have a significant affect in increasing the coarse recovery of pyrite from using SEDTP only. However, intermediate recoveries for SEX:SEDTP mixtures only improved slightly from that of either pure collector. Again the use of mixtures in the flotation of coarse material is a significant result.

From the overall recovery seen in Figure 3.5.3a only the 10:90 SEX:SEDTP mixture had a significant improvement, as the error associated with the 50:50 and 90:10 conditions was too large to distinguish from the results obtained with either pure SEX or SEDTP. The overall increase in final recovery from using SEDTP only was 4.3% (for the 10:90 mixture). However the standard deviation of the SEDTP final recovery was 3% and so the maximum increase was probably only 1.3% for the mixture, which was only very slight in comparison to the increase observed under the same conditions with galena (17% overall final recovery increase from using SEX or SEDTP only). The trend of increased recovery from that of using SEX and SEDTP when using a 10:90 mixture of the two collectors is consistent with the result seen with galena (cf. Section 3.5.1.1).

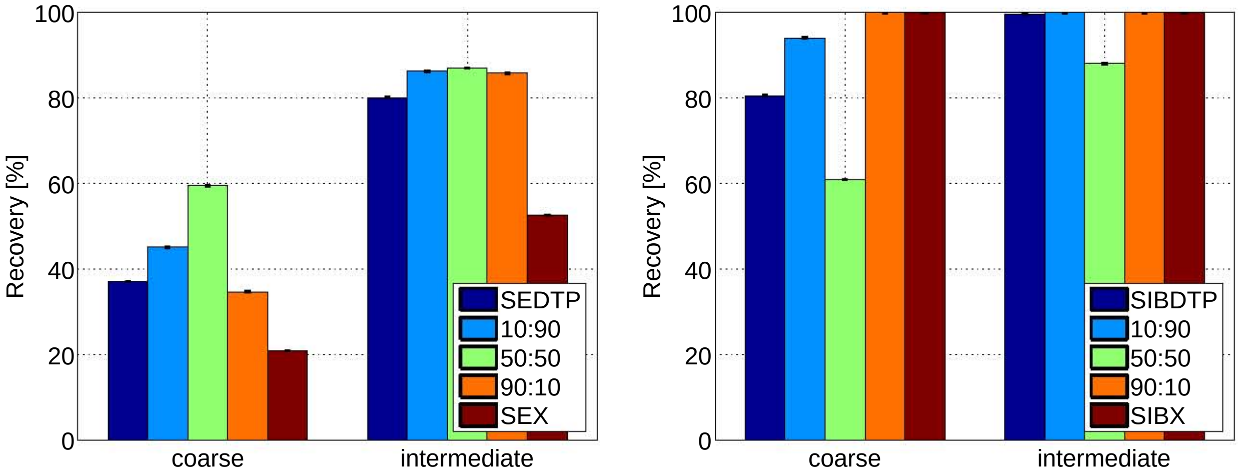
Figure 3.5.3b shows that using mixtures of SIBX and SIBDTP again resulted in a dilution effect of the collecting power of SIBX (not including the 50:50 mixture, which is considered an outlier in this case). This result is consistent with the trend observed for the same mixture on galena (cf. Table 3.5.3). The same trend is observed in the coarse fraction final recoveries as seen in Figure 3.5.4b and Table 3.5.5, where increasing the SIBX fraction in the mixture resulted in higher recoveries. The intermediate fraction is seen to have reached its maximum floatability under all conditions with the isobutyl chain length.

It is interesting to note that the rate of recovery increased across all fractions when using mixtures of SIBX and SIBDTP (cf. Table 3.5.5), which was also observed for galena in the coarse fraction (cf. Table 3.5.3).



(a) ethyl chain length **(b)** isobutyl chain length

Figure 3.5.3: Overall recovery (mass) of xanthate and dithiophosphate mixtures. [Pyrite; pH = 9; total dosage = 2.4x10^{-6}moles/g]



(a) ethyl alkyl chain length **(b)** isobutyl alkyl chain length

Figure 3.5.4: Sized final mass recoveries of xanthate and dithiophosphate mixtures. [Pyrite; pH = 9; total dosage = 2.4x10^{-6}moles/g]

Table 3.5.4: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of mixtures of ethyl xanthate and di-ethyl DTP. [Pyrite; pH = 9]

Collector	**Mass recovery [%]**		
	Overall	-150 +75 (μm)	-75 +38 (μm)
SEDTP	67.9	37.2	80.2
10:90	72.2	45.1	86.3
50:50	72.1	59.5	87.1
90:10	69.1	34.7	85.8
SEX	65.0	20.9	52.6
First order rate constant (min^{-1}) x10^{-2}			
SEDTP	10.8	3.0	7.9
10:90	11.9	2.9	9.4
50:50	9.0	8.6	9.1
90:10	10.8	1.9	8.8
SEX	8.4	1.0	6.9

Table 3.5.5: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of mixtures of isobutyl xanthate and di-isobutyl DTP. [Pyrite; pH = 9]

Collector	**Mass recovery [%]**		
	Overall	-150 +75 (μm)	-75 +38 (μm)
SIBDTP	83.1	80.6	99.7
10:90	88.3	94.1	100.0
50:50	73.9	61.0	88.1
90:10	90.4	100.0	100.0
SIBX	87.2	100.0	100.0
First order rate constant (min^{-1}) x10^{-2}			
SIBDTP	8.9	6.0	10.9
10:90	12.4	10.1	15.0
50:50	6.4	4.5	7.8
90:10	12.3	10.4	16.0
SIBX	10.3	9.4	13.8

3.5.1.3 Summary

Isobutyl chain length mixtures of xanthate and dithiophosphate did not enhance the flotation recovery of pyrite or galena beyond using SIBX only, however the coarse fraction rate of recovery of galena and all three (viz. overall, coarse and intermediate) for pyrite where seen to be greater than that of either pure collector. Recoveries of mixtures seemed to be within the additive contributions of the single collectors and a dilution effect of the collecting power of SIBX with the weaker collector SIBDTP was seen.

Most notably, the 10:90, SEX:SEDTP condition significantly improved the overall, coarse and intermediate recovery of galena, beyond using only SEX or SEDTP. With the largest increase in recovery occurring in the coarse fraction. This result was only very slight for pyrite and not deemed as significant, although for pyrite the 10:90 and 50:50 mixtures of SEX:SEDTP again increased the coarse particle recovery as was the case with galena at the 10:90 condition. This indicated increased galena hydrophobicity when adding a small amount of SEX to SEDTP.

Flotation response of pyrite and galena with SEX:SEDTP at the 90:10 condition did not significantly increase recovery. This seems to infer that observed increases in hydrophobicity with SEX:SEDTP mixtures were mineral specific. And most notably, flotation of the coarse fraction was enhanced when using mixtures of ethyl xanthate and di-ethyl DTP beyond that of using either single collector. The trends were consistent throughout both minerals, but increases in floatability as observed with ethyl mixtures were not as pronounced with pyrite as they were with galena.

3.5.2 Mixtures of xanthate and dithiocarbamate

Mixtures of xanthate and dithiocarbamate were investigated at both the ethyl and isobutyl chain lengths to observe any changes in flotation behaviour when compared to the constituent single collectors. An example of a collector mixture dosage is given in Table 3.5.1.

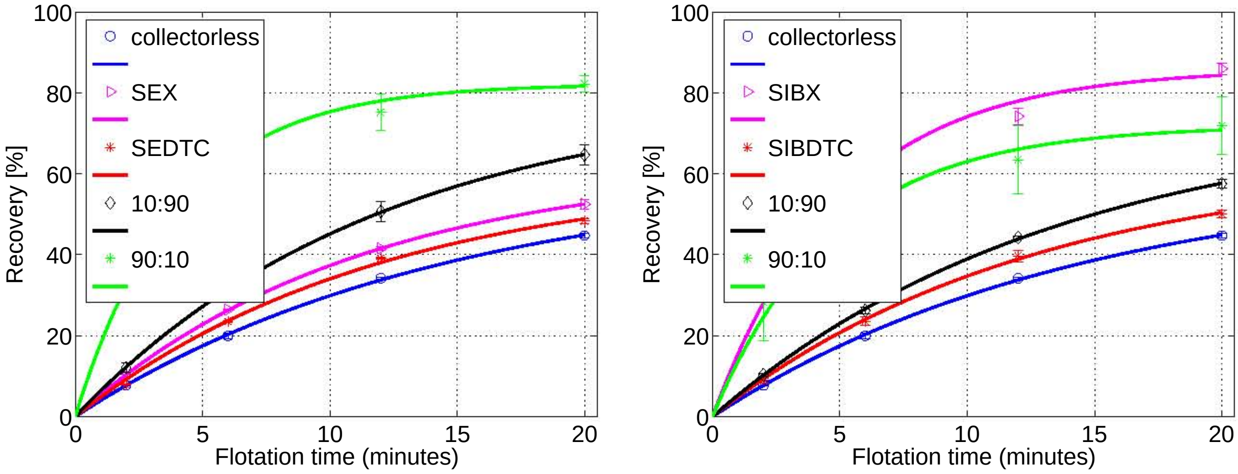
3.5.2.1 Galena

Bearing in mind that a 10:90 SEX:SEDTP mixture (cf. Section 3.5.1.1) significantly increased galena flotation behaviour beyond that of using its constituent single collectors, Figure 3.5.5a shows significant increases in overall recovery for 90:10 and 10:90 mixtures of SEX:SEDTC. As was the case for the SEX:SEDTP mixtures, Figure 3.5.6a and Table 3.5.6 show that the greatest increase in final recovery was in the coarse fraction. This result further supported the general observation that the use of collector mixtures significantly increased the flotation performance of the coarse fraction beyond that of using pure collectors.

The rate of flotation is significantly increased in all size fractions when using the 90:10 SEX:SEDTC mixture (cf. Table 3.5.6), where the coarse fraction is consistently the most affected, as was the case with final recoveries when compared to using either single collector. The 10:90 mixture however has a similar overall rate of recovery to that of using SEDTC only.

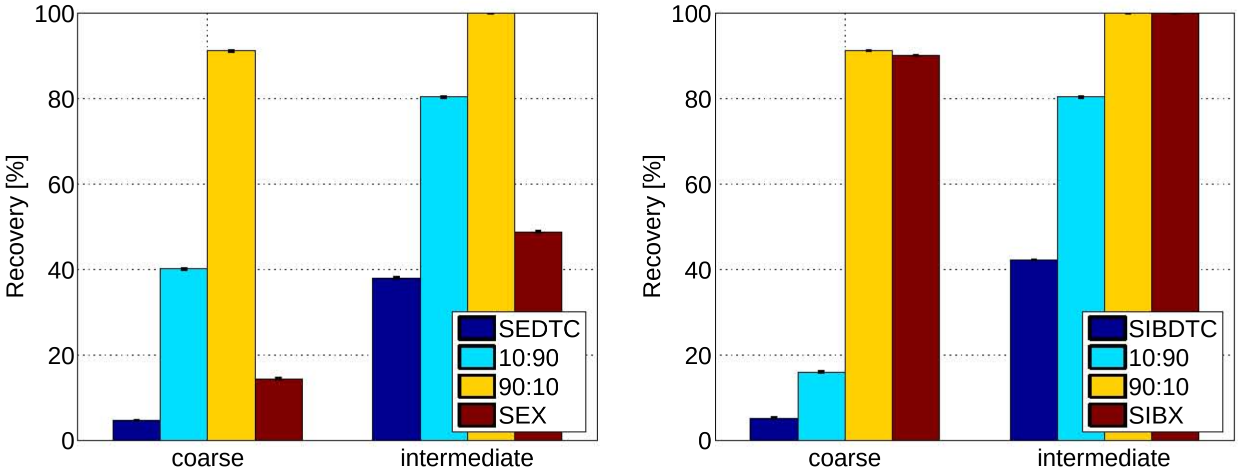
Isobutyl mixtures of xanthate and dithiocarbamate however did not increase flotation behaviour of galena beyond using SIBX only. This is similar to the previous findings for mixtures of xanthate and dithiophosphate for this alkyl chain length. This is clear in Figure 3.5.5b which shows that as the SIBX fraction in the mixture increased, the flotation response became more like that of using SIBX only, to the extent where the 90:10 SIBX:SIBDTC mixture condition gave identical coarse and intermediate fraction recoveries in Figure 3.5.5b and Table 3.5.7.

This dilution effect is also evident when looking at Table 3.5.7, where the 90:10 mixtures overall rate of recovery is almost identical to that of SIBX only and the 10:90 mixtures overall rate of recovery is identical to that of using SIBDTC only. The coarse and intermediate fraction rates of recovery are however seen to increase when adding a SIBDTC to SIBX (i.e. the 90:10 mixture), this is consistent with the results for the ethyl mixture (cf. Table 3.5.6).



(a) ethyl alkyl chain length **(b)** isobutyl alkyl chain length

Figure 3.5.5: Overall recovery (mass) of xanthate and dithiocarbamate mixtures. [Galena; pH = 9; total dosage = 3.8x10^{-7}moles/g]



(a) ethyl alkyl chain length **(b)** isobutyl alkyl chain length

Figure 3.5.6: Sized final mass recoveries of xanthate and dithiocarbamate mixtures. [Galena; pH = 9; total dosage = 3.8x10^{-7}moles/g]

Table 3.5.6: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of mixtures of ethyl xanthate and di-ethyl DTC. [Galena; pH = 9]

Collector	**Mass recovery [%]**		
	Overall	-150 +75 (μm)	-75 +38 (μm)
SEDTC	48.3	4.6	38.0
10:90	64.7	40.1	80.3
90:10	82.0	91.1	100.0
SEX	52.5	14.4	48.9
First order rate constant (min^{-1}) x10^{-2}			
SEDTC	8.3	6.9	2.3
10:90	8.3	2.4	7.2
90:10	25.0	40.0	37.1
SEX	9.0	0.69	3.2

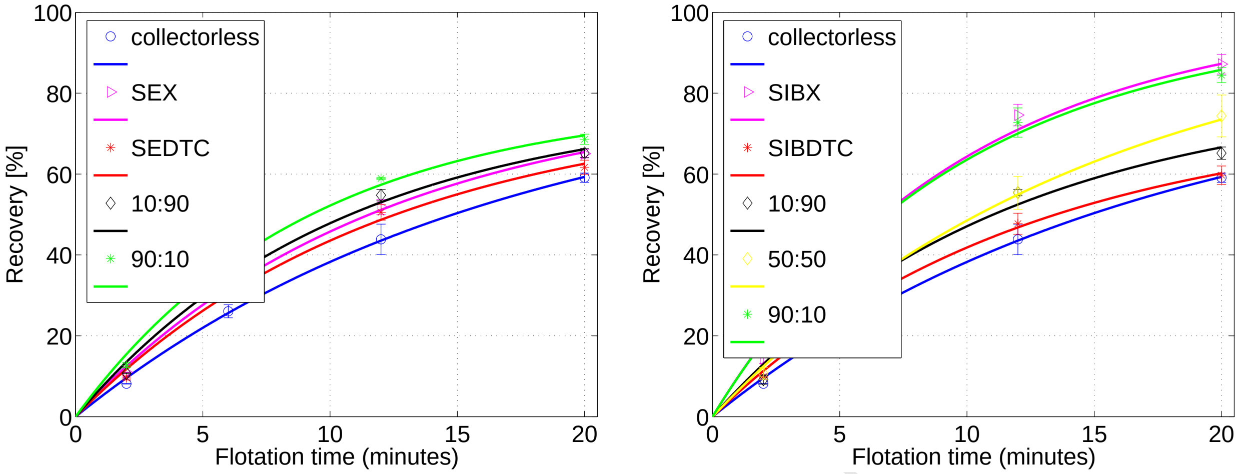
Table 3.5.7: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of mixtures of isobutyl xanthate and di-isobutyl DTC. [Galena; pH = 9]

Collector	**Mass recovery [%]**		
	Overall	-150 +75 (μm)	-75 +38 (μm)
SIBDTC	50.1	5.2	42.2
10:90	57.5	16.0	64.8
90:10	71.9	91.2	100.0
SIBX	86.0	90.1	100.0
First order rate constant (min^{-1}) x10^{-2}			
SIBDTC	7.9	3.1	2.6
10:90	7.3	0.8	4.4
90:10	20.9	33.6	32.4
SIBX	19.8	15.7	25.1

3.5.2.2 Pyrite

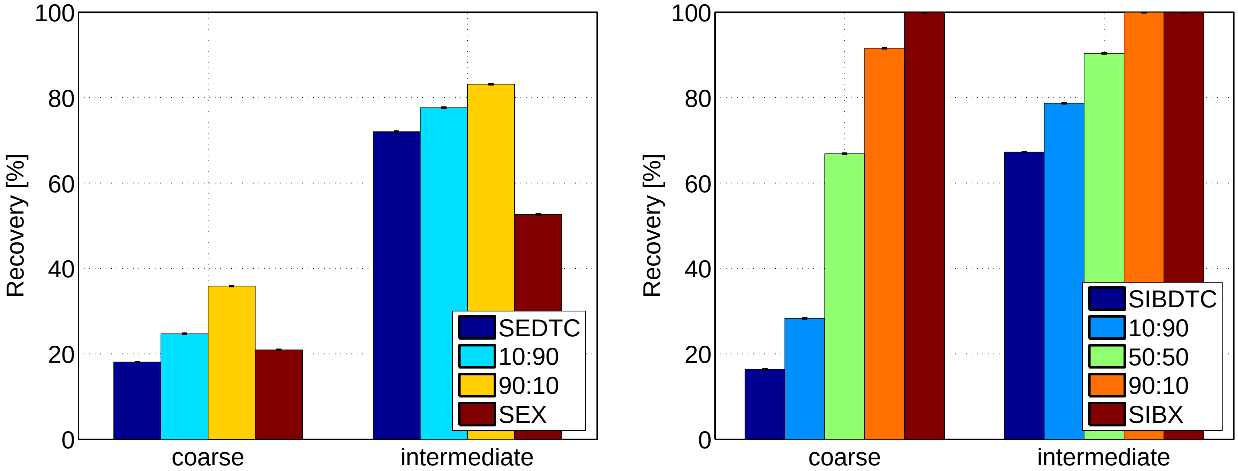
Recalling that isobutyl xanthate and dithiophosphate mixtures did not significantly increase the overall flotation behaviour of pyrite, we see a similar result in both Figures 3.5.7b and 3.5.8b for xanthate and dithiocarbamate mixtures.

Figure 3.5.8a and Table 3.5.8 indicate increases in the coarse and intermediate fraction recoveries of 10:90 and 90:10 SEX:SEDTC mixtures beyond using SEX only. This was also seen for coarse and intermediate recoveries under the same conditions for galena (cf. Table 3.5.6) showing that the trend was consistent for both minerals, but not as pronounced with pyrite as it was with galena. These increases in coarse and intermediate final recovery are only slight and overall final recovery is only increased marginally. Figure 3.5.7a shows the overall flotation performance of the mixtures to be similar to that of SEX only.



(a) ethyl chain length **(b)** isobutyl chain length

Figure 3.5.7: Overall recovery (mass) of xanthate and dithiocarbamate mixtures. [Pyrite; pH = 9; total dosage = 2.4x10^{-6}moles/g]



(a) ethyl alkyl chain length **(b)** isobutyl alkyl chain length

Figure 3.5.8: Sized final mass recoveries of xanthate and dithiocarbamate mixtures. [Pyrite; pH = 9; total dosage = 2.4x10^{-6}moles/g]

Table 3.5.8: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of mixtures of ethyl xanthate and di-ethyl DTC. [Pyrite; pH = 9]

Collector	**Mass recovery [%]**		
	Overall	-150 +75 (μm)	-75 +38 (μm)
SEDTC	61.7	18.1	72.0
10:90	65.2	24.7	77.6
90:10	68.6	35.9	83.1
SEX	65.0	20.9	52.6
First order rate constant (min^{-1}) x10^{-2}			
SEDTC	8.3	0.9	6.0
10:90	9.6	1.3	7.0
90:10	11.0	2.0	8.5
SEX	8.4	1.0	6.9

Table 3.5.9: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of mixtures of isobutyl xanthate and di-isobutyl DTC. [Pyrite; pH = 9]

Collector	**Mass recovery [%]**		
	Overall	-150 +75 (μm)	-75 +38 (μm)
SIBDTC	59.7	16.4	67.3
10:90	65.2	28.3	78.7
50:50	74.4	66.9	90.4
90:10	84.4	91.6	100.0
SIBX	87.2	100.0	100.0
First order rate constant (min^{-1}) x10^{-2}			
SIBDTC	8.3	0.8	5.1
10:90	8.8	1.5	7.2
50:50	6.6	4.8	8.5
90:10	10.5	8.6	13.5
SIBX	10.3	9.4	13.8

Coarse recovery for the isobutyl lengths increased linearly (R^2 = 0.98) with increasing SIBX molar fraction as is observed in Figure 3.5.9. This indicated that SIBX performance with pyrite was probably not influenced by the presence of SIBDTC and dependent only on the amount of SIBX added when in a mixture with SIBDTC. In this work, it was clear this was a dilution effect. This is also clear when looking at the overall rate of recovery in Table 3.5.9, where the 10:90 mixture rate is similar to that of using SIBDTC only, and the 90:10 rate is also identical to that of using SIBX only. This trend is also similar when looking at the coarse and intermediate fraction rates of recoveries across the different isobutyl collector conditions

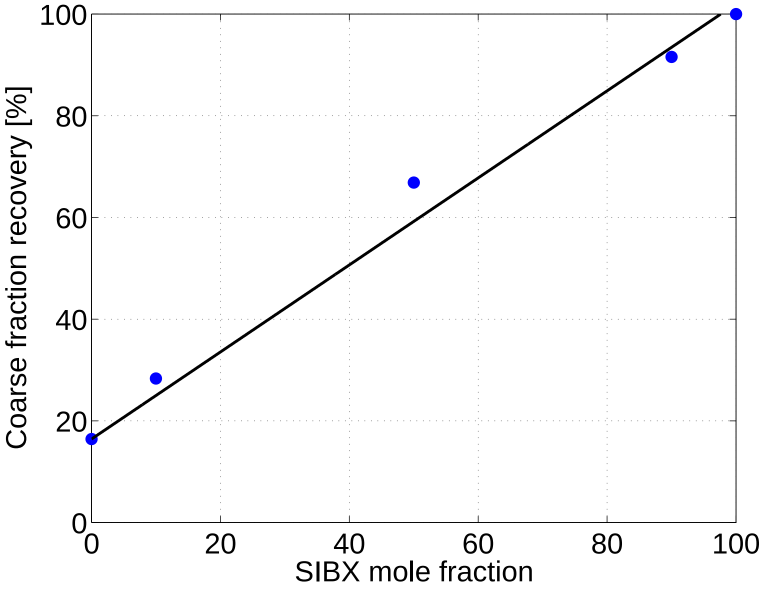


Figure 3.5.9: Final mass recoveries of the coarse fraction (-150+75 μm) as a function of SIBX mole fraction in SIBX:SIBDTC mixture. SIBDTC only final recovery intersects the coarse fraction recovery axis. The correlation coefficient for the straight-line is $R^2 = 0.988$. [Pyrite; pH = 9; total dosage = 2.4x10^{-6}moles/g]

3.5.2.3 Summary

Recovery of galena and pyrite generally increased in a linear manner as the proportion of SIBX in the SIBX:SIBDTC mixture increased. This was more evident for pyrite where the increase in coarse fraction recovery with SIBX percentage in the mixture had a linear correlation of $R^2 = 0.988$. The rate of coarse fraction recovery was seen to increase by the use of a 90:10 SIBX:SIBDTC mixture, but not the final recoveries of across all size fractions.

Most notably galena flotation with SEX:SEDTC mixtures (at both 10:90 and 90:10 conditions) significantly increased beyond that of using SEX. The 90:10 mixture of SEX:SEDTC with pyrite also gave increased flotability, but was not as prominent as with galena. The general trend of the 90:10 and 10:90 ethyl mixtures (with the former mixture giving the greatest increase in floatability) increasing mineral flotability was observed across both minerals. The effect was however more prominent with galena than with pyrite, which was also the case for xanthate and dithiophosphate mixtures (cf. Section 3.5.1.3).

3.6 The effect of sequence of collector addition when using collector mixtures

The results shown in preceding sections have been for cases where xanthate was added first and then the secondary collector. The reagent sequences were either, xanthate added first, DTC or DTP first, or both collectors added simultaneously. In general this sequence of addition did not affect the flotation behaviour of either galena or pyrite when mixtures of collectors were used. There were only three cases where the sequence of addition affected the flotation behaviour of the mineral. These were the three cases where increased flotation performance was observed. These three cases are presented next.

3.6.1 Flotation of galena with ethyl xanthate:di-ethyl DTP mixtures

Figure 3.6.1 shows the overall flotation behaviour of galena with 10:90 SEX: di-ethyl DTP mixture and that of the pure collector constituents. Recalling that this mixture increased galena flotation behaviour from using SEX only. The sized and overall final recoveries and rates of recoveries for the different sequences of addition are also shown in Table 3.6.1. The case for the simultaneous sequence of collector addition is omitted from Table 3.6.1 as it was clearly a worse result than the other two addition sequences (cf. Figure 3.6.1).

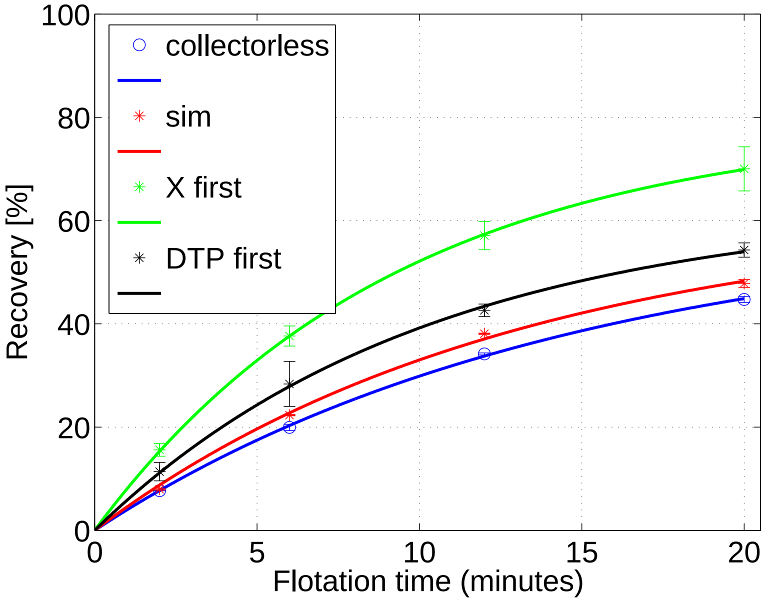


Figure 3.6.1: Overall mass recovery of the 10:90 SEX:SEDTP mixture. Simultaneous (sim); xanthate first (X) and dithiophosphate first (DTP). [Galena; pH = 9; total dosage = 3.8x10^{-7}moles/g]

It is clear that sequence of collector addition played a significant role in the collecting power of the 10:90 SEX: di-ethyl DTP mixture. Simultaneous addition of SEX and di-ethyl DTP decreased the collecting action of both collectors, giving a lower total recovery than either collector gave on its own (cf. Figure 3.6.1) .

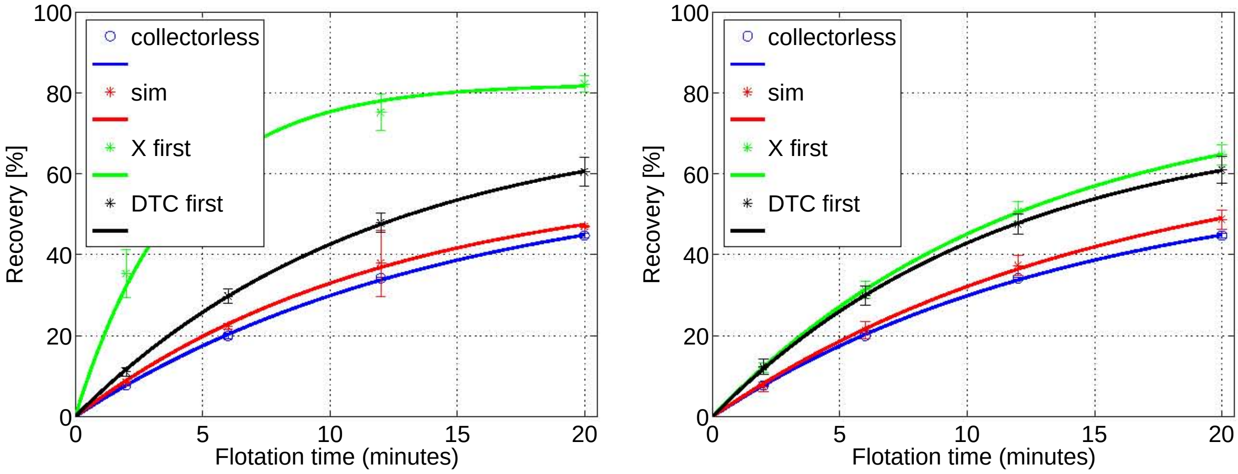
When di-ethyl DTP was added first, galena flotation performance was essentially identical to that of either pure collector, although it did increase coarse and intermediate fraction recoveries from that of either pure collector (cf. Table 3.6.1). The 10:90 DTP first condition however gave similar size fraction rates of recoveries to that of using SEX only. Adding SEX first resulted in the best outcome for galena flotation when using the 10:90 SEX: di-ethyl DTP mixture, this is seen when comparing the rates of recoveries and final recovery values across all size fraction in Table 3.6.1.

Table 3.6.1: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of the 10:90 mixture of ethyl xanthate and di-ethyl DTP for different sequences of collector addition. [Galena; pH = 9]

Collector	**Mass recovery [%]**		
	Overall	-150 +75 (μm)	-75 +38 (μm)
SEDTP	51.6	11.8	47.4
SEX	52.5	14.4	48.9
10:90 (X first)	70.0	62.9	87.5
10:90 (DTP first)	54.3	19.6	61.1
First order rate constant (min^{-1}) x10^{-2}			
SEDTP	9.9	7.2	6.8
SEX	9.0	0.69	3.2
10:90 (X first)	10.7	7.2	9.7
10:90 (DTP first)	9.8	1.6	4.3

3.6.2 Flotation of galena with an ethyl xanthate:di-ethyl DTC mixture

Figure 3.6.1 shows the overall flotation behaviour of galena with 90:10 and 10:90 SEX: di-ethyl DTC mixtures. These mixture conditions were seen to result in a significantly higher flotation rate and recovery from that of using SEX only. The final recoveries and rates of recovery are given in Tables 3.6.2 and 3.6.3 for the 10:90 and 90:10 case respectively.



(a) Sequence of addition 90:10; SEX:SEDT**C** **(b)** Sequence of addition 10:90; SEX:SEDT**C**

Figure 3.6.2: Overall mass recovery of xanthate and dithiocarbamate and their 10:90 and 90:10 mixtures at the ethyl chain length. Simultaneous (sim); xanthate first (X) and dithiocarbamate first (DTC). [Galena; pH = 9; total dosage = 3.8x10^{-7}moles/g]

As was the case for the 10:90 SEX:di-ethyl DTP mixture in the previous section, adding SEX and di-ethyl DTC simultaneously resulted in flotation behaviour poorer than that of using either pure collector alone for both 10:90 and 90:10 SEX:di-ethyl DTC mixtures. Sequence of addition played a smaller role in the 10:90 SEX:SEDTC conditions flotation response, but the rates and recoveries across all size fractions were higher for the case when xanthate was added first (cf. Table 3.6.2).

Table 3.6.2: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of the 10:90 mixture of ethyl xanthate and di-ethyl DTC for different sequences of collector addition. [Galena; pH = 9]

Collector	**Mass recovery [%]**		
	Overall	-150 +75 (μm)	-75 +38 (μm)
SEDTC	48.3	4.6	38.0
SEX	52.5	14.4	48.9
10:90 (X first)	64.7	40.1	80.3
10:90 (DTC first)	61.0	14.5	65.7
First order rate constant (min^{-1}) x10^{-2}			
SEDTC	8.3	6.9	2.3
SEX	9.0	0.69	3.2
10:90 (X first)	8.3	2.4	7.2
10:90 (DTC first)	8.7	0.75	4.6

Figure 3.6.2a shows the overall flotation behaviour of galena with 90:10 SEX: diethyl DTC

mixture changes with the sequence of collector addition in that adding xanthate first resulted in the best flotation performance of galena. When looking at Table 3.6.3 it is seen that adding di-ethyl DTC first resulted in a flotation response only slightly better than that of using either pure collector.

Table 3.6.3: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of the 90:10 mixture of ethyl xanthate and di-ethyl DTC for different sequences of collector addition.[Galena; pH = 9]

Collector	**Mass recovery [%]**		
	Overall	-150 +75 (μm)	-75 +38 (μm)
SEDTC	48.3	4.6	38.0
SEX	52.5	14.4	48.9
90:10 (X first)	82.0	91.1	100.0
90:10 (DTC first)	60.5	24.4	74.3
First order rate constant (min^{-1}) x10^{-2}			
SEDTC	8.3	6.9	2.3
SEX	9.0	0.69	3.2
90:10 (X first)	25.0	40.0	37.1
90:10 (DTC first)	8.6	1.3	6.0

3.6.3 Summary

Sequence of collector addition was significant for the two collector mixtures where significant increases in flotation behaviour were observed for galena (viz. 10:90 SEX:SEDTP and 90:10 SEX:SEDTC). In both cases conditioning galena with ethyl xanthate first resulted in a better flotation response of galena than adding the secondary collector first (viz. di-ethyl DTP or di-ethyl DTC). This was consistent throughout overall, coarse and intermediate final recoveries and rates of recoveries.

3.6.4 Summary of collector mixture results

Mixtures of SIBX:SIBDTP and SIBX:SIBDTC for both minerals, did not result in increased flotability above using SIBX only. It was clear that for pyrite and galena SIBX:SIBDTC mixtures resulted in recoveries which increased linearly with increasing SIBX molar fraction. This indicated a dilution effect on the collecting power of SIBX was occurring. The presence of only SIBDTC did not significantly affect the flotation behaviour of pyrite or galena and so the latter result was not unexpected (assuming no synergy is experienced). The linear relationship was more pronounced for pyrite than for galena. This was expected because pyrite flotation responded less to the presence of SIBDTC than galena. A similar result was observed for SIBX:SIBDTP mixtures with both minerals

Mixtures of SEX:SEDTP and SEX:SEDTC improved recovery of galena at the 10:90 condition beyond using SEX only. The increased flotation of the coarse fraction was however seen to continue through the ethyl mixture results. SEX:SEDTC at the 90:10 condition gave the largest increase in overall, coarse and intermediate recovery of galena, making the use of such a mixture almost as powerful as using SIBX only (mixture = 82% overall final mass recovery; SIBX = 86% overall final mass recovery). The increases in flotation performance of galena from using SEX only are shown in Table 3.6.4.

Table 3.6.4: Increases in overall final (after 20 minutes) recovery and recovery by size class from using ethyl xanthate only. [Galena; pH = 9; total dosage = 3.8x10^{-7}moles/g]

Galena (PbS)	**10:90 SEX:SEDTP**	**10:90 SEX:SEDTC**	**90:10 SEX:SEDTC**
Increase in final recovery from using SEX only			
Overall	18%	12%	30%
-150 +75 (μm)	49%	26%	77%
-75 +38 (μm)	39%	32%	51%

Again emphasis is placed on the large observed increases in final recovery of the coarse fraction (cf. Table 3.6.4). In general the rate of recovery also increases (cf. Table 3.6.5) when using the mixtures on galena. The largest increase in rate of recovery was seen for the 90:10 SEX:SEDTC mixture across all size fraction compared to using SEX only. This was consistent with the largest increase in recovery also occurring with this mixture.

Table 3.6.5: Comparison of first order rates between selected mixtures and ethyl xanthate only. [Galena; pH = 9; total dosage = 3.8x10^{-7}moles/g]

Galena (PbS)	**SEX only**	**10:90 SEX:SEDTP**	**10:90 SEX:SEDTC**	**90:10 SEX:SEDTC**
First order rate constant (min^{-1}) x10^{-2}				
Overall	9.0	10.7	8.3	24.8
-150 +75 (μm)	0.69	7.2	2.4	40.1
-75 +38 (μm)	3.2	9.7	7.2	37.1

SEX:SEDTP and SEX:SEDTC mixtures did not increase the flotability of pyrite beyond using the single collectors as significantly as they did with galena. There was a slight increase of a 1.3 % in over all recovery at the 10:90 SEX:SEDTP mixture condition, but this was deemed in-significant compared to the large 17% increase for galena flotation under the same conditions. There were also increases in coarse fraction recoveries with the use of 10:90 and 90:10 SEX:SEDTC mixtures, but again these only resulted in marginal increases in overall recovery.

SIBX was a superior collector when compared to all other collectors and collector mixtures tested in this thesis. The use of a collector mixture (as in this thesis) over that of SIBX alone would have to be motivated by a reason other than increased pulp phase flotability.

Sequence of collector addition was seen to have a marked influence on the collecting action of the 10:90 and 90:10 SEX:SEDTC and 10:90 SEX:SEDTP mixtures with galena. The simultaneous addition of collectors resulted in a flotation response poorer than that of using either single collector. The addition of SEX first and then the secondary collector resulted in the best flotation response of galena for the former mixtures.

In general the same trends were observed for both minerals. When a mixture was seen to significantly improve galena performance the flotation response of pyrite was markedly less than that for galena.

3.7 Batch flotation of a synthetic ore using a selected collector mixture

The aim of doing batch flotation tests was to see if the observations made in the pulp phase were sustained when a froth phase and energy (in the form of mixing by means of an impeller) were present. As mentioned in the Experimental chapter of this thesis (cf. Section 2.10) a synthetic ore made up (by mass) of 5% galena, 45% of a plagioclase-rich ore and 45% of a pyroxene-rich ore was used to carry out the batch flotation tests. The latter two minerals constituted the gangue portion of the synthetic ore. All minerals were prepared in the same manner as the microflotation feed (cf. Section 2.3) and were 100% -106 μm.

For each test 1 kg of this synthetic ore was used and the total collector dosage was kept constant to ensure an equivalent of 50% pseudo-monolayer coverage of the galena surface in the ore (cf. Section 2.10.1.1). Batch flotation tests were carried out using deionised water at pH 9 (using NaOH) and 15 ppm DOW 200 frother. The reagent conditions that were tested using batch flotation of the synthetic ore are listed in Table 2.10.5.

3.7.1 Results for the flotation of the complete ore

Figure 3.7.1 shows the total solids recovery from batch flotation tests carried out using no collector, pure di-ethyl DTC, ethyl xanthate and a 90:10 mixture of SEX:SEDTC. As mentioned previously, the 90:10 mixture was chosen because it resulted in the largest increase in galena floatability from using SEX only (cf. Table 3.6.4).

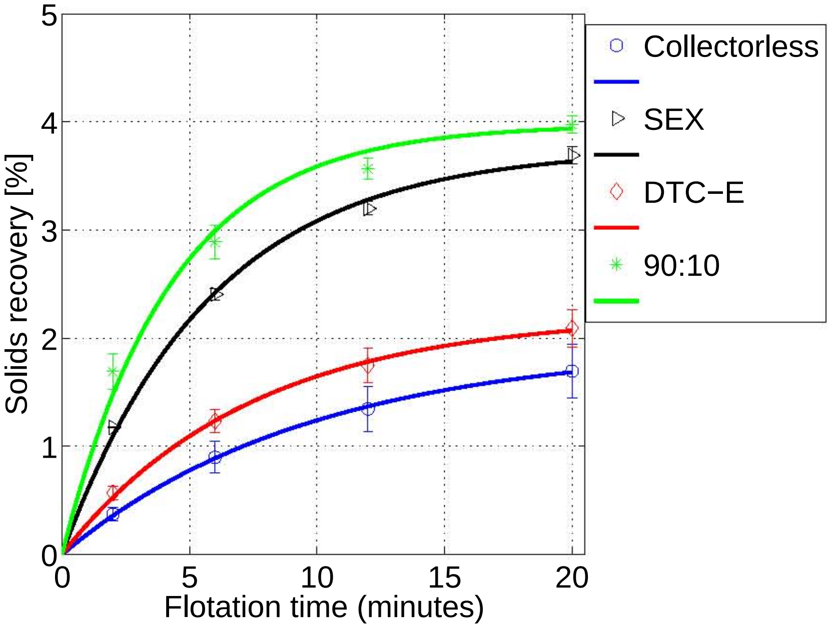


Figure 3.7.1: Batch flotation solids recovery as a function of flotation time. [pH = 9, total collector dosage = 5.9x10^{-7} moles collector / g of galena; 1 kg of synthetic ore made up by mass of 5% galena, 47.5 % plagioclase-rich ore and 47.5% pyroxene-rich ore]

The use of di-ethyl DTC did not significantly increase the solids recovery from the collectorless condition. The use of ethyl xanthate did result in a significantly higher solids recovery from using no collector. The 90:10 mixture shows an increase in solids recovery of 0.28% from that of using SEX only.

3.7.2 Lead and water recovery

The Pb recovery as a function of time shown in Figure 3.7.2 follows the same trend seen with solids recovery and rate of recovery (cf. Figure 3.7.4), in that di-ethyl DTC was seen to be the weakest collector, only improving the flotation of Pb (and thus galena) by a little from that of the collectorless condition. The 90:10 SEX:SEDTC mixture increased the final Pb recovery by a maximum of 5.3% from that of using SEX only which is consistent with the increased solids recovery seen in Figure 3.7.1.

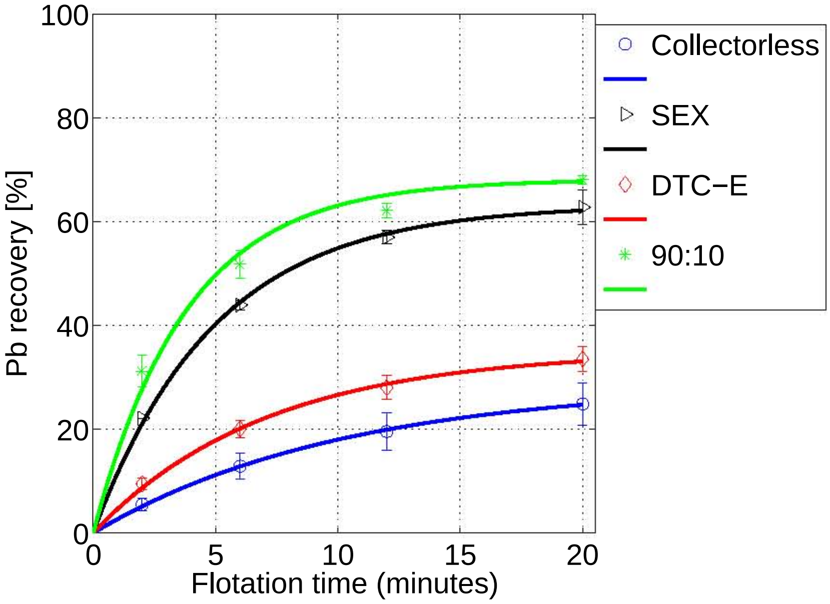


Figure 3.7.2: Batch flotation Pb recovery as a function of flotation time. [pH = 9, total collector dosage = 5.9x10^{-7} moles collector / g of galena; 1 kg of synthetic ore made up by mass of 5% galena, 47.5 % plagioclase-rich ore and 47.5% pyroxene-rich ore]

The increased floatability seen by the use of the 90:10 SEX:SEDTC mixture must however be understood in terms of froth effects. The effect of the froth phase can be observed by plotting the Pb recovery per unit of water recovered as in Figure 3.7.3.

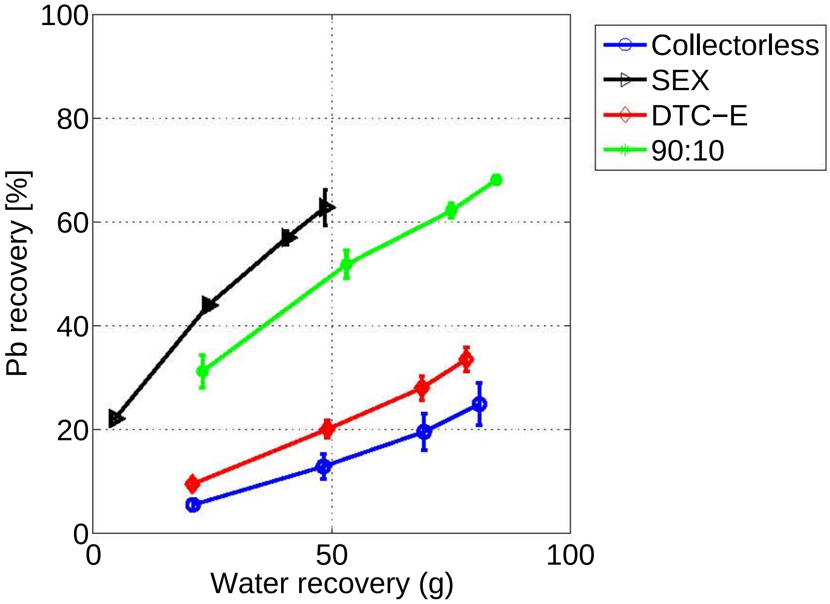


Figure 3.7.3: Batch flotation Pb recovery as a function of water recovery . [pH = 9, total collector dosage = 5.9x10^{-7} moles collector / g of galena; 1 kg of synthetic ore made up by mass of 5% galena, 47.5 % plagioclase-rich ore and 47.5% pyroxene-rich ore]

Figure 3.7.3 shows that using di-ethyl DTC resulted in a Pb recovery per unit of water similar to that of the collectorless condition, confirming that it was a consistently poor collector even when a froth phase was present. The use of SEX results in a significantly higher Pb recovery at lower water recoveries than the 90:10 SEX:SEDTC mixture. This indicated that the addition of SEDTC to SEX resulted in increased froth stability from that of using SEX.

Table 3.7.1: Comparison of final (after 20 minutes of flotation) Pb grade and recovery for batch flotation tests [pH = 9, total collector dosage = 5.9x10^{-7} moles collector / g of galena; 1 kg of synthetic ore made up by mass of 5% galena, 47.5 % plagioclase-rich ore and 47.5% pyroxene-rich ore].

Parameter	Collectorless	SEDTC	SEX	90:10 SEX:SEDTC
Final Pb recovery	24.9 %	33.5 %	62.7 %	68.0 %
Final Pb grade	31.3 %	25.0 %	20.4 %	19.9 %

Figure 3.7.4 shows the first order rate constant (cf. Equation 2.5.3; modelled on Pb recovery) of each of the batch floats. It is clear that the rate of recovery follows the same trend as the final solids recoveries observed in Figure 3.7.1. The collecting ability of the collectors is seen to be SEDTC < SEX < 90:10 SEX:SEDTC.

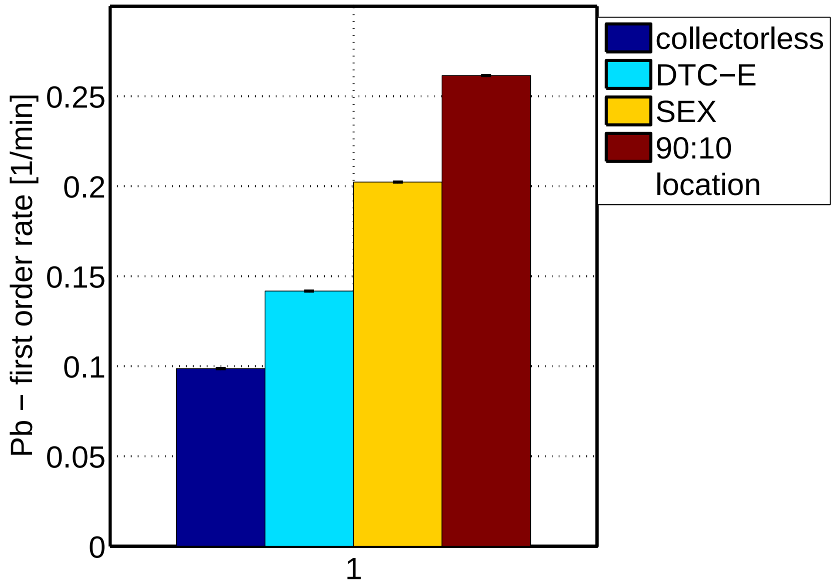


Figure 3.7.4: Batch flotation first order rate constants as a function of collector type. [pH = 9, total collector dosage = 5.9x10^{-7} moles collector / g of galena; 1 kg of synthetic ore made up by mass of 5% galena, 47.5 % plagioclase-rich ore and 47.5% pyroxene-rich ore]

3.7.3 Summary of batch flotation results

The set of batch flotation tests performed showed that the order of individual collector strength was identical to that obtained with pure galena in a microflotation cell, where SEX was observed to be a superior collector to di-ethyl DTC which gave similar flotation results to that of using no collector.

The use of a 90:10 SEX:SEDTC did result in a slightly higher solids and Pb recovery as a function of time, when compared to the use of SEX only. The water recovery however showed that the mixture resulted in higher water recoveries for a similar solids recovery to that of SEX. This indicated that the mixture had stabilised the froth. In summary, the observations of increased flotability seen in microflotation tests with the use of a 90:10 SEX:SEDTC mixture for galena, were also seen in a batch flotation cell.

Chapter 4

Discussion

This chapter discusses the findings presented in this thesis and relates them to the research objectives and key questions set out in the beginning of this investigation. The use of common thiol collector mixtures (viz. xanthate with dithiophosphate and xanthate with dithiocarbamate) is often considered to increase flotation performance of sulphide minerals. This improvement is termed synergistic, because the increase in performance is not simply additive and is greater than the *pro rata* contribution of the mixture's constituents.

This thesis took a fundamental approach in which the pulp phase floatability (and thus hydrophobicity) of two widely studied sulphide minerals (viz. galena and pyrite) was assessed using different collector mixtures. Mixture ratios were not intended to determine a point where optimum flotation performance was observed but rather to investigate whether there was any indication of synergism in the pulp phase. They were maintained 90:10 and 10:90 (constant molar dosage).

4.1 Mineral floatability with pure collectors

4.1.1 Establishing the baseline

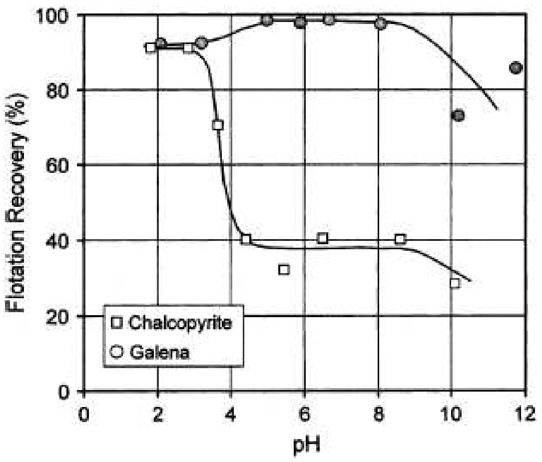
A baseline of how both pyrite and galena floated without the presence of collector and in the presence of each of the single collectors had to be established. This would allow the performance of collector mixtures to be assessed according to the baseline. The key questions were outlined in Section 1.9 and are summarised here again for convenience:

- Do differences in alkyl chain lengths of the thiol collectors have any effect on recoveries or rates of flotation as observed in a microflotation cell?
- Do collector mixtures have any effect on recoveries or rates of flotation compared to the constituent single collectors?
- Do different size classes respond differently in the above regard?
- Do differences observed in rates or recoveries during microflotation carry through to batch flotation?

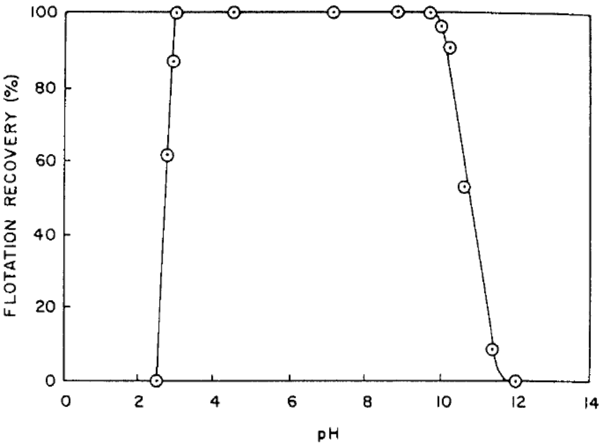
Reproducibility of microflotation tests and Malvern analysis of the flotation concentrates was found to be satisfactory for both minerals (cf. Section 3.2).

As mentioned previously, pure samples of pyrite and galena were used. Pyrite was chosen because of its widespread occurrence in sulphide ores. Galena has a unique regular cubic morphology and is frequently used in fundamental studies due to this particular morphological property.

Baseline observations for both minerals needed to coincide with accepted literature before findings with collector mixtures could be considered plausible. Galena is known to float well at pH 9, both without (cf. Figure 4.1.1a) and with (cf. Figure 4.1.1b) the addition of collector (Fuerstenau et al., 2007)



(a) Microflotation recovery of galena with no collector in distilled water as a function of pH. Copied from Kelebek and Yoruk (2002).



(b) Flotation recovery of galena as a function of pH with 1 x 10^{-5}mol/l ethyl xanthate. Copied from Fuerstenau (1982b).

Figure 4.1.1: Flotation behavior of galena

Flotation behaviour of pyrite has also been extensively studied, and is known to float at pH 9 with the addition of ethyl xanthate (cf. Figure 4.1.2).

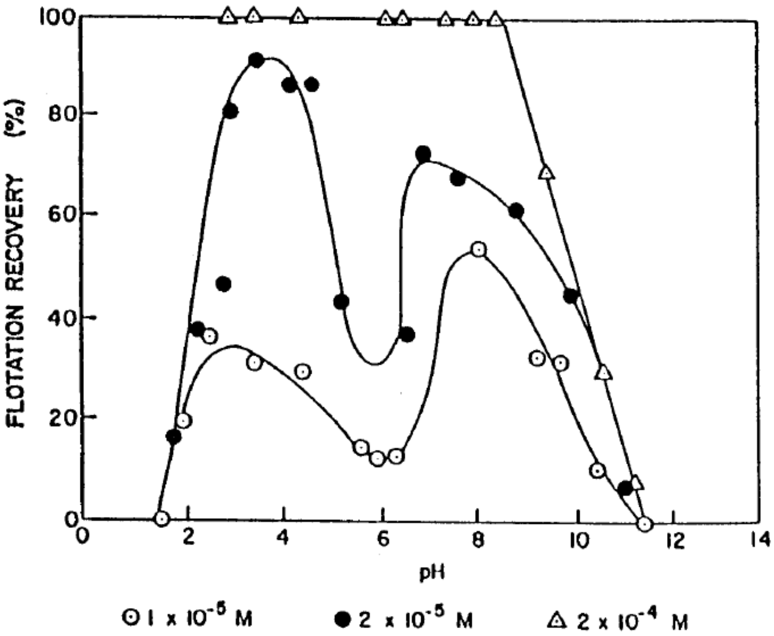


Figure 4.1.2: Recovery of pyrite as a function of flotation pH with various additions of potassium ethyl xanthate (Fuerstenau, 1982b).

Relating the findings of this thesis with those observed in Figures 4.1.1 and 4.1.2 must be done based only on trends. This is because when flotation results of either galena or pyrite are reported with ethyl xanthate concentrations given in mol/l, the reader has no indication of the surface coverage with collector or g/t dosage. This means that an excess of collector could be used to induce flotation almost independent of the conditions, with the exception of regions where the mineral is clearly depressed (e.g. pyrite at pH 12, cf. Figure 4.1.2). This is an original criticism pointed out by Crozier (1991) when discussing microflotation research.

The trends for both minerals as discussed in Section 1.5 are that at pH 9 both galena and pyrite were expected to float, with and without the addition of collector. This was the case in this thesis and is discussed in more detail further on.

The purpose of looking at different size fractions was because the three limiting regions (viz. fine, intermediate and coarse) are known to float differently (cf. Section 1.3.3). If changes in flotation behaviour were seen in a size class when changing collector conditions, then these could be related to the sub-process of flotation in the pulp phase.

Figure 1.3.3 outlines the basic relationship between hydrophobicity (and thereby implying surface coverage) and particle size in flotation. The larger the particle size is the more hydrophobic it will need to be in order to be floated successfully. There is a point of contention as to whether or not a collector would preferentially adsorb onto one size class above another, one of the views being that fine particles adsorb more collector than coarser particles due to their (the fines) higher specific surface free energy (J/m^2) (Trahar, 1981). The concept of active sites and distribution of their strength of activity is well known in fields of solid state chemistry such as catalysis. As mentioned in Section 1.3.3.2, Trahar (1981) contested this view because surface area estimation techniques using gas adsorption are not affected in this way. However there are many classical techniques to determine distribution of strength of sites such as NH_3- TPD (temperature programmed desorption), CO_2 – TPD, sorbent-IR-MS-TPD, etc. And these all illustrate that a solid surface consists of an energetically heterogeneous distribution of sites.

In this study it is assumed that the calculated dosages indicated, based on pseudo-monolayer surface coverage would result in each particle surface, regardless of size, being approximately 50% covered with collector molecules. It should be understood however that both minerals had about 50% of their material in the fine fraction (-38 μm) (cf. Table 2.3.1) which has two implications. Firstly most of the available surface area (and thus adsorption sites) were contained in this fraction, and secondly most collector would be adsorbed on this fraction because it also contains the most particles and thus the highest probability of collision between a particle and collector molecules. The latter point is an intuitive argument and will be used throughout this discussion when referring to the different strength of collectors and their likelihood of adsorbing onto one size class above another. On the other hand it should be noted that the smaller particles have lower momentum and thus have a potentially lower collision/attachment efficiency with a bubble.

Adding to the above discussion of assumptions in size class floatability, a study by Abreu and Skinner (2011) found that the distribution of contact angles (in the flotation feed) in three similar size classes to the ones used in this study (viz. coarse, intermediate and fine) were similar at a low collector coverage. It is assumed that in this thesis the 50% pseudo monolayer coverage of the mineral also represents a low collector coverage. This is plausible, because all collectors in the ethyl alkyl chain length group exhibited poor collecting action on both minerals at this coverage. The significance of this is that there would be a similar hydrophobicity across all three size classes, however as previously stated, based on Figure 1.3.4 the larger and very small particles require higher contact angles to float implying that there would be better flotation for the intermediate size class, followed by fine and then coarse particles.

4.1.2 Size class floatability

The collectorless recovery (at pH 9) of galena was observed to be 44.7%, with the fines fraction (-38 μm) making up 69.6% of the overall 44.7% mass recovery. The collectorless recovery (at pH = 9) of pyrite was observed to be 59.1%, with the fines fraction (-38 μm) making up 67.5% of the overall 59.1% mass recovery. The collectorless coarse fraction recovery was negligible for both minerals under these conditions. This observation lead to the proposition that the fine fraction was recovered mainly by entrainment, as fines are usually considered difficult to float and should act in a similar manner to the coarse fraction.

Poor fine fraction flotation is thought to be due to a low probability of collision with bubbles, and a tendency to skirt around the edges of bubbles instead of colliding with them (due to low momentum) (King, 1982). This proposition is further supported by the finding that in pulp phase sub-flotation processes (viz. collision, attachment and stability) entrainment increases with decreasing particle size (Neethling and Cilliers, 2009). This deduction is intuitive, as smaller particles have a lower mass and thus are affected less by the gravitational force acting on them and are more likely to be swept up with vortices created by the upward moving bubble stream.

This proposition of fines entrainment was further confirmed when, even additions of potassium amyl xanthate (which was observed to be the strongest collector for both minerals), did not significantly affect recovery of the fine fraction.

The intermediate size fraction responded positively to the addition of longer chain xanthates, such as SIBX, with an increase in recovery. Thus the flotation of this fraction was probably not due to entrainment. However, some of the intermediate fraction was recovered during collectorless flotation, which may indicate that there was entrainment, or simply that some of it was naturally hydrophobic and hence floatable.

A consistent finding for pure collector and collectorless results for both minerals was that the coarse fraction (-150 +75 μm) was less amenable to flotation in terms of both rate of flotation and solids recovery. This was in line with this fraction requiring the highest hydrophobicity to float (Pease et al., 2006; Crawford and Ralston, 1988; Trahar, 1981). The flotation of coarse particles is of key operational importance and hence careful attention was paid in this study to the effect of different reagents and mixtures thereof on coarse particle flotation.

4.1.3 A review of expected collector surface species on pyrite and galena

The dominant xanthate surface species on pyrite is thought to be dixanthogen (Buckley, 1994; Leppinen et al., 1989; Fuerstenau, 1982b; Finkelstein and Poling, 1977), with higher alkyl chain lengths being more easily oxidised to the dimer (Chander, 1999; Harris, 1988). However it should be understood that it is not only dimers that are formed and adsorbed onto pyrite, but rather a combination of chemisorbed xanthate ions or radicals and xanthate dimers (Nagaraj and Brinen, 2001). It should also be noted that iron-hydroxide is thought to be an intermediate in the formation of dixanthogen in the presence of pyrite (Harris, 1988). The reaction scheme is shown in equations 4.1.1 and 4.1.2.

$$2X^{-} \rightleftharpoons 2X_{ads} + 2e^{-} \tag{4.1.1}$$

$$2X_{ads} \qquad \underrightarrow{pyrite}\, as\, a\, catalyst \qquad X_2 \tag{4.1.2}$$

This is significant because at pH 9 ferrous (Fe^{2+}) hydroxy species ($FeOH_2$) are expected to be dominant on the pyrite surface (Leja, 2004).

Dithiophosphate species responsible for hydrophobicity on pyrite are also ascribed to the thiol dimer (Finkelstein and Goold, 1972), but above pH 6 the DTP dimer does not form on pyrite (Fuerstenau, 1982b), which meant that under the conditions used in this study the DTP dimer was not expected to be the surface species on either galena or pyrite. Nagaraj and Brinen (2001) found evidence of both the DTC dimer and a metal-thiol complex being present on the pyrite surface using SIMS. Their findings were, however, inconclusive.

Galena is not as easily oxidised as pyrite (Ralston, 1991) and thus less likely to promote the transfer of electrons required in the formation of a collector dimer. The dominant xanthate surface species has been found to be the chemisorbed xanthate ion (Kartio et al., 1999; Woods, 1994).

Stowe et al. (1995) found the DTP ion to be the dominant species on the galena surface by ToF-SIMS mapping of the surface. Reduction potentials for a galena-DTC (Finkelstein and Goold, 1972) system (cf. table 1.5.2) also suggest that the oxidation of DTC and DTP is not probable on galena and so the metal-thiolate (DTC-Galena) is thought to be responsible for galena's surface hydrophobicity.

4.1.4 Collector strength

The order of collector strength of the thiols used in this investigation has been reported to be dithiocarbamate > xanthate > dithiophosphate (Bagci et al., 2007; Bradshaw, 1997; Nagaraj, 1988). This is based on the chemical nature of the collector's binding centre (cf. Section 1.4.4). Although in this study heats of adsorption were not measured the sequence of ability to float the sulphides used did not match this order, as for both galena and pyrite and for both chain lengths (ethyl and isobutyl), dithiocarbamate was found to have no affect on their flotation performance when compared to the collectorless condition. A possible reason could be that DTC required higher dosages than xanthate and dithiophosphate to achieve similar results. This was not investigated.

It is of interest to see if there would be an increase in flotation performance of either mineral when mixing DTC and xanthate, because when in a mixture not only would there would be less xanthate than with a pure collector test, but DTC would not be expected to make much of a contribution, if their contributions to floatability were assumed to be additive. This would mean that if there were an increase in floatability of either mineral significantly greater than when using xanthate only, the increase could be considered to be synergistic.

Xanthate and DTP were found to have very similar behaviour in the case of both galena and pyrite for the ethyl alkyl chain length. This finding was expected since the contact angles were reported to be similar for both galena and pyrite contacted with the ethyl alkyl chain length of both collectors (Wark and Wark, 1932). They however also found di-ethyl DTC to have a similar contact angle, which suggests, it could float pyrite and galena under these conditions. It may however have been that the dosages used in this study and that of Wark and Wark (1932) for DTC are not comparable and so the contact angles across these two studies are not comparable in the case of DTC.

Di-ethyl DTP was, however, seen to float the pyrite coarse fraction significantly better than ethyl xanthate (cf. Figure 3.4.9d), which indicated that it produced a higher degree of hydrophobicity on coarse pyrite than ethyl xanthate. This observation was restricted to the coarse fraction since there was not a better overall flotation performance across all size fractions. However, the increase in flotation performance compared to using no collector was only slight, with very little coarse material responding to the presence of the ethyl alkyl chain lengths of collectors. The use of di-ethyl DTP also resulted in a higher rate of coarse fraction recovery when compared to ethyl xanthate. This may have been the result of DTP being reported as being the weakest adsorber of the three collectors (Nagaraj, 1988). As mentioned previously, most of the collector would be expected to be adsorbed onto the fine fraction, mainly due to these particles having most of the surface area and thus adsorption sites. It may be speculated that if it was the weakest collector it would adsorb more slowly than either DTC or xanthate onto the fine particles. Thus its concentration in the pulp would be relatively greater. This could allow it to have greater possibility of adsorbing onto coarser particles, resulting in better coarse particle flotation.

the relatively poor floatability of di-ethyl DTP observed here is consistent with Fuerstenau et al. (2007) (Figure 4.1.3) that both galena and pyrite would not float well with di-ethyl DTP at pH 9 or above. With regards to ethyl xanthate, it may also be the case that a 50% monolayer coverage is not sufficient to allow the short chain lengths to impart adequate hydrophobicity to the surface.

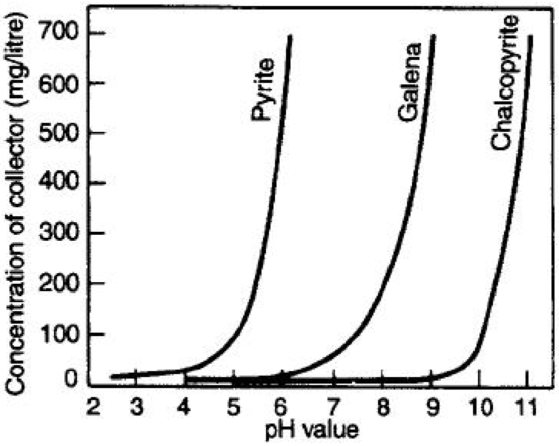


Figure 4.1.3: Critical contact curves for several sulphide minerals as a function of di-ethyl dithiophosphate concentration and pH. [Graph copied from Wills and Napier-Munn (2006)]

In the case of the isobutyl alkyl chain length xanthate and dithiophosphate behaviour differed between the minerals. As mentioned previously, isobutyl xanthate floated pyrite more strongly than it did galena. The same was true for di-isobutyl DTP with galena and pyrite, with the DTP having identical collecting power to SIBX on pyrite. However as mentioned earlier the DTP dimer is not expected to form in the presence of pyrite above pH 6 (Fuerstenau, 1982b) and so this result is unexpected because the dimer coated surface (X_2-Pyrite) is expected to float better due to its greater hydrophobicity (Finkelstein and Poling, 1977).

DTP is also known for its ability to reject pyrite in a basic medium (Fuerstenau et al., 2007; Mingione, 1984), but this observation was made in the presence of other sulphide minerals and cannot be extended to a situation where only the pyrite surface is presented to the DTP collector radical.

The almost identical overall flotation behaviour of ethyl xanthate and di-ethyl DTP on both pyrite and galena meant that their performance as mixtures across both minerals would highlight whether or not a synergistic effect is observed. In the case of SIBX it was not possible to judge the effects of mixtures since this collector already resulted in 100% recovery. Hence the rate of flotation was used as an indicator of the effect of using mixtures.

4.1.5 The effect of alkyl chain length

The aim of varying collector alkyl chain length was to establish a baseline from which to assess changes in floatability of both minerals when a collector mixture was used. As mentioned previously, higher chain lengths are known to have stronger collecting properties (Harris, 1988; Ackerman et al., 1987). The solubility of an isobutyl thiol was shown to be 10 times less than an ethyl thiol (Harris, 1988) and so increased floatability would be expected with higher chain lengths. As a particle coated with a higher chain length thiol would be less soluble (i.e. more hydrophobic) in water and thus more likely to attach to a bubble and be recovered.

The investigation of xanthate alkyl chain lengths was extended to normal butyl and amyl (normal pentyl) for both minerals. Higher chain lengths of all collectors did float both galena and pyrite better than their ethyl counter parts, as expected from the extensive literature on such systems. The amyl alkyl chain length of xanthate was observed to be superior to all other collector conditions. Thus the findings of this section were consistent with general literature i.e. the higher the molecular weight of the the alkyl chain length the better the flotation performance, thereby validating the methodology used in this thesis.

The main difference between galena and pyrite flotation when increasing xanthate chain lengths is that pyrite reached a flotation recovery maximum for the isobutyl and higher chain lengths even though the overall recovery was not 100%. Galena flotation, on the other hand, continued to increase in both rate and final recovery as the length of the alkyl chain increased. This seems to indicate a maximum floatability inherent in the pyrite sample. That is, there is a non-floating component present which is the residual which would not float even at the amyl chain length. This assumption is reinforced by the observation that the rates and recoveries for SIBX, PNBX and PAX are not exceeded for any collector conditions during this study. In general the trends seen with galena flotation were also observed in pyrite flotation.

In adding to the above considerations, the central assumption made here was that both minerals had an equal surface coverage of collector. This was validated to some extent in preliminary experiments (cf. Figure 2.6.1), where the same molar dosages on both minerals did not produce similar flotation results. However when pyrite was dosed with approximately 6 times the amount of xanthate compared to that used in the case of galena (which resulted in the same approximate surface coverage of the mineral surface with collector molecules because of the different specific surface areas of the minerals), did their flotation responses match. It was also noted that galena was recovered at a higher rate than pyrite with xanthates as the chain length increased. Attachment and collection efficiency are both functions of the density of the particles. On the one hand denser particles have a greater momentum which favours attachment. On the other hand such particles are subjected to greater gravitational forces which could increase the possibility of detachment. In the case of galena the former may well dominate i.e galena's significantly higher specific gravity (pyrite ≈5.1; galena ≈7.6) results in a greater momentum than pyrite, enhancing the probability for a successful collision with an air bubble and thus for attachment to occur. The first order rate calculated for each collector condition is an indication of the efficiency of particle collection (E_{coll}) as described by Equation 4.1.3:

$$E_{coll} = E_c \, E_a \, E_s \tag{4.1.3}$$

The three parameters in Equation 4.1.3 are: efficiency of particle-bubble collision (E_c), adhesion (E_a) and stability or detachment (E_s). As mentioned above, the increased specific gravity of a galena particle may however also negatively affect the stability of attachment, as the particles would now be more likely to detach due to increased load on the bubble.

The particle shape of galena is know to be more regular to that of pyrite (cf. Section 3.3) and so attachment of a cubic particle to a bubble may be more favoured than that of a rectangular and irregular particle of pyrite. It should be noted that the particle size distributions of galena and pyrite were seen to be similar (cf. Figure 3.2.1), making a comparison like this reasonable.

4.2 Thiol collector mixtures

The main focus of this thesis is to investigate changes in pulp phase hydrophobicity of the two sulphides studied. The assumption is that the bubble particle attachment tenacity as observed in a microflotation cell is a dynamic indicator of particle hydrophobicity. The hypothesis presented in the beginning of this thesis is given again below:

> Pulp phase floatability of a sulphide mineral is enhanced synergistically by the use of mixtures of both X:DTC and X:DTP. The reason for this is that each collector will have different characteristics of adsorption onto the mineral surface. This will result in a more extensive adsorption of collectors onto the surface which consists of a wide distribution of sites of different energies. This will cause a more evenly distributed collector coating which in turn will lead to increased particle hydrophobicity.

Keeping the theme of hydrophobicity in mind, the statement by Nagaraj and Ravishankar (2007) should be considered:

> “Flotation is a delicate balance between buoyancy and gravitational forces; any perturbation (chemical, physical, or operational) can tip the balance. Flotation outcome cannot be predicted exactly, but probabilities of the various sub-processes can be estimated, some better than others. More accurately, flotation is pseudo-probabilistic or pseudo-deterministic. Collector, modifier and frother work in concert.”

Two important points should be borne in mind during the discussion of the results on collector mixtures. The first is that changes (or lack thereof) in flotation rate and recovery of both galena and pyrite observed when using mixtures are an indication that there has indeed been a change in the surface hydrophobicity and thus buoyancy) as all other parameters remained constant.

The second point to consider is that, while changes in the pulp phase microflotation results may indicate increased performance, these have to be considered in the context that all flotation reagents "work in concert" and these might not follow through to real flotation systems. Bradshaw (1997), however, found that in that pulp phase, thermodynamic and adsorption observations were sustained in a batch flotation system when floating pyrite with mixtures of cyclo-hexyl DTC and PNBX.

It should also be appreciated that the literature available on thiol collector mixtures is limited and that the review by Bradshaw and O'Connor (2000) and Lotter and Bradshaw (2010) is used as the primary resource for discussing results.

4.2.1 Xanthate and Dithiophosphate mixtures

The first set of mixtures to be investigated were xanthate with dithiophosphate at both the ethyl and isobutyl alkyl chain lengths with 10:90 and 90:10 molar ratios. The mineral pulp was conditioned with xanthate first. The addition of dithiophosphate first and the simultaneous addition of both collectors were also investigated. The latter sequence of addition was only tested for galena. This would help in elucidating possible mechanisms responsible for increased hydrophobicity.

The distinctly different possibilities of collector surface species discussed previously on both galena and pyrite could help in formulating a mechanism responsible for the flotation behaviour observed in this thesis when using xanthate dithiophosphate mixtures.

The most significant increase in floatability beyond an additive effect (when using xanthate:DTP mixtures) was observed for a 10:90 ethyl xanthate : di-ethyl DTP mixture on galena (when xanthate was added first). The results are summarised in Table 4.2.1.

Table 4.2.1: Overall and sized mass recoveries (after 20 minutes) and first order rate constants of the 10:90 mixture of ethyl xanthate and di-ethyl DTP for different sequences of collector addition. [Galena; pH = 9]

Collector	**Mass recovery [%]**		
	Overall	-150 +75 (μm)	-75 +38 (μm)
SEDTP	51.6	11.8	47.4
SEX	52.5	14.4	48.9
10:90 (X first)	70.0	62.9	87.5
10:90 (DTP first)	54.3	19.6	61.1
First order rate constant (min^{-1}) x10^{-2}			
SEDTP	9.9	7.2	6.8
SEX	9.0	0.69	3.2
10:90 (X first)	10.7	7.2	9.7
10:90 (DTP first)	9.8	1.6	4.3

The significant increase in coarse fraction recovery with the use of the 10:90 ethyl xanthate : di-ethyl DTP mixture is an important finding. This is in light of an increasing demand for the ability to float coarser particles since this would generally result in energy savings in the comminution circuit. As expected, the coarse fraction does not exhibit large increases in rate, even when recoveries increase significantly (Muganda et al., 2011b). The intermediate fraction does, however, show an increase in rate when the 10:90 mixture is used.

The increased flotation performance of this collector mixture could possibly be attributed to two observations in literature, viz. Possible preferential DTP adsorption from the xanthate/DTP mixture (Wakamatsu and Numata, 1979) or greater coverage of both collectors on galena's surface (Plaskin and Zaitseva, 1960).

Preferential DTP adsorption could be discounted, because the experimental conditions were chosen to ensure that only a 50% pseudo monolayer coverage would be reached at total collector dosage and hence there would be an excess of adsorption sites remaining even after the mineral surface had been conditioned with both collectors. This is however also based on two assumptions, viz. that the area occupied by one DTC molecule (cf. Section 2.6.1) is a good estimate for all collectors used and that all the available surface area estimated by BET gas adsorption is suitable for collector adsorption. Preferential adsorption in any event, when using single mineral systems, will not correspond to a synergistic increase in recovery. It will simply float the mineral at the rate and recovery of that pure collector.

Lotter and Bradshaw (2010) proposed that a more even coverage of chemisorbed collector will to lead to increased hydrophobicity. Plaskin and Zaitseva (1960) have proposed that chemisorbed xanthate and dithiophosphate cover a galena surface more evenly. As mentioned in the previous section, oxidation of either xanthate or DTP in the presence of galena is unlikely (Finkelstein and Poling, 1977) and so under the conditions of this study they are assumed to chemisorb as thiols. The observed increase in floatability was most prominent in the coarse fraction.

An explanation for why a xanthate-DTP mixture should increase the hydrophobicity of galena particles may be due to the fact that xanthate is a stronger adsorber than dithiophosphate (Nagaraj, 1988). Hence when the mineral is conditioned with xanthate first and then DTP, it may follow that xanthate preferentially occupy free adsorption sites on fine particles first, which leaves more adsorption possibilities for the DTP on coarser particles. Combining this with the fact that DTP is a weaker adsorber (Nagaraj, 1988) it may be that its concentration in the aqueous phase will be greater with the consequence that it may have a greater chance of interacting with coarser particles. Recalling that with pure collector results di-ethyl DTP was seen to recover coarse particles at a faster rate than ethyl xanthate, this reasoning seems plausible, in that there may now be more DTP adsorbing onto coarse particles than in the case of the pure collector scenario.

The effect of changing the sequence of reagent addition was also tested, to see whether the addition of xanthate first, DTP first or both collectors simultaneously would change the flotation performance. It was found (cf. Section 3.6.1) that the 10:90 SEX:SEDTP mixture showed quite different results between the three sequences of addition (viz. X first, DTP first or simultaneous addition).

The 10:90 mixture resulted in the highest recovery of galena when xanthate was added first (cf. Table 4.2.1). When di-ethyl DTP was added first, the flotation performance was similar to using only di-ethyl DTP. The simultaneous addition of collectors resulted in a flotation performance of galena worse than using either pure collector. These first two results support the argument set out previously, which proposed that when xanthate is added first it to adsorbs onto the fine fraction thus leaving more DTP to adsorb onto the coarse fraction. This will improve the overall hydrophobicity by enhancing the adsorption of DTP onto sites unaffected by xanthate thus resulting in increased recovery. When the DTP was added first, it may have adsorbed onto fine instead of coarse particles. Because there are more fine particles in the pulp due to their higher volume percent in the feed, it may follow that no increased floatability would be observed. As discussed previously, it should also be noted that the fine fraction did not respond to addition of stronger xanthates (PAX) leading to the conclusion that these fine particles are mostly recovered by entrainment. Therefore, even if there was increased floatability due to a more even and favourable collector distribution on the fine fraction, it may not have been observable under these conditions.

In this part of the study two points that stand out very clearly. Firstly, no improvement in flotation is observed when an identical mixture (10:90 or 90:10 xanthate:DTP) of a higher chain length is used. This is discussed in more detail in subsequent sections. And secondly that pyrite did not exhibit the increases in flotation behaviour with the same mixture as was observed in the case of galena. There was a slight improvement in coarse particle recovery for the 10:90 mixture with pyrite, but again it was not as significant as with galena.

The second point may reinforce the theory of "collector specific sites" in that pyrite may have less of the "DTP specific" sites available and so is not subject to the same mechanisms which increased the flotability of galena under identical conditions. It also illustrates that collector mixture-mineral interactions may be mineral specific.

4.2.2 Xanthate and Dithiocarbamate mixtures

The experiments performed with dithiocarbamate and xanthate mixtures were identical to those in the previous section, where xanthate:dithiophosphate mixtures were investigated.

A marked increase in galena flotation performance was seen for ethyl xanthate with di-ethyl DTC mixtures at the 10:90 and 90:10 conditions (cf Table 4.2.2 and 4.2.3). The increases were not as significant with pyrite, although the trends in increased recovery of the coarse and intermediate fraction recoveries were the same as those with galena. This was also the case with xanthate:dithiophosphate mixtures, further supporting the proposition that pyrite was not as amenable to flotation as galena.

Table 4.2.2: Increases in overall final (after 20 minutes) recovery and recovery by size class from using ethyl xanthate only. [Galena; pH = 9; total dosage = 3.8x10^{-7}moles/g]

Galena (PbS)	**10:90 SEX:SEDTC**	**90:10 SEX:SEDTC**
Increase in final recovery from using SEX only		
Overall	12%	30%
-150 +75 (μm)	26%	77%
-75 +38 (μm)	32%	51%

Table 4.2.3: Comparison of first order rates between the 10:90 and 90:10 ethyl xanthate : di-ethyl DTC mixtures and ethyl xanthate only. [Galena; pH = 9; total dosage = 3.8x10^{-7}moles/g]

Galena (PbS)	**SEX only**	**10:90 SEX:SEDTC**	**90:10 SEX:SEDTC**
First order rate constant (min^{-1}) x10^{-2}			
Overall	9.0	8.3	24.8
-150 +75 (μm)	0.69	2.4	40.1
-75 +38 (μm)	3.2	7.2	37.1

The means by which this large increase in hydrophobicity of galena is postulated to occur is through the formation of thiol dimers, which would not normally occur using pure collectors (Finkelstein and Poling, 1977). As discussed previously, the chemisorbed thiol of either DTP, DTC or xanthate is expected to be the dominant surface species for galena at pH 9. It is proposed that a DTC/surface catalysed reaction occurs in which the xanthate is oxidised to dixanthogen, thereby creating a more hydrophobic surface coverage. This is similar to the theory put forward by Lotter and Bradshaw (2010) in which they proposed the DTC-catalysed oxidation of xanthate to its dimer. Those authors did not propose the exact mechanism by which the reaction is proposed to occur. The determination of the exact nature of the surface species remains elusive. Bradshaw (1997) proposed that chemisorbed thiols such as DTC, which tend to adsorb more evenly on the minerals surface (Woods, 1994), will act as anchor sites to which the dixanthogen may attach. The dimer tends to weakly physisorb onto the mineral surface (Nagaraj and Ravishankar, 2007) and so may not adsorb as evenly as the chemisorbing monomer. Thus such an anchor site may provide the opportunity to adsorb more evenly.

The anchor site theory is plausible as it is important to understand that a thiol dimer is expected to be significantly more hydrophobic than its monomer contemporary. This is thought to be because the O-C-S2-S2-C-O [binding centre of the dithiolate] group has a free energy of solution of about 15 kJ/mol, compared to a -CH3 group of about 8.8 kJ/mol or a CH2 group of about 3.7 kJ/mol (Woods, 1988). This indicates that the dimer sulphydryl group will tend to repel quite readily from water molecules due to its highly hydrophobic nature along with its two alkyl chain lengths. Rotation of the molecule about the S-S bond is possible to minimise interactions of alkyl groups with water molecules (Clayden et al., 2001; Woods, 1988). Thus is can be concluded that a dimer molecule will tend to interact with alkyl chains from chemisorbed species to minimise interaction with water molecules.

The lack of increased hydrophobicity with mixtures of increased chain length compared to using SIBX only could be ascribed to the possibility that once a certain degree of hydrophobicity is observed, any further increases will not produce significantly better flotation. That is, the mineral has already achieved maximum floatability with SIBX.

The argument that DTC needs to act as a catalyst at all, is strongly supported by the observation that when DTC was allowed to contact with the mineral first, the flotation behaviour of the 90:10 (SEX:SEDTC) was not significantly better than either pure collector result (cf. Section 3.6.2). This sequence of collector addition may have resulted in all the available DTC having been adsorbed onto the fine fraction before the xanthate was added and therefore did not have the opportunity to act as a catalyst in the dimer formation of xanthate. DTC is considered to be the strongest adsorber of the three collectors used (Nagaraj, 1988) and so its complete adsorption in the prescribed conditioning time (i.e. 6 minutes) is plausible.

4.2.2.1 Ratio of collectors

An observation which should be noted was that when adding the stronger collector to a greater concentration of the weaker collector (viz. 10:90 SEX:SEDTP and 90:10 SEX:SEDTC), the greatest increase in recovery was observed. This may have indicated that the stronger adsorbing collector would occupy adsorption sites on finer particles (as discussed previously) for two reasons. Firstly, a stronger collector would adsorb faster and thus its highest likelihood of interaction would be with a fine particle due to the greater surface area and the greater number of particles. Secondly, finer particles probably have a greater concentration of high energy sites due to the comminution process requiring higher energies to reduce them to that size (Trahar, 1981). This may have allowed the weaker adsorbing collector more likelihood of interacting with coarser particles, as less fine particle sites are now available.

4.2.3 Cases of observed minimal improved performance

Lesser improvements in recovery were observed for all mixtures tested with pyrite, while the trends were generally the same. In addition, SIBX was always seen to be the superior collector, including flotation with galena. This was especially evident when di-isobutyl DTC was in a mixture with SIBX. There was a linear increase in recovery when the SIBX fraction in the mixture increased (cf. Figure 3.5.9). This observation was more pronounced with pyrite than with galena, but not unexpected so since di-isobutyl DTC did not greatly affect the flotation behaviour of either mineral.

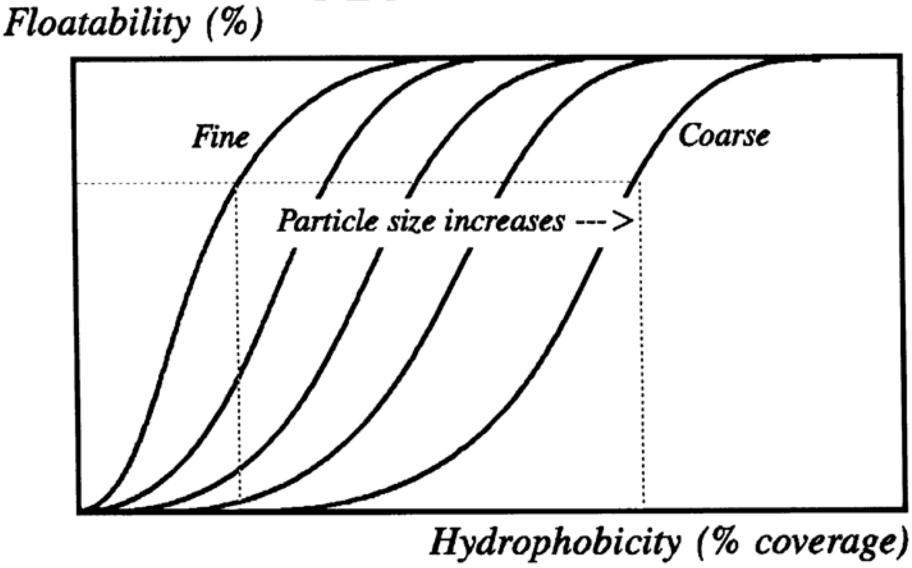


Figure 4.2.1: Qualitative representation of the influence of particle size on the relationship between floatability and hydrophobicity. Copied from Trahar (1981)

The hydrophobicity required to float a particular size class as seen in Figure 4.2.1 may reach an equilibrium point at the upper part of the curve where increasing floatability does not significantly improve with increasing hydrophobicity. It could be proposed that the arguments that resulted in an increase in hydrophobicity with both ethyl X:DTP and X:DTC mixtures on galena could also have occurred with the isobutyl mixtures. This could be reasonable if the hydrophobicity which the single ethyl collectors imparted on galena was on the lower end of the curve (low hydrophobicity and floatability) while the hydrophobicity imparted by the single isobutyl collectors was on the higher end of the curve. This may well have been the case because the coarse recovery for single ethyl collectors on both galena and pyrite was relatively poor compared to the intermediate fraction.

Pyrite floatability did not increase as significantly as was observed in the case of galena when using mixtures. As mentioned previously dixanthogen is expected to be the dominant surface species on pyrite when xanthate is the collector. Xanthate was added first and so the physisorbing dimers which were given the opportunity to adsorb first are weakly held to the mineral surface (Nagaraj and Ravishankar, 2007). These may block adsorption sites due to their conformation which tends to expose as little of itself to water molecules as possible.

As mentioned previously, pyrite and galena had different morphologies (cf. Section 3.3). Galena has a more cubic and regular shape than pyrite. The increased irregularity of the pyrite particle surface may be the reason why it was found to have BET surface area about 6 times higher than that of galena for a similar particle size distribution. Muganda et al. (2011a) found that even though two minerals (chalcopyrite and pyrite) were found to have similar contact angle distributions of size classes within the flotation feed (and thus hydrophobicity), their flotation response was markedly different. They attributed this to differences in specific gravity of the minerals and because of this they attributed the minerals with different critical contact angles. If this reasoning is extended to the present study, it can be assumed that galena would have required a higher critical contact angle than pyrite to float similarly, because of its significantly higher specific gravity (pyrite ≈5.1; galena ≈7.6). There are two arguments that can be put forward for the observed difference in flotation between pyrite and galena.

Firstly, pyrite did not float as well as galena with the use of certain mixtures due to its surface chemistry not resulting in a better distribution of reagents from that occurring when using single collectors. This may have been due to pyrite not having as many "DTP specific sites" as galena when SEX:SEDTP mixtures were used.

Secondly, the irregular shape of pyrite may result in less stability of attachment (E_s) as well as less adhesion (E_a) compared to the more regularly shaped galena particles.

In either case these arguments further support the proposition that galena flotation was enhanced due to a significant increase in hydrophobicity resulting from a better distribution of collectors on the mineral surface.

4.3 Preliminary batch flotation

All of the above investigations were carried out in the pulp phase. However as is well known arguably the most important phase in the flotation system is the froth phase. In order to determine whether the observations made in the present study were sustained when a froth was present a set of preliminary investigations were carried out using a standard batch flotation cell. To that end batch flotation of a synthetic ore made up by mass of galena (5%), a plagioclase-rich ore (47.5%) and a pyroxene-rich ore (47.5%) was carried out to see whether observations made in the pulp phase (microflotation) would be sustained when a froth phase was present. The latter two minerals constituted the gangue portion of the ore. The dosage was kept constant to ensure an equivalent 50% pseudo monolayer of galena only. It was assumed that the collectors would not adsorb onto the gangue minerals.

The collector mixture chosen was the 90:10 SEX:SEDTC condition, as it had shown the greatest increase in galena floatability from using either pure collector (cf. Table 4.2.2). The pure collectors and collectorless condition were also tested as baseline cases. The batch flotation results are summarised in Table 4.3.1 for convenience.

Table 4.3.1: Comparison of batch flotation results [pH = 9, total collector dosage = 5.9x10^{-7} moles collector / g of galena; 1 kg of synthetic ore made up by mass of 5% galena, 47.5 % plagioclase rich ore and 47.5% pyroxene rich ore].

Parameter	Collectorless	SEDTC	SEX	90:10 SEX:SEDTC
Final solids recovery	1.7 %	2.09 %	3.69 %	3.98 %
Final Pb recovery	24.9 %	33.5 %	62.7 %	68.0 %
Final Water recovery	80.9 g	78.9 g	48.6 g	84.5 g
Pb first order rate constant (min^{-1}) x10^{-2}	9.8	14.2	20.2	26.2

The use of di-ethyl DTC did not result in marked increases in solids, Pb or water recovery from that of using no collector. The finding that the solids and Pb recovery did not increase significantly from the collectorless condition were consistent with microflotation studies done on galena, where DTC did not significantly increase the pulp phase floatability of galena compared to the collectorless condition. The observation that the water recovery did not increase significantly from using no collector indicated that di-ethyl DTC did not have any significant influence on the froth zone under these conditions. In summary it is clear that di-ethyl DTC did not display strong collecting abilities in microflotation or batch flotation. The lack of influence on the froth phase with the use of di-ethyl DTC is not unexpected because only higher alkyl chain lengths are known to affect the froth phase as is the case with DTP (Mingione, 1984).

Water recovery is taken as the measure of froth stability, where a high water recovery points towards a stabilised froth and a low water recovery points to a destabilised froth and thus low mass pull (Wiese et al., 2010). SEX did show marked increases in Pb recovery when compared to the collectorless condition and at a significantly lower water recovery as well. The lower water recovery indicated a lowered froth activity with the use of SEX.

The 90:10 mixture recovered more Pb, solids and water than any other condition. The significant increase in water recovery when using the mixture compared to the use of SEX only, where a similar solids recovery had been observed, indicated that the distribution of reagents on the mineral surface when using the 90:10 mixture was significantly different to that of using SEX only. According to Ata et al. (2004), more hydrophobic particles result in a decrease in water recovery and thus a stabilised froth, this would mean that the use of SEX only resulted in a more hydrophobic surface than that of using the 90:10 SEX:SEDTC mixture. Tao et al. (2000) however states that there is much controversy about the degree of hydrophobicity which would stabilise or destabilise the froth. In either case a change in hydrophobicity would have occurred with the use of the 90:10 mixture which resulted in increased, Pb, solids and water recovery.

4.4 Summarising remarks

Most studies reported in the literature pertaining to the effect of using mixed collector systems have included the froth phase. The present study however focused on the pulp phase phenomenon but appreciated the huge importance that the froth phase has on flotation performance. More specifically these observations pertain to the use of X:DTP (Adkins and Pearse, 1992; Mingione, 1984; Plaskin et al., 1954) and X:DTC mixtures (Bradshaw, 1997; Jiwu et al., 1984; Falvey, 1969). Dithiophosphates have been known to have frothing properties at higher chain lengths (Mingione, 1984), with frother requirements having been minimised in copper flotation circuits with the use of di-isobutyl DTP (Nagaraj and Ravishankar, 2007).

The marked increase in pulp phase floatability of galena when using a 90:10 SEX:SEDTC mixture was sustained when a froth phase was added, by means of batch flotation tests. The use of this mixture had a froth stabilisation effect and thus this may have contributed to the higher solids and Pb recoveries than the use of SEX only. It is however appreciated that the conditions under which microflotation and batch flotation occur, are significantly different and so observations made in one device may not be sustained in the other.

It may have been possible that isobutyl mixtures had less scope for improvement in flotation from that of using single collectors. Because SIBX on its own had already resulted in good floatation of both pyrite and galena when compared to the poor floatability of its ethyl counterpart under the same conditions.

It is thus possible that using ethyl mixtures may induce selective hydrophobicity on one sulphide mineral relative to another.

At first glance it seems that there can be no plausible reason for using a thiol mixture since SIBX was shown to be a superior collector of both galena and pyrite compared to SEX. There is however one significant result that could be useful in separation of galena and pyrite. The 90:10 SEX: SEDTC mixture resulted in flotation of galena similar to that of using SIBX. This may present an opportunity to selectively separate galena from pyrite.

Another positive side of this application would be that the 90:10 mixture is economically viable, as xanthate is the major constituent in the mixture. In addition, the mixture ratio was not tested for a metallurgical optimum result, which means there could be a mixture with even less DTC (and thus less cost) which gives a similar result.

All of this indicates that synergism is more complex than just increasing hydrophobicity or acting on the froth phase. Different chain lengths could possibly have different effects on the different sub-processes of flotation and thus different size classes.

Understanding the use of collectors and remaining within the application of such findings one is reminded of the statement by Nagaraj (2005):

> “The process of reagent selection and optimisation in base metal sulphide flotation as practised today is rather informal and reductionist on the part of both reagent manufacturers and plant metallurgists... If the objective is to develop a robust solution to a problem or challenge in the plant, and to increase value or profitability in the operation, a holistic or total system approach is necessary.”

Chapter 5

Conclusions

Microflotation performances of two of the most widely studied sulphide minerals viz. pyrite and galena were assessed using pure collectors or mixtures of either xanthate with di-alkyl dithiophosphate (DTP) or xanthate with di-alkyl dithiocarbamate (DTC). Both minerals were found to be mineralogically pure using XRD. All tests were carried out at pH 9 to simulate the natural pH commonly found on concentrators.

Tests were conducted using all three collectors, whether in mixtures or pure, with the ethyl and isobutyl alkyl chain length. Molar dosage used was determined using the BET surface area of each mineral and kept constant throughout all tests. The dosage was designed to be equivalent to a 50% pseudo monolayer coverage of the mineral surface area based on the cross sectional footprint area of a DTC anion.

Pure collector tests established a baseline against which to assess the performance of mixtures. Galena and pyrite exhibited very poor collectorless flotation in the coarse fraction (-150 +75μm). The intermediate fraction (-75 +38μm) had better recoveries than the coarse fraction. The fine fraction (-38μm) was probably recovered mostly by entrainment as it did not respond to any changes in collector conditions and entrainment is independent of the surface properties of particles. The coarse fraction was found to be the relatively least amenable to flotation throughout this study, which was to be expected as it requires the most hydrophobicity to float.

The order of single collector strength was found to be similar for both minerals. The order of collector strength was xanthate > dithiophosphate > dithiocarbamate. The latter collector was expected to be the strongest according to literature but was found to have no collecting properties under the conditions used in this thesis. The second significant result was that as alkyl chain length increased so did the collector performance. This result is consistent with the reported literature and hence these results were validated.

Ethyl alkyl chain lengths of xanthate and DTP were found to have very similar performance. This was observed on both minerals. SEX and SEDTP gave poor recoveries of the coarse size fraction of both the minerals. The isobutyl alkyl chain length of xanthate was observed to be the stronger collector. However on pyrite SIBX performed only slightly better than di-isobutyl DTP.

Pyrite was found to be less amenable to flotation than galena and the higher chain length xanthates were found to recover galena at significantly higher rates than pyrite. This trend was also observed for mixtures of collectors. The observed differences may be attributed to the effect of particle shape and/or density differences between the two minerals which would affect the efficiency of collection and thus recovery.

Ethyl alkyl chain length mixtures increased the recovery of galena. This increase was greater than the expected *pro rata* contributions of the mixture's constituents. 10:90 ethyl xanthate: di-ethyl DTP mixtures improved the flotation rate and recovery of galena. With most of this improved recovery being in the coarse fraction.

90:10 and 10:90 mixtures of ethyl xanthate:di-ethyl DTC gave improved overall recoveries of especially the coarse fraction. In similar studies when mixtures are shown to have a much greater effect than the additive effect each collector this has been ascribed to a range of particle sizes. The observed improvements in flotation performance may be attributed to a more favourable distribution of reagents in the mineral surface.

Two different explanations are proposed to interpret the synergistic improvements in flotation in the xanthate:DTP and in the xanthate:DTC mixtures. Minerals are proposed to have "thiol-specific" sites available for the adsorption of collector. These are sites where the energy and/or conformation of the site is the most favourable for collector adsorption. Thus, a mixture of xanthate and DTP may result in a larger and more uniform distribution of reagents on the mineral surface.

In the case of xanthate:DTC mixtures, this proposed mechanism may still hold. However, the overriding mechanism by which synergism may be achieved could be through the DTC/surface-catalysed formation of highly hydrophobic dixanthogens.

The sequence of collector addition only affected the three cases mentioned previously (viz. 10:90 SEX:SEDTP; 10:90 and 90:10 SEX:SEDTC; all for galena). It was found that the simultaneous addition of collectors resulted in flotation performance poorer than that of using either pure collector. The addition of xanthate first resulted in the best flotation performance of the three mixtures mentioned previously. The addition of either DTP or DTC first to a mixture resulted in a flotation performance similar to that of using either single collector. These results supported the proposal that the observed increases in floatability may result from a more homogeneous distribution of reagents on the mineral surface when these mixtures were used.

The use of collector mixtures with pyrite was not as pronounced as with galena.

Isobutyl collector mixtures did not improve the flotation of either galena or pyrite relative to pure SIBX, which was observed to be the strongest collector. When SIBX:SIBDTC mixtures were used flotation was seen to increase with increasing SIBX content in the mixture. This increase was observed to be linearly additive for both minerals and indicated that a *pro rata* contribution to hydrophobicity occurred. The same was true for SIBX:SIBDTP mixtures. It is possible previously observed synergistic increases in flotation as reported in literature with mixtures at the higher chain lengths, may have been due to froth phase effects.

The use of certain mixtures increased the pulp phase flotability of galena and, these observations were sustained when carried out using a batch flotation cell with an artificial ore.

The marked increase in coarse fraction flotation with mixtures of collectors is a significant finding because of the increasing importance of coarse particle flotation on modern concentrators where the focus is often on minimising energy consumption and hence fines production.

There is also potential in using well established reagents in mixtures when they are able to selectively render the surface of one sulphide more hydrophobic than another. While this selectivity has been achieved by using single collectors such as DTP (Nagaraj and Ravishankar, 2007; Mingione, 1984) to reject pyrite in the presence of copper ores, it has not been demonstrated for galena. Thus the increases in recovery of galena and not pyrite under the same conditions, may provide an opportunity for selective separation of these minerals. It is however appreciated that these effects may be confounded when a real ore is used.

5.1 Recommendations for future work

While improvements in pulp phase floatability indicate increased particle hydrophobicity, it cannot be assumed that these will always result in observable improvements when a froth phase is present. There is great potential in using existing and well established reagents to achieve better metallurgical results, instead of developing a new set of collectors. Recommendations for future test work to further and expand on findings in this thesis are given below:

- The present study focused on the pulp phase behaviour. In the context of the research results reported in this thesis it is recommended that further insights would be gained in a batch or column cell where a frother is present.
- Surface analytical techniques which are able to determine the nature of the surface sites is of key importance in seeking explanations for the observations made in this study.
- ToF-SIMS should be used to identify surface products and reagent distribution of a statistically representative sample of the mineral surface when using collector mixtures. This needs to be done together with work identifying surface activity when: no collector is used, 10% or 90% of collector A is added alone; 10% or 90% of collector B is added alone and this would help to identify how evenly collectors adsorb alone and whether there are changes in surface activity when using different sequences of addition or molar ratios of mixtures.

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Appendices

Appendix A

Microflotation of galena

Flotation of galena			First order parameters	
Collector	**Overall recovery**	**SD (%)**	**Rmax (%)**	**Rate (min^{-1})**
Xanthate				
SEX	52.5%	1.2%	62.9	0.0899
SIBX	86.0%	1.2%	86.0	0.1981
PNBX	91.9%	0.1%	91.9	0.2717
PAX	93.6%	0.0%	93.6	0.4579
Dithiophosphate				
DTP-E	51.6%	0.7%	60.2	0.0990
DTP-IB	72.0%	1.6%	73.7	0.1624
Dithiocarbamate				
DTC-E	48.3%	0.6%	60.3	0.0831
DTC-IB	50.1%	0.9%	63.3	0.0795
collectorless pH 9	44.7%	0.6%	60.1	0.0687
Xanthate and Dithiophosphate mixtures				
Simultaneous addition				
90-10 ethyl	67.6%	8.1%	76.0	0.1097
10-90 ethyl	47.8%	0.8%	61.4	0.0772
90-10 Iso-Butyl	89.8%	1.3%	89.8	0.2697
10-90 Iso-Butyl	74.6%	0.3%	76.4	0.1612
Xanthate first				
90-10 ethyl	60.7%	8.5%	65.5	0.1253
10-90 ethyl	70.0%	4.3%	79.1	0.1067
90-10 Iso-Butyl	76.6%	0.5%	76.6	0.1850
10-90 Iso-Butyl	76.7%	1.2%	76.7	0.1972
Dithiophosphate first				
90-10 ethyl	65.6%	0.8%	74.6	0.1045
10-90 ethyl	54.3%	1.4%	62.9	0.0976
90-10 Iso-Butyl	76.6%	6.7%	76.6	0.2323
10-90 Iso-Butyl	78.5%	1.8%	78.7	0.1778
Xanthate and Dithiocarbamate mixtures				
Simultaneous addition				
90-10 ethyl	47.0%	0.2%	58.92	0.0819
10-90 ethyl	48.7%	2.4%	67.79	0.0643
90-10 Iso-Butyl	73.3%	3.0%	73.74	0.1743
10-90 Iso-Butyl	50.5%	1.8%	62.82	0.0829
Xanthate first				
90-10 ethyl	82.0%	2.0%	82.20	0.2481
10-90 ethyl	64.7%	2.4%	79.98	0.0831
90-10 Iso-Butyl	71.9%	7.1%	71.91	0.2092
10-90 Iso-Butyl	57.5%	1.0%	75.06	0.0732
Dithiocarbamate first				
90-10 ethyl	60.5%	3.5%	74.01	0.0856
10-90 ethyl	61.0%	3.4%	73.84	0.0870
90-10 Iso-Butyl	91.0%	0.7%	90.96	0.4099
10-90 Iso-Butyl	55.4%	0.4%	68.10	0.0841

	Final solids recovery [%]		
Collector	**Fines (-38 µm)**	**Intermediate (-75 +38 µm)**	**Coarse (-150 +75 µm)**
Xanthate			
SEX	75.8	48.8	14.4
SIBX	71.3	100.0	90.1
PNBX	65.9	100.0	100.0
PAX	70.3	100.0	100.0
Dithiophosphate			
DTP-E	76.0	47.3	11.8
DTP-IB	76.9	89.1	44.0
Dithiocarbamate			
DTC-E	77.0	38.0	4.6
DTC-IB	77.9	42.2	5.2
		7.3	5.6
collectorless pH 9	65.2	41.1	8.8
Xanthate and Dithiophosphate mixtures			
Simultaneous addition			
90-10 ethyl	72.6	83.2	40.7
10-90 ethyl	76.2	39.5	2.5
90-10 Iso-Butyl	68.6	100.0	100.0
10-90 Iso-Butyl	72.9	97.5	52.8
Xanthate first			
90-10 ethyl	71.7	68.3	31.1
10-90 ethyl	63.7	87.5	62.9
90-10 Iso-Butyl	63.5	94.1	82.6
10-90 Iso-Butyl	70.7	98.9	64.2
Dithiophosphate first			
90-10 ethyl	74.9	77.9	33.5
10-90 ethyl	68.4	61.1	19.6
90-10 Iso-Butyl	80.3	100.0	78.5
10-90 Iso-Butyl	76.3	100.0	58.7
Xanthate and Dithiocarbamate mixtures			
Simultaneous addition			
90-10 ethyl	71.1	44.0	3.9
10-90 ethyl	75.5	41.0	5.9
90-10 Iso-Butyl	71.1	93.6	55.3
10-90 Iso-Butyl	77.6	43.4	6.1
Xanthate first			
90-10 ethyl	69.0	100.0	91.1
10-90 ethyl	68.4	80.3	40.1
90-10 Iso-Butyl	66.0	100.0	91.2
10-90 Iso-Butyl	74.8	64.8	16.0
Dithiocarbamate first			
90-10 ethyl	71.2	74.3	24.4
10-90 ethyl	82.2	65.7	14.5
90-10 Iso-Butyl	72.0	100.0	100.0
10-90 Iso-Butyl	77.0	57.5	11.2

	-38 µm		-75 +38 µm		-150 +75 µm	
Collector	**Rmax**	**Rate (min^{-1})**	**Rmax**	**Rate (min^{-1})**	**Rmax**	**Rate (min^{-1})**
Xanthate						
SEX	83.0	0.1291	100.0	0.0319	100.0	0.0070
SIBX	72.5	0.2117	100.0	0.2505	90.1	0.1572
PNBX	67.2	0.2386	100.0	0.4260	100.0	0.4472
PAX	71.2	0.2922	100.0	0.7152	100.0	1.3930
Dithiophosphate						
DTP-E	84.5	0.1219	86.8	0.0396	12.4	0.1231
DTP-IB	78.9	0.1865	94.8	0.1264	44.0	0.1541
Dithiocarbamate						
DTC-E	89.6	0.1039	100.0	0.0234	5.8	0.0694
DTC-IB	90.2	0.1039	100.0	0.0263	10.8	0.0314
collectorless pH 9	77.5	0.0948	100.0	0.0252	16.0	0.0380
Xanthate and Dithiophosphate mixtures						
Simultaneous addition						
90-10 ethyl	78.5	0.1399	100.0	0.0857	57.0	0.0597
10-90 ethyl	89.3	0.1009	100.0	0.0241	100.0	0.0012
90-10 Iso-Butyl	70.8	0.2008	100.0	0.3956	100.0	0.4614
10-90 Iso-Butyl	76.7	0.1594	99.7	0.1491	52.8	0.1753
Xanthate first						
90-10 ethyl	77.1	0.1387	82.7	0.0840	31.1	0.1607
10-90 ethyl	68.5	0.1409	100.0	0.0968	81.0	0.0723
90-10 Iso-Butyl	66.9	0.1620	94.1	0.1811	82.6	0.1988
10-90 Iso-Butyl	71.7	0.2094	98.9	0.1791	64.2	0.1880
Dithiophosphate first						
90-10 ethyl	78.7	0.1666	100.0	0.0660	88.5	0.0235
10-90 ethyl	72.4	0.1527	100.0	0.0432	72.5	0.0155
90-10 Iso-Butyl	80.5	0.2338	100.0	0.3449	78.5	0.4291
10-90 Iso-Butyl	77.2	0.20473	100.0	0.15478	58.7	0.156
Xanthate and Dithiocarbamate mixtures						
Simultaneous addition						
90-10 ethyl	81.9	0.0927	100.0	0.0247	6.7	0.0398
10-90 ethyl	95.5	0.0812	100.0	0.0251	6.1	0.1161
90-10 Iso-Butyl	73.9	0.1641	93.6	0.1656	55.3	0.1943
10-90 Iso-Butyl	90.0	0.1037	100.0	0.0277	6.2	0.1381
Xanthate first						
90-10 ethyl	69.7	0.2352	100.0	0.3706	91.1	0.4006
10-90 ethyl	74.0	0.1358	100.0	0.0715	100.0	0.0244
90-10 Iso-Butyl	67.0	0.2532	100.0	0.3238	91.2	0.3357
10-90 Iso-Butyl	82.3	0.1273	100.0	0.0444	100.0	0.0079
Dithiocarbamate first						
90-10 ethyl	76.5	0.1464	100.0	0.0588	100.0	0.0128
10-90 ethyl	88.9	0.1354	100.0	0.0464	100.0	0.0075
90-10 Iso-Butyl	73.3	0.2687	100.0	0.6167	100.0	0.8907
10-90 Iso-Butyl	84.0	0.1322	100.0	0.0378	100.0	0.0054

Mass balance

Collector	-150 +75 µm	-75 +38 µm	-38 µm	Recovery	difference
Xanthate	Final recovery (mass in grams)				
SEX	0.1058	0.4075	1.0853	53.3%	0.80%
SIBX	0.6625	0.8340	1.0209	83.9%	2.1%
PNBX	0.7350	0.8340	0.9434	83.7%	8.1%
PAX	0.7350	0.8340	1.0062	85.8%	7.7%
Dithiophosphate					
DTP-E	0.0869	0.3951	1.0882	52.3%	0.69%
DTP-IB	0.3235	0.7430	1.0998	72.2%	0.3%
Dithiocarbamate					
DTC-E	0.0337	0.3166	1.1020	48.4%	0.1%
DTC-IB	0.0383	0.3518	1.1147	50.2%	0.1%
collectorless pH 9	0.0643	0.3428	0.9335	44.7%	0.05%
Xanthate and Dithiophosphate mixtures					
Simultaneous addition					
90-10 ethyl	0.2991	0.6942	1.0390	67.7%	0.11%
10-90 ethyl	0.0186	0.3297	1.0904	48.0%	0.12%
90-10 Iso-Butyl	0.7350	0.8340	0.9816	85.0%	4.75%
10-90 Iso-Butyl	0.3878	0.8131	1.0426	74.8%	0.15%
Xanthate first					
90-10 ethyl	0.2285	0.5694	1.0255	60.8%	0.13%
10-90 ethyl	0.4663	0.7710	1.0289	75.5%	0.10%
90-10 Iso-Butyl	0.6073	0.7847	0.9084	76.7%	0.03%
10-90 Iso-Butyl	0.4719	0.8248	1.0118	77.0%	0.24%
Dithiophosphate first					
90-10 ethyl	0.2462	0.6496	1.0720	65.6%	0.03%
10-90 ethyl	0.1441	0.5094	0.9792	54.4%	0.12%
90-10 Iso-Butyl	0.5770	0.8340	1.1494	85.3%	8.74%
10-90 Iso-Butyl	0.4317	0.8336	1.0919	78.6%	0.11%
Xanthate and Dithiocarbamate mixtures					
Simultaneous addition					
90-10 ethyl	0.0287	0.3670	1.0174	47.1%	0.1%
10-90 ethyl	0.0433	0.3419	1.0799	48.8%	0.1%
90-10 Iso-Butyl	0.4062	0.7807	1.0170	73.5%	0.1%
10-90 Iso-Butyl	0.0449	0.3616	1.1107	50.6%	0.1%
Xanthate first					
90-10 ethyl	0.6661	0.8340	0.9248	80.8%	11.3%
10-90 ethyl	0.2162	0.6383	1.0941	65.0%	0.1%
90-10 Iso-Butyl	0.6706	0.8340	0.9446	81.6%	9.7%
10-90 Iso-Butyl	0.1179	0.5403	1.0710	57.6%	0.1%
Dithiocarbamate first					
90-10 ethyl	0.1791	0.6196	1.0184	60.6%	0.1%
10-90 ethyl	0.1068	0.5479	1.1770	61.1%	0.1%
90-10 Iso-Butyl	0.7350	0.8340	1.0300	86.6%	4.3%
10-90 Iso-Butyl	0.0820	0.4797	1.1018	55.5%	0.1%

Microflotation of pyrite

Flotation of pyrite			First order parameters	
Collector	**Overall recovery**	**SD (%)**	**Rmax**	**Rate (min^{-1})**
Xanthate				
SEX	65.0%	1.0%	80.3	0.0845
SIBX	87.2%	2.4%	100.0	0.1031
PNBX	86.9%	0.1%	100.0	0.1049
PAX	90.0%	0.7%	100.0	0.1133
Dithiophosphate				
DTP-E	67.9%	2.1%	77.3	0.1087
DTP-IB	83.1%	2.6%	100.0	0.0876
Dithiocarbamate				
DTC-E	61.7%	1.8%	77.4	0.0827
DTC-IB	59.7%	2.3%	74.5	0.0824
Collectorless pH 9	59.1%	1.1%	84.9	0.0599
Xanthate and Dithiophosphate mixtures				
Xanthate first				
90-10 ethyl	69.1%	0.0%	78.8	0.1076
50-50 ethyl	72.1%	0.2%	87.1	0.0899
10-90 ethyl	72.2%	3.8%	80.2	0.1191
90-10 Iso-Butyl	90.4%	1.3%	99.5	0.1229
50-50 Iso-Butyl	73.9%	1.1%	100.0	0.0643
10-90 Iso-Butyl	88.3%	3.1%	97.4	0.1235
Dithiophosphate first				
90-10 ethyl	70.3%	2.0%	80.0	0.1074
50-50 ethyl	75.8%	1.2%	88.2	0.0981
10-90 ethyl	74.4%	2.3%	83.0	0.1182
90-10 Iso-Butyl	88.0%	0.0%	95.7	0.1378
50-50 Iso-Butyl	80.6%	0.9%	100.0	0.0788
10-90 Iso-Butyl	87.6%	1.1%	95.2	0.1418
Xanthate and Dithiocarbamate mixtures				
Xanthate first				
90-10 ethyl	68.6%	1.3%	78.2	0.1101
50-50 ethyl	50.8%	1.1%	83.3	0.0476
10-90 ethyl	65.2%	0.2%	77.5	0.0960
90-10 Iso-Butyl	84.4%	1.9%	97.7	0.1051
50-50 Iso-Butyl	74.4%	1.5%	100.0	0.0664
10-90 Iso-Butyl	65.2%	5.2%	80.4	0.0880
Dithiocarbamate first				
90-10 ethyl	72.0%	2.5%	83.8	0.1001
50-50 ethyl	65.7%	1.7%	82.1	0.0433
10-90 ethyl	47.3%	1.2%	79.2	0.0934
90-10 Iso-Butyl	83.4%	3.8%	97.0	0.1015
50-50 Iso-Butyl	78.3%	2.4%	100.0	0.0743
10-90 Iso-Butyl	61.9%	0.4%	79.6	0.0786

	Final solids recovery [%]		
Collector	**Fines (-38 µm)**	**Intermediate (-75 +38 µm)**	**Coarse (-150 +75 µm)**
Xanthate			
SEX	86.75	52.63	20.94
SIBX	73.48	100.00	100.00
PNBX	74.00	100.00	100.00
PAX	75.59	100.00	100.00
Dithiophosphate			
DTP-E	72.82	80.16	37.18
DTP-IB	75.94	99.66	80.61
Dithiocarbamate			
DTC-E	72.04	72.02	18.09
DTC-IB	71.59	67.25	16.41
Collectorless pH 9	73.41	62.97	13.53
Xanthate and Dithiophosphate mixtures			
Xanthate first			
90-10 ethyl	73.83	85.81	34.73
50-50 ethyl	69.66	87.07	59.52
10-90 ethyl	74.93	86.32	45.12
90-10 Iso-Butyl	76.08	100.00	100.00
50-50 Iso-Butyl	71.64	88.07	61.02
10-90 Iso-Butyl	78.38	100.00	94.07
Dithiophosphate first			
90-10 ethyl	74.43	86.69	36.53
50-50 ethyl	69.54	92.04	72.10
10-90 ethyl	74.01	93.13	50.61
90-10 Iso-Butyl	73.44	100.00	100.00
50-50 Iso-Butyl	71.67	98.41	81.70
10-90 Iso-Butyl	75.66	100.00	99.11
Xanthate and Dithiocarbamate mixtures			
Xanthate first			
90-10 ethyl	73.41	83.14	35.87
50-50 ethyl	63.21	54.14	11.61
10-90 ethyl	73.77	77.63	24.70
90-10 Iso-Butyl	73.98	100.00	91.56
50-50 Iso-Butyl	69.46	90.36	66.85
10-90 Iso-Butyl	71.69	78.68	28.33
Dithiocarbamate first			
90-10 ethyl	73.51	88.25	46.04
50-50 ethyl	61.11	48.29	7.38
10-90 ethyl	73.68	78.91	25.74
90-10 Iso-Butyl	73.18	100.00	89.79
50-50 Iso-Butyl	69.13	97.34	78.71
10-90 Iso-Butyl	69.85	74.35	22.95

Collector	**-38 µm**		**-75 +38 µm**		**-150 +75 µm**	
Xanthate	**Rmax**	**Rate (min^{-1})**	**Rmax**	**Rate ($\text{min}^{-1)}$**	**Rmax**	**Rate (min^{-1})**
SEX	100.0	0.1065	66.2	0.0692	100.0	0.0096
SIBX	80.7	0.1398	100.0	0.1379	100.0	0.0936
PNBX	78.6	0.1689	100.0	0.1392	100.0	0.0857
PAX	82.1	0.1483	100.0	0.1449	100.0	0.1085
Dithiophosphate						
DTP-E	78.8	0.1428	100.0	0.0785	82.5	0.0298
DTP-IB	83.1	0.1323	100.0	0.1093	100.0	0.0599
Dithiocarbamate						
DTC-E	80.9	0.1202	100.0	0.0586	100.0	0.0089
DTC-IB	79.9	0.1202	100.0	0.0512	100.0	0.0081
Collectorless pH 9	87.1	0.0956	100.0	0.0426	100.0	0.0061
Xanthate and Dithiophosphate mixtures						
Xanthate first						
90-10 ethyl	79.2	0.1508	100.0	0.0882	100.0	0.0195
50-50 ethyl	81.6	0.1019	100.0	0.0905	71.0	0.0861
10-90 ethyl	79.7	0.1617	100.0	0.0943	100.0	0.0292
90-10 Iso-Butyl	80.4	0.1770	100.0	0.1601	100.0	0.1041
50-50 Iso-Butyl	97.6	0.0683	100.0	0.0779	100.0	0.0448
10-90 Iso-Butyl	83.4	0.1611	100.0	0.1495	100.0	0.1006
Dithiophosphate first						
90-10 ethyl	79.5	0.1553	100.0	0.0879	100.0	0.0203
50-50 ethyl	81.4	0.1007	100.0	0.1043	77.1	0.1182
10-90 ethyl	78.4	0.1677	100.0	0.1089	100.0	0.0336
90-10 Iso-Butyl	77.8	0.1737	100.0	0.1732	100.0	0.1345
50-50 Iso-Butyl	90.8	0.0815	100.0	0.1028	100.0	0.0767
10-90 Iso-Butyl	82.2	0.1518	100.0	0.1694	100.0	0.1558
Xanthate and Dithiocarbamate mixtures						
Xanthate first						
90-10 ethyl	78.5	0.1581	100.0	0.0847	100.0	0.0203
50-50 ethyl	82.5	0.0747	100.0	0.0351	100.0	0.0055
10-90 ethyl	80.5	0.1388	100.0	0.0699	100.0	0.0126
90-10 Iso-Butyl	80.3	0.1454	100.0	0.1352	100.0	0.0855
50-50 Iso-Butyl	87.0	0.0835	100.0	0.0849	100.0	0.0483
10-90 Iso-Butyl	79.8	0.1302	100.0	0.0717	100.0	0.0149
Dithiocarbamate first						
90-10 ethyl	79.0	0.1532	100.0	0.0898	100.0	0.0261
50-50 ethyl	83.9	0.0665	100.0	0.0299	100.0	0.0034
10-90 ethyl	80.8	0.1370	100.0	0.0721	100.0	0.0137
90-10 Iso-Butyl	79.7	0.1395	100.0	0.1302	100.0	0.0818
50-50 Iso-Butyl	88.4	0.0797	100.0	0.1027	100.0	0.0685
10-90 Iso-Butyl	79.3	0.1175	100.0	0.0623	100.0	0.0116

Mass balance					
Collector	**-150 +75 µm**	**-75 +38 µm**	**-38 µm**	**Recovery**	**difference**
Xanthate	Final recovery (mass in grams)				
SEX	0.1231	0.4121	1.4132	64.9%	0.08%
SIBX	0.5880	0.7830	1.1970	85.6%	1.57%
PNBX	0.5880	0.7830	1.2054	85.9%	1.0%
PAX	0.5880	0.7830	1.2314	86.7%	3.3%
Dithiophosphate					
DTP-E	0.2186	0.6277	1.1862	67.7%	0.11%
DTP-IB	0.4740	0.7803	1.2371	83.0%	0.08%
Dithiocarbamate					
DTC-E	0.1064	0.5639	1.1735	61.5%	0.2%
DTC-IB	0.0965	0.5266	1.1661	59.6%	0.1%
Collectorless pH 9	0.0796	0.4930	1.1958	58.9%	0.1%
Xanthate and Dithiophosphate mixtures					
Xanthate first					
90-10 ethyl	0.2042	0.6719	1.2027	69.3%	0.16%
50-50 ethyl	0.3500	0.6817	1.1347	72.2%	0.08%
10-90 ethyl	0.2653	0.6759	1.2205	72.1%	0.11%
90-10 Iso-Butyl	0.5880	0.7830	1.2393	87.0%	3.40%
50-50 Iso-Butyl	0.3588	0.6896	1.1670	73.8%	14.42%
10-90 Iso-Butyl	0.5531	0.7830	1.2767	87.1%	13.21%
Dithiophosphate first					
90-10 ethyl	0.2148	0.6788	1.2125	70.2%	0.13%
50-50 ethyl	0.4239	0.7206	1.1329	75.9%	1.54%
10-90 ethyl	0.2976	0.7292	1.2056	74.4%	1.42%
90-10 Iso-Butyl	0.5880	0.7830	1.1963	85.6%	2.46%
50-50 Iso-Butyl	0.4804	0.7706	1.1675	80.6%	6.94%
10-90 Iso-Butyl	0.5827	0.7830	1.2325	86.6%	6.00%
Xanthate and Dithiocarbamate mixtures					
Xanthate first					
90-10 ethyl	0.2109	0.6509	1.1958	68.6%	0.03%
50-50 ethyl	0.0683	0.4239	1.0297	50.7%	14.47%
10-90 ethyl	0.1453	0.6078	1.2017	65.2%	14.34%
90-10 Iso-Butyl	0.5384	0.7830	1.2052	84.2%	0.21%
50-50 Iso-Butyl	0.3931	0.7075	1.1315	74.4%	9.25%
10-90 Iso-Butyl	0.1666	0.6161	1.1679	65.0%	9.35%
Dithiocarbamate first					
90-10 ethyl	0.2707	0.6910	1.1974	72.0%	0.03%
50-50 ethyl	0.0434	0.3781	0.9955	47.2%	18.44%
10-90 ethyl	0.1514	0.6179	1.2003	65.7%	18.31%
90-10 Iso-Butyl	0.5279	0.7830	1.1920	83.4%	0.04%
50-50 Iso-Butyl	0.4628	0.7621	1.1261	78.4%	16.45%
10-90 Iso-Butyl	0.1349	0.5822	1.1379	61.8%	16.46%

Appendix B

Malvern analysis of microflotation concentrates samples

Each reagent condition (e.g. di-ethyl DTP only) was done in duplicate and thus there were always two concentrates for each time interval (e.g. CA1 and CB1). Each individual sample (e.g. CA1 only) did not have enough mass to be accurately analysed by the Malvern Mastersizer. The Malvern has obscuration limits and when adding a sample the obscuration for this size class (above 5 µm) needed an obscuration of between 5% and 20 %.

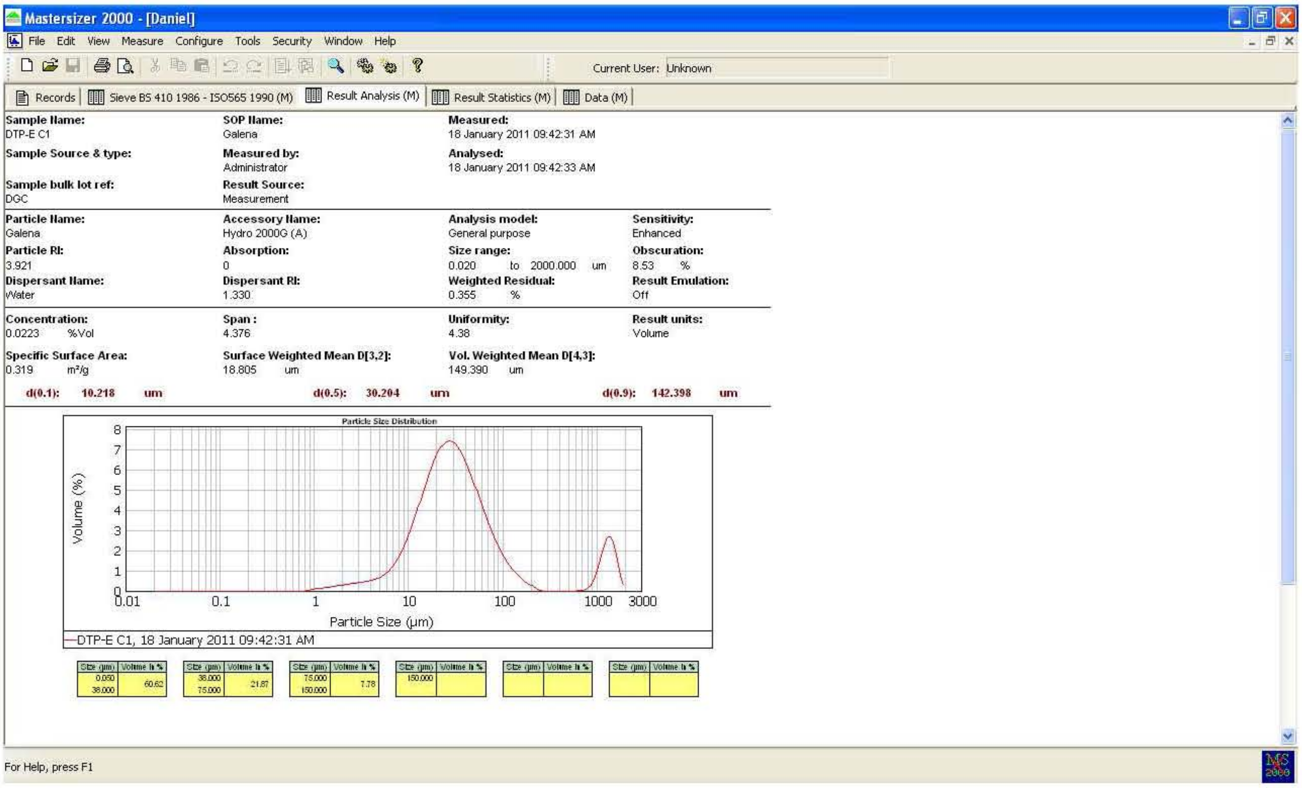
Keeping these limits in mind, the two duplicate concentrates were combined and analysed as one sample to meet the optimal obscuration value (about 15%). High impeller speeds had to be used for analysis of galena due to its high specific gravity. Thus the use of dispersant was avoided as it would introduce bubbles into the pulp and these would interfere with particle size measurements.

The particle size limit had to be set, because any particle size above this would be non real and may have been the results of particles sticking together and so not an accurate representation. All flotation samples were sieved to 100% -106 µm. Thus using the principle of equivalent sphere diameter (Malvern, 2005), the upper particle size limit that would make sense from a Malvern reading was ~150 µm. Equivalent spherical diameter (or ESD) of an irregularly-shaped object is the diameter of a sphere of equivalent volume. The calculation is given below.

Volume of 106 µm cube = $1.19\text{x}10^6$ μm^3

Diameter of sphere with equivalent volume to the cube = 131 µm, it has been estimated it at 150 µm for this thesis, to include any particles with irregular shapes (e.g. long particles for pyrite). The raw data obtained from the Malvern had to be processed according to the steps below:

1. The raw data has a peak at 1000 µm which is clearly a bubble in the pulp.
2. Resetting the sizes for all results to be re-calculated within the limits of 0.1 µm and 151 µm.
3. Setting the user sizes for Malvern to group the volume % into the size fractions of your choice, in this case,0.1 -38 µm; 38 - 75 µm; 75 - 150 µm.
4. Export the data to a text file according to the user sizes.



Current User: Unknown

Sample Name: DTP-E C1
SOP Name: Galena
Measured: 18 January 2011 09:42:31 AM
Sample Source & type:
Measured by: Administrator
Analysed: 18 January 2011 09:42:33 AM
Sample bulk lot ref: DGC
Result Source: Measurement

Particle Name: Galena
Accessory Name: Hydro 2000G (A)
Analysis model: General purpose
Sensitivity: Enhanced
Particle RI: 3.921
Absorption: 0
Size range: 0.020 to 2000.000 um
Obscuration: 8.53 %
Dispersant Name: Water
Dispersant RI: 1.330
Weighted Residual: 0.355 %
Result Emulation: Off

Concentration: 0.0223 %Vol
Span : 4.376
Uniformity: 4.38
Result units: Volume
Specific Surface Area: 0.319 m²/g
Surface Weighted Mean D[3,2]: 18.805 um
Vol. Weighted Mean D[4,3]: 149.390 um

d(0.1): 10.218 um **d(0.5): 30.204 um** **d(0.9): 142.398 um**

Size (μm)	Volume In %
0.050 38.000	60.62

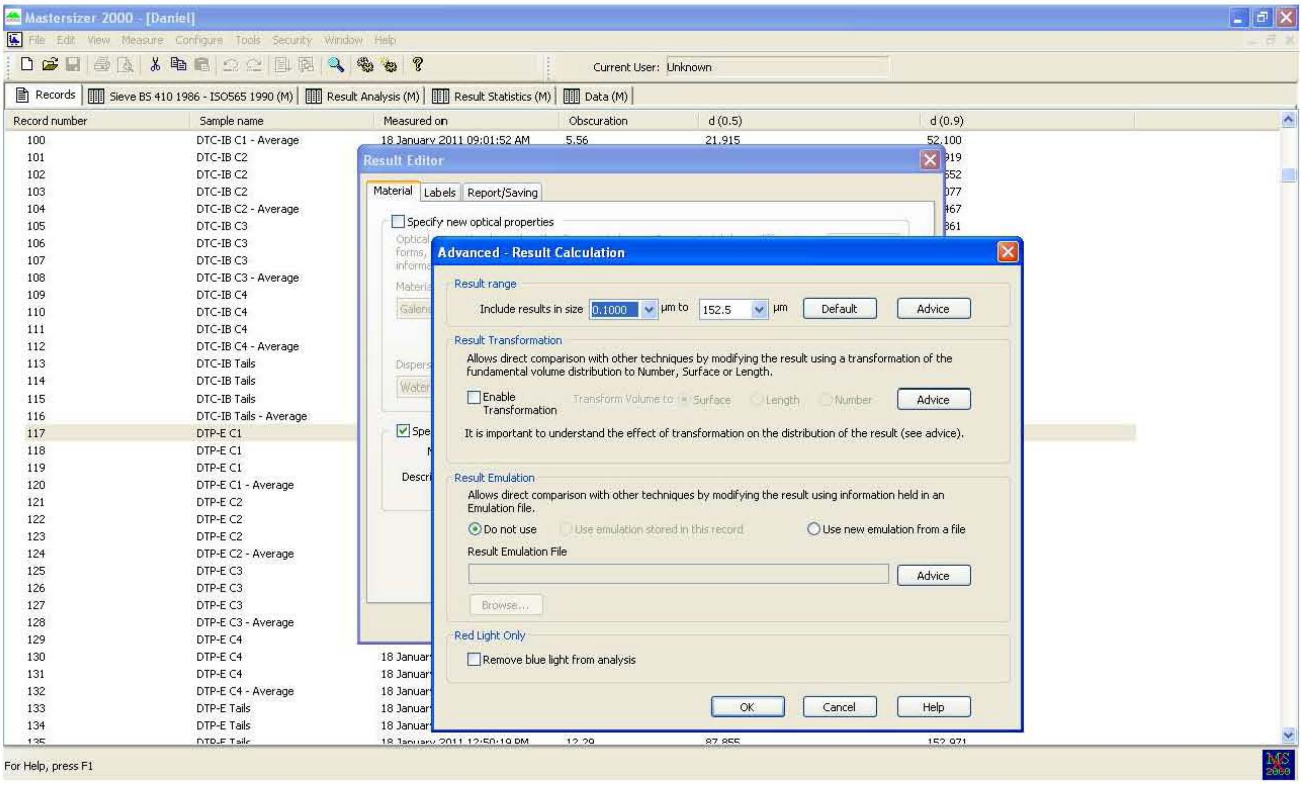
Size (μm)	Volume In %
38.000 75.000	21.87

Size (μm)	Volume In %
75.000 150.000	7.78

Size (μm)	Volume In %
150.000	

Size (μm)	Volume In %

Size (μm)	Volume In %



Current User: Unknown

Record number	Sample name	Measured on	Obscuration	d (0.5)	d (0.9)
100	DTC-IB C1 - Average	18 January 2011 09:01:52 AM	5.56	21.915	52.100
101	DTC-IB C2				919
102	DTC-IB C2				552
103	DTC-IB C2				077
104	DTC-IB C2 - Average				467
105	DTC-IB C3				361
106	DTC-IB C3				
107	DTC-IB C3				
108	DTC-IB C3 - Average				
109	DTC-IB C4				
110	DTC-IB C4				
111	DTC-IB C4				
112	DTC-IB C4 - Average				
113	DTC-IB Tails				
114	DTC-IB Tails				
115	DTC-IB Tails				
116	DTC-IB Tails - Average				
117	DTP-E C1				
118	DTP-E C1				
119	DTP-E C1				
120	DTP-E C1 - Average				
121	DTP-E C2				
122	DTP-E C2				
123	DTP-E C2				
124	DTP-E C2 - Average				
125	DTP-E C3				
126	DTP-E C3				
127	DTP-E C3				
128	DTP-E C3 - Average				
129	DTP-E C4				
130	DTP-E C4	18 Januar			
131	DTP-E C4	18 Januar			
132	DTP-E C4 - Average	18 Januar			
133	DTP-E Tails	18 Januar			
134	DTP-E Tails	18 Januar			
135	DTP-E Tails	18 January 2011 12:50:19 PM	12.29	87.855	152.971

Result Editor

☐ Specify new optical properties

☑ Spe

Advanced - Result Calculation

Result range

Include results in size 0.1000 μm to 152.5 μm

Result Transformation

Allows direct comparison with other techniques by modifying the result using a transformation of the fundamental volume distribution to Number, Surface or Length.

☐ Enable Transformation   Transform Volume to: ● Surface ○ Length ○ Number

It is important to understand the effect of transformation on the distribution of the result (see advice).

Result Emulation

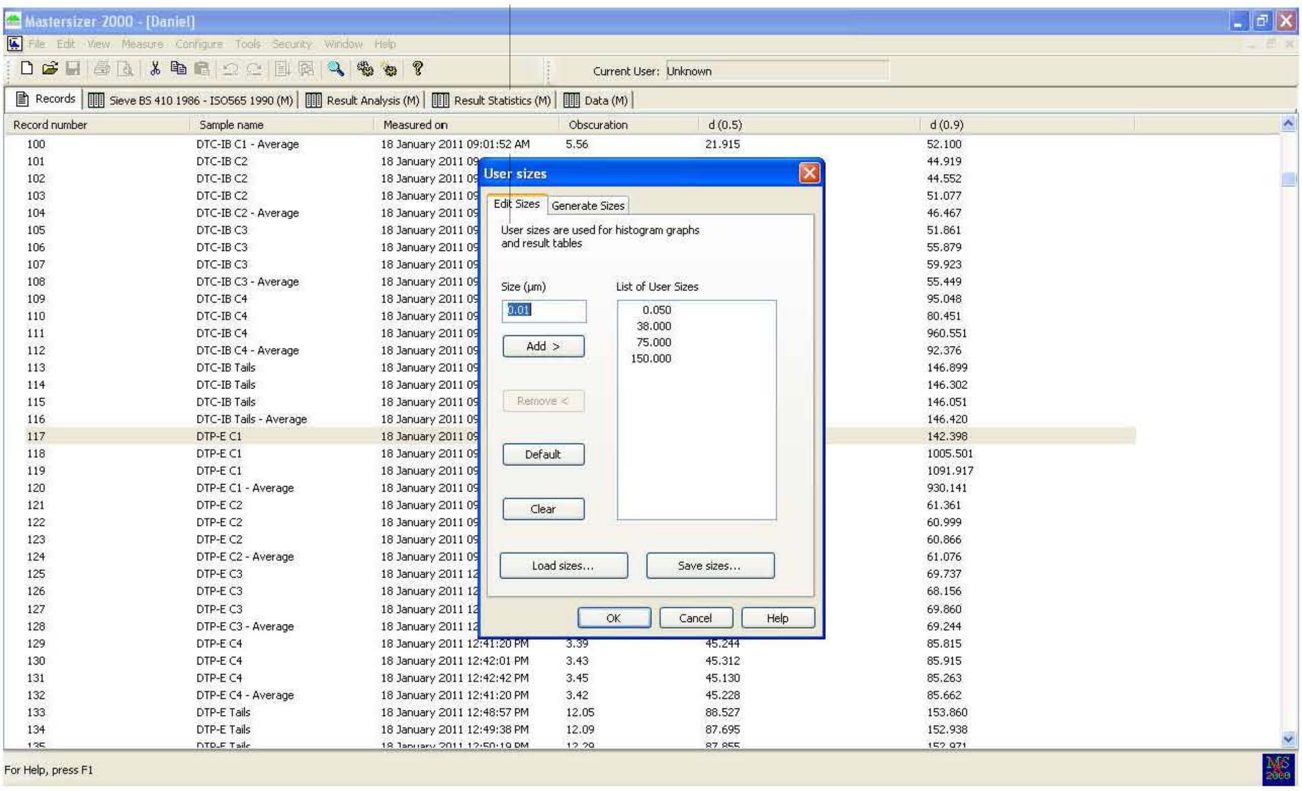
Allows direct comparison with other techniques by modifying the result using information held in an Emulation file.

● Do not use ○ Use emulation stored in this record ○ Use new emulation from a file

Result Emulation File

Red Light Only

☐ Remove blue light from analysis



Current User: Unknown

Record number	Sample name	Measured on	Obscuration	d (0.5)	d (0.9)
100	DTC-IB C1 - Average	18 January 2011 09:01:52 AM	5.56	21.915	52.100
101	DTC-IB C2	18 January 2011 09			44.919
102	DTC-IB C2	18 January 2011 09			44.552
103	DTC-IB C2	18 January 2011 09			51.077
104	DTC-IB C2 - Average	18 January 2011 09			46.467
105	DTC-IB C3	18 January 2011 09			51.861
106	DTC-IB C3	18 January 2011 09			55.879
107	DTC-IB C3	18 January 2011 09			59.923
108	DTC-IB C3 - Average	18 January 2011 09			55.449
109	DTC-IB C4	18 January 2011 09			95.048
110	DTC-IB C4	18 January 2011 09			80.451
111	DTC-IB C4	18 January 2011 09			960.551
112	DTC-IB C4 - Average	18 January 2011 09			92.376
113	DTC-IB Tails	18 January 2011 09			146.899
114	DTC-IB Tails	18 January 2011 09			146.302
115	DTC-IB Tails	18 January 2011 09			146.051
116	DTC-IB Tails - Average	18 January 2011 09			146.420
117	DTP-E C1	18 January 2011 09			142.398
118	DTP-E C1	18 January 2011 09			1005.501
119	DTP-E C1	18 January 2011 09			1091.917
120	DTP-E C1 - Average	18 January 2011 09			930.141
121	DTP-E C2	18 January 2011 09			61.361
122	DTP-E C2	18 January 2011 09			60.999
123	DTP-E C2	18 January 2011 09			60.866
124	DTP-E C2 - Average	18 January 2011 09			61.076
125	DTP-E C3	18 January 2011 12			69.737
126	DTP-E C3	18 January 2011 12			68.156
127	DTP-E C3	18 January 2011 12			69.860
128	DTP-E C3 - Average	18 January 2011 12			69.244
129	DTP-E C4	18 January 2011 12:41:20 PM	3.39	45.244	85.815
130	DTP-E C4	18 January 2011 12:42:01 PM	3.43	45.312	85.915
131	DTP-E C4	18 January 2011 12:42:42 PM	3.45	45.130	85.263
132	DTP-E C4 - Average	18 January 2011 12:41:20 PM	3.42	45.228	85.662
133	DTP-E Tails	18 January 2011 12:48:57 PM	12.05	88.527	153.860
134	DTP-E Tails	18 January 2011 12:49:38 PM	12.09	87.695	152.938

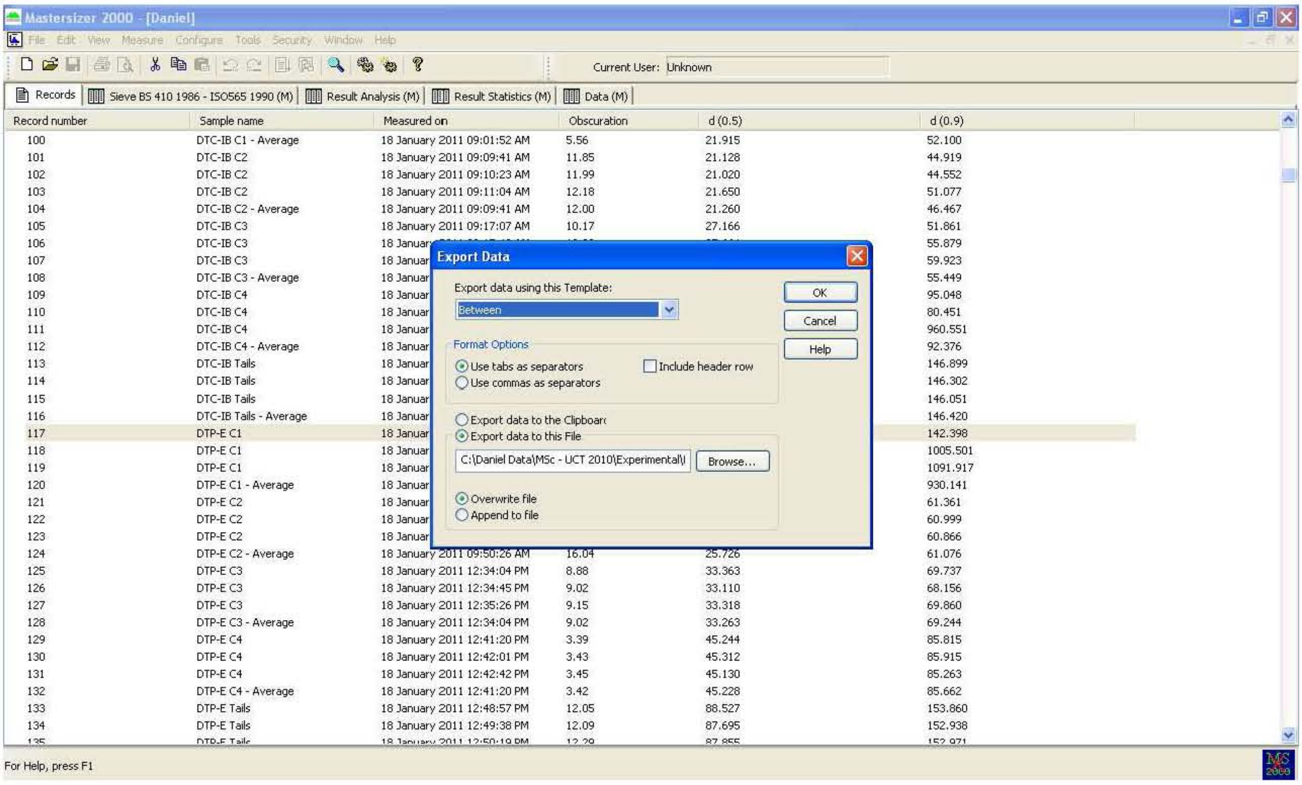
User sizes

Edit Sizes | Generate Sizes

User sizes are used for histogram graphs and result tables

Size (µm): 0.01

List of User Sizes:
0.050
38.000
75.000
150.000



Current User: Unknown

Record number	Sample name	Measured on	Obscuration	d (0.5)	d (0.9)
100	DTC-IB C1 - Average	18 January 2011 09:01:52 AM	5.56	21.915	52.100
101	DTC-IB C2	18 January 2011 09:09:41 AM	11.85	21.128	44.919
102	DTC-IB C2	18 January 2011 09:10:23 AM	11.99	21.020	44.552
103	DTC-IB C2	18 January 2011 09:11:04 AM	12.18	21.650	51.077
104	DTC-IB C2 - Average	18 January 2011 09:09:41 AM	12.00	21.260	46.467
105	DTC-IB C3	18 January 2011 09:17:07 AM	10.17	27.166	51.861
106	DTC-IB C3	18 Januar			55.879
107	DTC-IB C3	18 Januar			59.923
108	DTC-IB C3 - Average	18 Januar			55.449
109	DTC-IB C4	18 Januar			95.048
110	DTC-IB C4	18 Januar			80.451
111	DTC-IB C4	18 Januar			960.551
112	DTC-IB C4 - Average	18 Januar			92.376
113	DTC-IB Tails	18 Januar			146.899
114	DTC-IB Tails	18 Januar			146.302
115	DTC-IB Tails	18 Januar			146.051
116	DTC-IB Tails - Average	18 Januar			146.420
117	DTP-E C1	18 Januar			142.398
118	DTP-E C1	18 Januar			1005.501
119	DTP-E C1	18 Januar			1091.917
120	DTP-E C1 - Average	18 Januar			930.141
121	DTP-E C2	18 Januar			61.361
122	DTP-E C2	18 Januar			60.999
123	DTP-E C2	18 Januar			60.866
124	DTP-E C2 - Average	18 January 2011 09:50:26 AM	16.04	25.726	61.076
125	DTP-E C3	18 January 2011 12:34:04 PM	8.88	33.363	69.737
126	DTP-E C3	18 January 2011 12:34:45 PM	9.02	33.110	68.156
127	DTP-E C3	18 January 2011 12:35:26 PM	9.15	33.318	69.860
128	DTP-E C3 - Average	18 January 2011 12:34:04 PM	9.02	33.263	69.244
129	DTP-E C4	18 January 2011 12:41:20 PM	3.39	45.244	85.815
130	DTP-E C4	18 January 2011 12:42:01 PM	3.43	45.312	85.915
131	DTP-E C4	18 January 2011 12:42:42 PM	3.45	45.130	85.263
132	DTP-E C4 - Average	18 January 2011 12:41:20 PM	3.42	45.228	85.662
133	DTP-E Tails	18 January 2011 12:48:57 PM	12.05	88.527	153.860
134	DTP-E Tails	18 January 2011 12:49:38 PM	12.09	87.695	152.938

Export Data

Export data using this Template: Between

Format Options
● Use tabs as separators
○ Use commas as separators
☐ Include header row

○ Export data to the Clipboar
● Export data to this File
C:\Daniel Data\MSc - UCT 2010\Experimental\

● Overwrite file
○ Append to file