Investigating the role of dithiophosphate in the flotation of base metal sulfides

Thomas Ignatius Jordaan

Centre for Minerals Research

Department of Chemical Engineering

University of Cape Town

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Abstract

The behaviour of sodium diethyl dithiophosphate (SEDTP) in flotation systems is of major interest to the Platinum Group Mineral (PGM) and Base Metal Sulphide (BMS) industry. Operationally, SEDTP has proved to be a point of contention as there are conflicting views regarding the role of collector with regard to its behaviour at the air-water and solid-water interface in the flotation process. The main objective of this thesis is to attempt to elucidate the surfactant behaviour of SEDTP and in particular its role at both the air-water and solid-water interface.

To interpret its behaviour at the air-water interface, bubble pressure tensiometry was used to investigate the effect that SEDTP had on equilibrium surface tension. This was compared to the surface tension of a polypropylene glycol (PPG) frother, which was selected as a benchmark due to it being a surface active agent at the air-water interface and its general use in the industry as a frother. One of the most common collectors used in the PGM industry, sodium ethyl xanthate (SEX), was used as a benchmark collector, which is not known to affect the surface tension. Reagent concentrations were pushed high enough for the air-water surfactant, the frother, to reduce the surface tension (5-100 mM). The maximum concentrations of the three different reagents were tested at pH 7, 9 and 11. The pH was kept constant for other experiments at pH 9 and throughout the investigation the make-up water was deionized water (DIW).

To investigate SEDTP's behaviour at the air-water interface, a frothing column was used to determine its effect on foam stability. Reagent dosages used were similar to those used on plant operations, which are much lower than those used in surface tension experiments. Foam stability experiments were carried out at pH 9 using synthetic plant water (SPW) the constitution of which is shown in the thesis. Solids were subsequently introduced to investigate the effect that SEDTP had on froth stability (3-phase) and compare it to foam stability (2-phase). The solids used were samples from a PGM-containing silicate ore, milled to 60% passing 75 micron. As with the foam stability investigation, the froth stability experiments were carried out at pH 9.

The pulp phase floatability of pyrite and galena with SEDTP was measured to investigate the effect that SEDTP had on particle hydrophobicity. Collector-less and pure reagent flotation recoveries were established to relate the effect that reagents had on the floatability. The

microflotation of pyrite was carried out at pH 4 and pH 9 to investigate the effect of pH on the flotation of pyrite when using either SEDTP or SEX as single reagents and in the presence of a PPG frother. The effect of frother type and chain length in a mixture containing SEDTP was also investigated on pyrite at pH 4. Microflotation of galena was done at pH 4 to test the relative effect of SEDTP either as a single reagent or in conjunction with a frother compared to pyrite at the same conditions. Collector dosages for all microflotation experiments were determined so as achieve 50% of a single monolayer surface coverage on the mineral surface. This was done by determining the BET surface area of the mineral and using the known surface area footprint of a single collector molecule. Frother concentrations were similar to those used in previous studies. Furthermore, to minimize surface oxidation of the minerals, the samples were stored in nitrogen in a desiccator and acid-washed prior to the experiments. SPW was used to simulate a plant-like solution.

Equilibrium surface tension results showed that the reagents used reduced the surface tension in the order: PPG frother, SEDTP, SEX. This is ascribed to the role of these reagents when adsorbing at the air-water interface. Foam stability tests were shown to be more sensitive than surface tension measurements in predicting the surface activity of SEDTP at much lower concentrations than the concentrations used for surface tension experiments. SEDTP did not have any significant effect on foam stability when used as a single reagent. However, when combined with a frother there was a significant improvement in the foam stability. SEX did not display any foam stabilizing effect with either a frother or in a collector mixture with a frother. This is consistent with the surface tension results, thus indicating that, compared to SEX, SEDTP has surface active properties, and more so when in the presence of a frother.

The presence of solids in the froth stability experiments diminished the role of SEDTP at the air-water interface since no froth stabilizing effect was observed when it was combined with a frother compared to the two-phase foam system. This may be due to SEDTP partially adsorbing on the solid particles (as was shown by UV-Vis experiments) and thus not being available to affect the air-water interface. The collector mixture containing SEDTP and SEX decreased the froth stability. This may be attributed to increased particle hydrophobicity upon the addition of a collector, which could lend to the destabilization of the froth.

Microflotation mineral recoveries are indicative of the bubble-particle attachment efficiency and hydrophobicity. At pH 9, no single reagents improved the recovery of pyrite. Combining SEDTP with a frother did, however, improve the recovery significantly. This was not observed for SEX as a single reagent or when combining SEX with a frother. However a 90 SEDTP: 10

SEX collector mixture containing frother exhibited further synergy by improving the total recovery and flotation rate of pyrite.

At pH 4, single reagent flotation improved reagent-less flotation in all cases. The more acidic conditions would give rise to a more reducing environment which accommodates adsorption of surfactants at the solid-water interface. A 90 SEDTP: 10 SEX collector mixture showed synergy in terms of recovery, i.e. the combined effect was much greater than would have been expected from a weighted sum of each individual contribution. It has been proposed that this may be due to the heterogeneity of the surfaces, viz. the stronger collector adsorbing onto the coarser size fraction and weaker, possibly more selective collectors adsorbing onto a finer particle fraction. Once again, a mixture of SEDTP and a frother improved the flotation recovery synergistically, which is not observed when SEX is combined with a frother.

Surfactant type, size and structure all contribute to the strength of the surfactant at the air-water interface. However, variable frother types (alcohols and PPG’s) at different molecular weights all displayed a similar synergistic effect with SEDTP. Furthermore, the mineral specificity of this synergistic phenomenon was tested on a second mineral, galena. The galena responded similarly to pyrite, in that an SEDTP-frother mixture significantly improved flotation rate and recovery above any single reagent.

The findings in the thesis indicate that SEDTP plays a surfactant role as indicated by its ability to reduce surface tension and improve foam stability. However the presence of solids reduced this effect. In microflotation experiments, SEDTP displayed a synergistic effect when combined with a frother, therefore indicating that it also plays a collecting role by adsorbing at the solid-water interface.

This synergistic effect between SEDTP and a frother can be explained by the ability of SEDTP, as well as the frothers, to adsorb at both the air-water interface and the solid-water interface. Furthermore, the presence of one of these surfactants at an interface improves the adsorption of the other in order to maintain electroneutrality. It is proposed that these observations provide supporting evidence for the classical Leja-Schulman penetration theory on the respective role of frothers and collectors in flotation. This theory proposes that during bubble-particle attachment, these interfaces come into contact with one another and condense to form a new mixed collector-frother monolayer at the bubble-particle film. The combination of surfactants that have bubble stabilizing ability and increase particle hydrophobicity at the bubble-particle interface will ultimately improve the flotation of the particles. However, it was shown in this dissertation, that this synergistic interaction is significant only in the case of SEDTP. SEX showed no evidence of this mechanism operating at all. This may be because all available

xanthate molecules are adsorbed onto the solid surface and are unavailable to act at the air-water interface. In addition, it was shown that SEX is an extremely poor surfactant at the air-water interface. These findings have important ramifications for the current processing of PGMs and BMS where DTP is widely used.

Abbreviations

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

BMS – base metal sulphides

CCC – critical coalescence concentration

CMC – crtitical micelle concentration

DIW – deionized water

DTC - di-alkyl dithiocarbamate

DTP - di-alkyl dithiophosphate

K/k – first order rate of flotation

Ka – dissociation constant

mM – milli Molar concentration

MS – metal sulphide

MX – metal thiolate

MX_2 – metal dithiolate

PAX – Potassium Amyl Xanthate

PGM – platinum group minerals

pKa – negative logarithm of Ka

PPG – polypropylene glycol

R – alkyl group

SEDTC - sodium di-ethyl dithiocarbamate

SEDTP - sodium di-ethyl dithiophosphate

SEX - sodium ethyl xanthate

SPW – synthetic plant water

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X^- - thiol radical

X_2 – thiol dimer, dithiolate

1. Introduction and Literature Review

1.1 Introduction

The mining sector is an integral part of global economy. The need to extract hard commodities from the Earth’s crust persists and the demand continues to rise to support the ever growing human population. Base metals such as iron, copper, lead and zinc are used in tools in almost every industry as well as our everyday life. Platinum group minerals are very important, for example, as catalytic converters, which greatly reduce the toxic emissions of combustion.

As mining continues to deplete ore reserves, the need for innovation in the mining sector has become more important to benefit from mining of lower grade, complex ore bodies.

Mining is the up-stream process of extractive metallurgy. Extractive metallurgy includes all the processes an ore may undergo to extract the sought after mineral from the gangue. This includes treatment using pyrometallurgy, hydrometallurgy, electrowinning or mineral processing. These processes are often used in combination to process the same ore. Focusing on mineral processing, comminution is the reduction and classification of grain sizes suited to liberate a mineral from an ore. The product of the comminution circuit is most frequently fed to a flotation plant which makes use of the chemical and physical differences between the desired mineral and gangue to produce a concentrate which is rich in the valuable mineral.

There are two fundamental operations in mineral processing: the liberation of the valuable minerals from their waste gangue materials, and concentration by separating the minerals from the gangue. Several beneficiation processes exist and one such important process is froth flotation. The use of flotation in the mining sector started about a century ago and is the most important beneficiation process used to extract valuable minerals from a milled ore (Nagaraj & Ravishankar, 2007)

Thiol collectors are readily used in many different flotation operations, most prominently for base metal sulphides (BMS) (Klimpel, 1994), precious metals such as gold (Allan & Woodcock, 2001), and platinum group minerals (PGM) (Hadler, Aktas & Cilliers, 2005). The most popular thiol collector used is xanthate, followed by dithiophosphate (DTP). Often they are used together in a mixture where the flotation performance is improved beyond the sum of their individual parts. In these cases, the thiol collectors are said to behave synergistically.

Collectors interact at the solid-water interface to adsorb onto the valuable mineral surface. Xanthate has been shown to adsorb onto the mineral surface and this correlates with an improvement in flotation. However, in some cases, there is no evident adsorption of DTP onto various minerals, yet it still enhances flotation performance as a single collector or as a co-collector (Petrus et al., 2011; McFadzean, Castelyn & O'Connor, 2012; McFadzean & O'Connor, 2014; Taguta, 2015).

Thiol collectors are ionic, heteropolar molecules with a non-polar hydrocarbon chain, which renders the particle hydrophobic, and a polar sulphydryl group that interacts with the mineral surface. At a mineral surface, physisorption or chemisorption of thiol collectors may occur. For physisorption, no collector-mineral interaction occurs whereas there is collector-mineral interaction for chemisorption. The Gibbs free energy of adsorption is greater for chemisorption than physisorption.

Mineral surfaces are often semi-conductors which may allow electrochemical reactions to occur, involving the oxidation of the collectors to dithiolates, which are largely responsible for the collecting ability of thiolates. The formation of the collector surface species is dependent on the electrochemical potential, pH and thermodynamics of the system.

Generally, alkaline conditions inhibit the adsorption of collectors as metal hydroxides tend to form on sulphide surfaces whereas acidic conditions promote thiol adsorption due to more surface sites being available as there is a lower concentration of interfering hydroxides (Grano et al., 1997).

Structurally, collectors are similar to frothers: they are hetero-polar molecules consisting of polar headgroups and non-polar hydrocarbon chains (Bradshaw, Harris & Connor, 1998). Therefore, it is possible that collectors may interact at the air-water interface as well as the solid-water interface, as frothers are shown to do. According to surfactant literature, anionic molecules like thiol collectors are fundamentally poor surfactants at the air-water interface. However, a mixture of different types of surfactants at the air-water interface and solid-water interface is commonly beneficial to flotation performance. Therefore, the attachment of the collectors at the air-water interface, and frothers at the solid-liquid interfaces, even to a minimal extent, could lead to a significant improvement in flotation performance. An investigation of these phenomena is central to this dissertation.

1.2 Flotation background

The flotation process separates hydrophobic and hydrophilic materials with the use of bubbles in water. In a flotation cell, there are two operationally important phases present, defined as the froth phase and the pulp phase. Conventionally, the desired material or mineral is transported from the pulp phase to the froth phase where it is able to be collected, whilst the gangue minerals are suppressed in the pulp phase. A reverse flotation method may also be used, where the desired mineral stays in the pulp and the gangue is floated and thus separated. A flotation cell is shown in Figure 1.

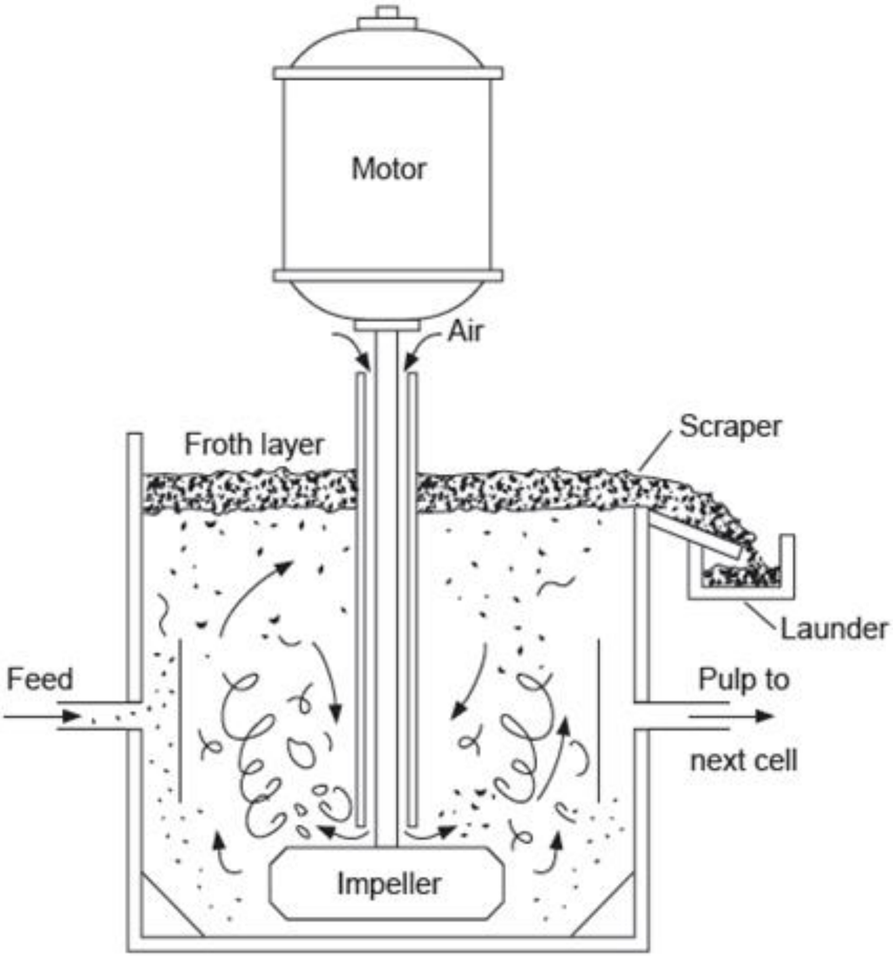


Figure 1: Flotation Cell (Froth Flotation: North American Mixing Forum, 2015)

Shortly described, a solution consisting of the solid mineral/ore to be floated, together with frothers, collectors, and modifiers is added to a flotation cell, each with a specified conditioning time. The impeller motor is turned on and after the respective conditioning times are reached, the air flow is turned. This liquid body of the cell consisting of the slurry is referred to as the pulp phase. In some cases, reagents are added to the mill instead of the cell. However, the addition to the cell generally proves more beneficial (e.g. Wiese et al. 2005). A froth phase forms as bubbles accumulate at the top of the cell. The froth product is collected in the launder and this concentrate is sent off to the next stage of mineral processing.

1.2.1 Sub-processes in Flotation

A flotation cell is a complex system. Simultaneous reactions occur, along with hydrodynamic processes. The sub-processes in flotation include (adapted from Bradshaw (1997)):

1. A reagent adsorbs onto the desired mineral, rendering it more hydrophobic. Adsorption is controlled by the properties of the reagent, the pulp (pH, pulp potential etc.) and the mineral.
2. Air is injected into the pulp, forming bubbles with a specific size and distribution. Reagents interact at the air-water interface, affecting the stability, strength and rising velocity of the bubble (Smar, Klimpel & Aplan, 1994)
3. The air bubble and the desired mineral particle come into contact with one another. This could lead to another adsorption reaction, then, in the case of detachment, a desorption reaction.
4. This bubble-particle complex rises through the pulp phase.
5. Particles move from the pulp into the froth phase. Preferably, this occurs through bubble-particle attachment as this is selective but entrainment does occur. Elutriation, a process whereby particles fall back into the pulp phase from the froth, also occurs.

When considering a flotation system, there are a range of different aspects one must consider. The three basic aspects are physical-mechanical, chemical and operational as described by Nagaraj (2005), shown in Figure 2.

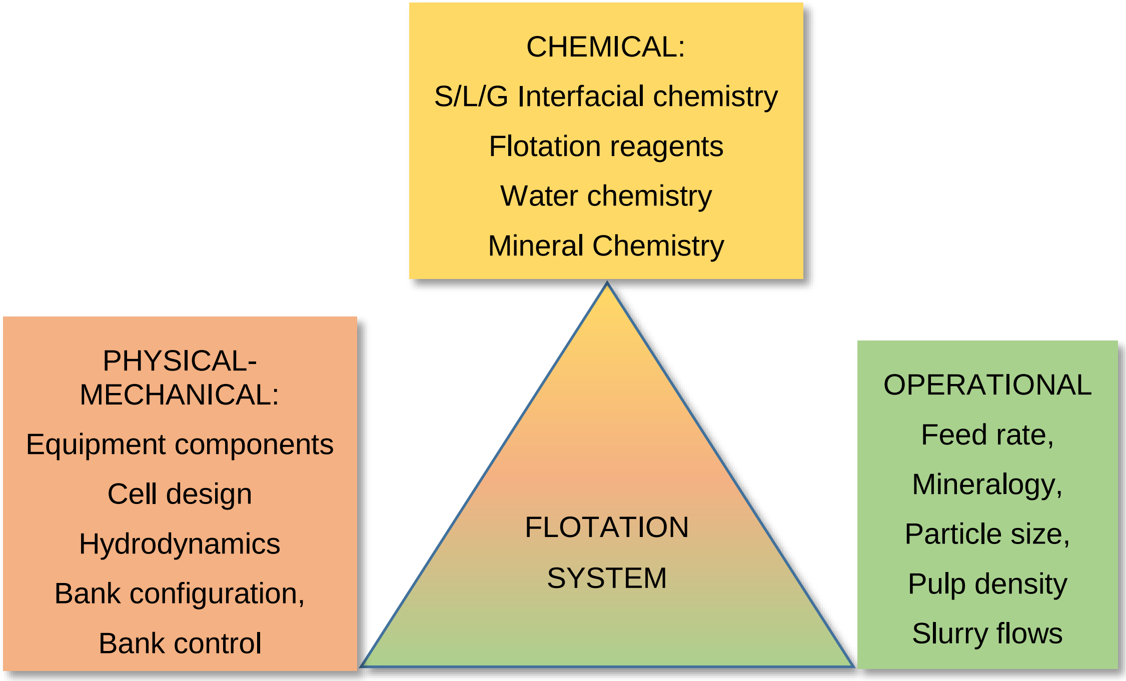


Figure 2: Klimpel's (1994) parameters concerning flotation system

All these aspects can be seen as interdependent rather than separate, (e.g. particle size, a physical aspect, is directly related to surface area which affects chemical aspects).This project is focusing on the chemical aspect of flotation, specifically flotation reagents.

1.3 Effects of chemical factors on flotation

1.3.1 Flotation reagents

Reagents added in a flotation cell have the predominant chemical effect in flotation. Reagent suite selection is an important consideration when attempting to float an ore. Flotation reagents are divided up into major classes: frothers, modifiers and collectors, with some degree in overlap of function between them (Klimpel, 1994).

1.3.1.1 Modifiers

This class of reagents includes depressants, pH modifiers and activators. In literature they are referred to as modifiers or regulators. As their name suggests, they change the action of the collector on the target mineral surface and thus govern the selectivity process. In the presence of a regulator, the collector should only adsorb onto the targeted mineral. Activators react directly with the mineral surface, making the surface more suitable for collector interaction, thus enhancing flotation (Bradshaw, Harris & Connor, 1998). A common activator, copper sulphate, is used in the activation of sulphide minerals in platinum bearing ore such as the Merensky ore (Bradshaw et al. 2006; Wiese et al. 2006). Depressants reduce the collection of unwanted gangue minerals in the ore by decreasing their hydrophobicity. Depressants are typically inorganic (sodium silicate) and organic (polysaccharides) salts. Common depressants include carboxyl methyl cellulose and guar gum, typically used for talc which poses an obstacle in PGM flotation due to its natural floatability (Shortridge et al., 2000). Modifying the pH will also either enhance or decrease the floatability of a mineral by altering its surface characteristics. In the case of lime and certain organic acids, pH modifiers can also be used as depressants simultaneously (Bulatovic, 2010).

1.3.1.2 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 and control the bubble size by controlling coalescence in the pulp. They are heteropolar surface-active compounds that lower the surface tension of water and have the ability to adsorb on the air bubble–water interface (Bulatovic, 2010; Farrokhpay & Zanin, 2012). 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 heteropolar 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 (Bradshaw, Harris & Connor, 1998). Commercial frother types are alcohols, polypropyl glycols, alkoxyparaffins and polyglycol ethers. Similar to the behaviour of collectors at the solid-water interface, the increase in hydrocarbon chain length of frothers increases their adsorption at the air-water interface as is shown by surface tension measurements of PPG's (Wakamatsu, Numata & Park, 1979)

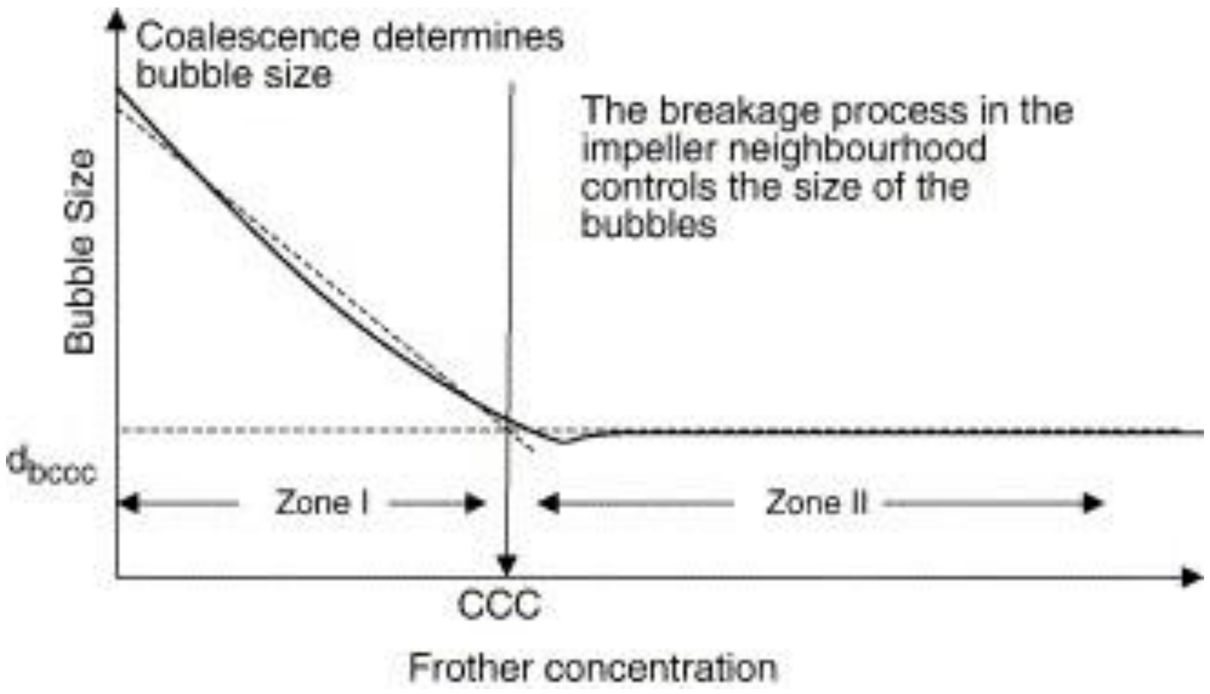


Figure 3: Effect of frother concentration on bubble size (Grau, Laskowski & Heiskanen, 2005)

Cho & Laskowski (2002) studied the effect of frothers on bubble size. They found that frother concentration only played its significant role in bubble size reduction when multi-hole spargers were used. At lower frother concentrations, the bubble size was larger. The bubble size decreases with increasing frother concentration up to the critical coalescence concentration above which coalescence can be prevented. This relationship is shown in Figure 3. Fuerstenau & Wayman (1958) showed that increasing frother concentrations decrease the bubble rise velocity. A bubble that rises slower will have a higher probability of bubble-particle contact and attachment.

Booth & Freyberger (1962) state that higher concentrations of frother give a closely knit froth phase which has high mineral recoveries. However these high recoveries decrease the grade due to the froth being able to retain heavier mineral loads and increased gangue recovery. At lower concentrations, a looser froth prevails which has lower recoveries but increased grade. Cooper et al. (1985) noted that lower frother concentrations gave a coarse bubble size distribution. Ultimately this leads to the destruction of bubble-particle attachments due to bubble collapse near froth surface.

Furthermore, as described by the Leja-Schulman theory (Leja & Schulman, 1954), frothers play an integral role in flotation, not only at the air-water interface but also aiding the adsorption of collectors onto mineral surfaces. Klimpel & Hansen, (1988) states that polypropyl glycol (PPG) frothers can compensate for the recovery deficiencies of thiol collectors (e.g. xanthate at low PPG concentrations). At higher concentrations, the PPG's display poor selectivity.

Wakamatsu et al. (1979) showed that PPG’s are good promotors of galena flotation. This is further discussed in Section 1.3.6 which looks at frother-collector synergy

1.3.1.3 Collectors

Collectors are heteropolar molecules with a non-polar hydrocarbon chain on one end (renders particle hydrophobic) and a polar group which interacts with the mineral surface (Bradshaw, Harris & Connor, 1998). Inductively this means they will concentrate at the mineral-water interface and preferably the mineral-bubble interface. Collectors are either described as non-ionic or ionic (cationic and anionic). Different collectors have variable affinities for different minerals and therefore must be chosen carefully (Klimpel, 1994). The collectors of interest in this study are anionic sulphydryl or thiol collectors. Among these thiol collectors are xanthates and dithiophosphates, the two collectors this study will be focusing on.

When considering collectors, their dosages must be selected at an optimum concentration for the flotation system in question. Schumann (1942) states that the flotation of galena is hindered by over-dosage of xanthate. Taggart (1951) reported a decrease in the particle-bubble contact angle at high collector dosage. Klimpel (1984) indicated that an increase in collector concentration increased the mineral recovery but in turn hindered the flotation rate. By increasing the bubble-particle contact angle through oil addition, foam stability is increased up to a threshold, after which increasing contact angle decreases foam stability. On the other hand, the flotation process needs to be selective to remove gangue material, so the target minerals need to be sufficiently hydrophobic to float.

1.4.1.3.1 Xanthates

Xanthates are the most important collector for sulphides. They tend to decompose at lower pH values but remain stable at higher pH values (Klimpel, 1994). 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. The chemical structure of alkyl xanthates is shown in Figure 4.

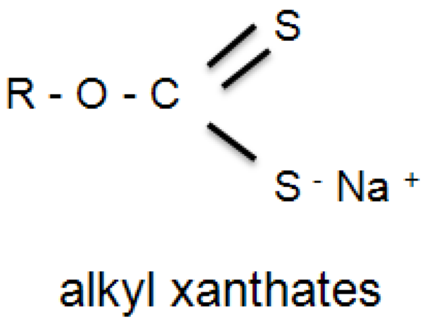


Figure 4: Chemical structure of alkyl xanthate

1.4.1.3.2 Dithiophosphates

Dithiophosphates (DTP), like xanthates, are used in the collection of sulphide ores. DTP is stored at high pH and is soluble. Unlike xanthate, DTP has good pyrite rejection. It is often used a co-collector with xanthate. Although it is not as cheap as xanthate, it is still one of the cheapest collectors. Some longer chain length DTP's have shown frothing ability due to residual alcohol formation during their synthesis (Mingione, 1984; Adkins & Pearse, 1992; Wiese, Harris & Bradshaw, 2005). Manufacturers sell low frothing versions of DTP when a high degree of froth control is needed (Cytec, 2002). This frothing property of DTP only becomes significant at chain lengths of C4 or higher (Mingione, 1984)

DTP is less readily oxidized than xanthate and its mineral complexes are more soluble than xanthate. The chemical structure of di-alkyl dithiophosphate is shown in Figure 5.

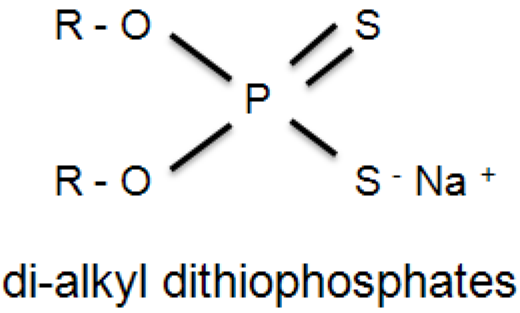


Figure 5: Chemical structure of di-alkyl dithiophosphate

1.3.2 Collector and mineral interaction

As previously stated, collectors interact with mineral surfaces to render the mineral particle hydrophobic. This reaction is considered an adsorption reaction. Interactions between various thiol collectors and mineral surfaces have been widely studied. The accepted adsorption processes identified are chemisorption at metal ion sites on a surface and physical adsorption

(Bulatovic, 2010). The former is a chemical interaction between the collector and the mineral which leads to the precipitation of a metal-thiol onto the mineral (e.g. CuDTP), the latter constitutes physisorption of dithiolates onto the mineral surface (DTP_2), weakly held by van der Waal's forces (Bradshaw, Harris & Connor, 1998). According to Buckley & Woods (1997) the adsorption process for thiol collectors, is either a chemical reaction and/or the result of electrochemical oxidation on the mineral surface. This reaction occurs by two separate electron transfer reactions where anodic reaction involving the collector is coupled with a cathodic reaction (usually the reduction of oxygen).

1.3.2.1 Collector surface species formation

When considering the adsorption of two thiol collectors, DTP and xanthate, their adsorbed surface species must be considered. The adsorption of thiol collectors has been described by the mixed potential mechanism (Tolun & Kitchener, 1964) which consists of four mechanisms:

i. Chemisorption of thiol collector: formation of a monolayer of the thiol collector on the mineral surface (formation must take place below the thermodynamic potential for the formation of metal thiol compound). There is no movement of ions from the mineral surfaces in their lattice sites, therefore it is restricted to the monolayer (Bradshaw, Harris & Connor, 1998). These adsorbed species are intermediates to the formation of dithiolates and metal thiols explained below.

ii. Catalytic oxidation: the mineral surface provides a passage for electrons from the oxidized collector to the reduced oxygen on the adsorption sight (e.g. the formation of dixanthogens). The mineral does not take part in this reaction, but it is essential in catalysing it.

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

Reaction 1: Oxidation of thiols to dimers

Dithiolate formation on mineral surfaces is not essential; however it does increase the hydrophobicity. This requires oxidation of the thiols (X^-) to their dimers (X_2) as follows (Chander, 1999). In the context of surficial adsorption it occurs as follows (Grano et al., 1997)

$$(1) Site + X^- \rightarrow Site \cdot X + e^-$$

$$(2) Site \cdot X + X^- \rightarrow Site \cdot X^2 + e^-$$

Reaction 2: Surficial adsorption of dimers

Where (1) indicates the chemisorption of the thiol onto the adsorption site and (2) indicates the oxidation of the two thiols to form a dithiolate. In the latter case, the adsorption site is occupied by the dithiolate but is only held by weak Van Der Waals forces.

iii. Metal thiol formation: mineral participate in the adsorption process by providing metal ions. This is viewed as an electrochemical reaction:

$$(1)\ MS \rightarrow M^{2+} + S^{0} + e^{-}$$

as well as a chemical reaction:

$$(2)\ M^{2+} + 2X^{-} \rightarrow MX_2$$

Where (1) and (2) together give the overall adsorption mechanism:

$$MS + 2X^{-} \rightarrow MX_2 + S^{0} + e^{-}$$

This is known as the electrochemical mechanism whereby most thiol collectors adsorb. For the electrochemical (oxidation) step, Eh is the controlling factor and for the chemical step, pK is the controlling factor

iv. The fourth mechanism is the metathetical substitution of the oxidized product on the mineral surface by thiol collectors which was proposed by Taggart, del Guidice & Ziehl, (1934).Although no charge transfer seems to occur, the products are formed via an EC process:

$$MS + X^{-} \rightarrow MX + S^{-}$$

Where:

MS is the oxidised species on the mineral surface,
X^{-} is the oxidised anion.

1.3.2.2 Interactions with pyrite

Pyrite is the most abundant mineral in the earth’s crust. Therefore, in mining operations, it is usually a gangue mineral and the flotation thereof would decrease grades. In PGM flotation, pyrite is targeted as a valuable mineral since PGM’s may be associated with it. Ekmekci & Demirel (1997) showed that collectorless flotation of pyrite is highly dependent on pH – almost complete recovery of pyrite is possible at pH 4. The acidic condition allowed metal deficient or elemental sulphide to form at the surface, which is suitable for flotation. The dissolution of pyrite is shown below:

$$FeS_2 \rightarrow Fe^{2+} + 2S^0 + e^-$$

Furthermore, increasing pH up to pH 9 decreased recovery, which is attributed to an increase in rate of formation and stability of hydrophilic oxidation products such as iron hydroxides. These are formed in two steps: hydrolysis of ferrous ions to ferrous hydroxide and then oxidation of ferrous hydroxide to ferric hydroxide, shown below:

$$Fe^{2+} + H_2O \rightarrow Fe(OH)_2 + 2H^+$$

$$Fe(OH)_2 + OH^- \rightarrow Fe(OH)_3 + e^-$$

In summary, the dissolution reaction of pyrite is favoured in acidic conditions and the hydrolysis and oxidation reactions are favoured in alkaline conditions. This is highly important as not only do the products of these reactions enhance/reduce the flotation of pyrite, they also determine whether further adsorption of collectors can occur.

1.3.2.2.1 Xanthates and dithiophosphate

The dithiolate of xanthate, dixanthogen, is thought to be the species responsible for the flotation of pyrite up to pH 11 (Fuerstenau, Kuhn & Elgillani, 1968; Finkelstein & Poling, 1977; Leppinen, Basilio & Yoon, 1989). However, Nagaraj & Brinen (2001) report the formation of the dimer of xanthate as well as the metal thiolate. Whether the presence of the metal thiolate on pyrite is responsible is contested by Fuerstenau et al. (1968) who state that the metal thiolate is highly soluble at moderate xanthate concentrations and the presence of ferric ions oxidizes the xanthate collectors to dixanthogen.

Dithiophosphate behaves similarly to xanthate in flotation in acidic conditions where the dithiolate is responsible for flotation and metal thiolates are also found on the surface (Nagaraj & Brinen, 2001). One of the reasons dithiophosphate is used as a collector is because of its ability to reject pyrite in neutral and alkaline conditions (Mu, Peng & Lauten, 2016). In comparison to xanthate, this difference arises due to their relative abilities to oxidize to their dimers.

Research indicates that the dithiolate formation of $(DTP)_2$ from DTP^- is more difficult than the formation of X_2 from X^- (Fuerstenau, Huiatt & Kuhn, 1971), but on the other hand, SEDTP is more stable in acidic solution than SEX (with reference to their pK_a, discussed in Section 1.4.3.2). To some extent, this is dependent on the dissolution of mineral surface species, which aids in the oxidation of the thiol collectors (Valli, Malmensten & Persson, 1994). The authors describe the adsorption of a thiol collector onto pyrite as follows: (i) the disulphide ions in pyrite are oxidised to oxosulphur anions with high oxidation potentials, most probably $S_2O_8^{2-}$ and/or $S_2O_7^{2-}$. These strong oxidizing agents are not removed from the mineral surface before the oxidation reaction with the thiol collectors takes place. (ii) The thiolate anions are oxidised to their dithiolates by the oxidizing agent on the mineral surface. (iii) The highly hydrophobic dithiolate is adsorbed onto the mineral surface.

1.3.2.3 Interactions with galena

Galena is an abundant source of lead and silver and is commonly associated with copper-lead-zinc deposits which also contain silver. The flotation of galena is achieved relatively easily as various sources indicate that near complete flotation of galena is possible with no collectors at pH 2-8 (Ralston, 1991; Kelebek & Yoruk, 2002). This flotation recovery is ascribed to the formation of metastable elemental sulphur in these conditions.

1.3.2.3.1 Xanthates and dithiophosphate

As opposed to pyrite, xanthate does not oxidize and form dixanthogen on the galena surface. Instead, the metal thiolate forms on the mineral surface and this is responsible for complete flotation of galena achieved at pH 2-11 (Fuerstenau, Chander & Woods, 2007). This is thought to be similar for DTP on galena surface. The reduction potential for DTP on galena is not favourable for oxidation from DTP to its thiolate (Finkelstein & Goold, 1972) and the presence of DTP on the galena surface has been confirmed with ToF-SIMS (Stowe, Chryssoulis & Kim, 1995)

These mechanisms highlight the importance of the redox environment and pH in the adsorption of collectors onto mineral surface. The minerals act as semi-conductors for electrochemical interactions to occur (Martin et al., 1989; Rao & Reddi, 2000). The pulp chemistry has an integral role in determining whether these reactions can take place and if they are favourable.

1.3.3 Collector selectivity

Collectors display variable selectivity in flotation. This is a crucial aspect when selecting reagent suites for the extraction of specific minerals. The selectivity of the collector increases in tandem with a decrease in collector strength. In the case of DTP and xanthate, generally xanthate is the stronger, less selective collector and DTP the weaker, more selective collector (Bagci, Ekmekci & Bradshaw, 2007; Lotter & Bradshaw, 2010).

The driving factor behind the collector strength/selectivity is the atoms situated in the reactive head group that are associated with the donor atoms. According to Bagci et al. (2007), collector strength is determined by the electronegativity of the reactive head group. A higher electronegativity leads to enhanced electron accepting ability and a lower electronegativity leads to enhanced electron donating ability. This determines how collectors behave at different interfaces. The electronegativity of different atoms associated with collectors are shown below in brackets (Bagci, Ekmekci & Bradshaw, 2007):

O (3.5) > N (3.07) > S (2.44) > P (2.06)

From the chemical structures of xanthate and DTP, the selectivity/strength can be deduced. DTP, with two O-R groups, is expected to have the greater electron withdrawing effect whereas xanthate only has one O-R group. The central phosphate in the DTP structure is also more electronegative than the central carbon in xanthate, adding to its greater electron withdrawing effect and intuitively its greater selectivity/weaker strength.

1.3.3.1 Effect of collector chain length

Early work done by Wark & Wark, (1933) showed that for dithiophosphate, xanthate and dithiocarbamates, there was an increase in contact angle with increasing alkyl chain length. This relationship is shown in a microflotation study by (McFadzean, Castelyn & O'Connor, 2012). the ethyl chain lengths equivalents of xanthate (SEX), dithiophosphate (SEDTP) and dithiocarbamate (SEDTC) show, in Figure 6, (Fig. 1.) below, consistently lower recoveries than their respective isobutyl (fig 2 below) chain length equivalents (SIBX, SIBDTP, SIBDTC respectively).

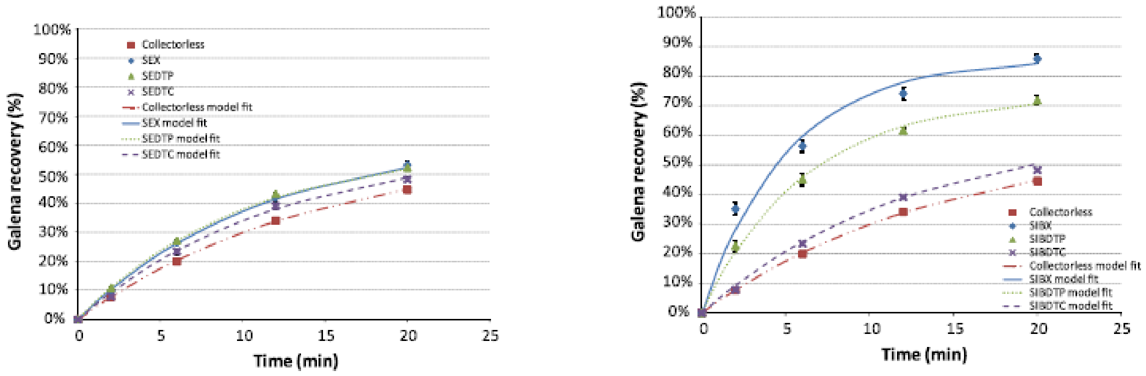


Fig. 1. Overall galena recovery using ethyl chain length xanthate, dithiophosphate and dithiocarbamate (pH 9; 3.8 × 10^{-7} moles/g).

Fig. 2. Overall recovery using isobutyl chain length xanthate, dithiophosphate and dithiocarbamate (pH 9; 3.8 × 10^{-7} moles/g).

Figure 6: Performance of ethyl collectors (Fig. 1.) and isobutyl collectors (Fig. 2.)(McFadzean, Castelyn & O'Connor, 2012)

This is consistent with the work done by Ackerman et al. (1987) where ethyl xanthates performed more poorly than amyl xanthates. Another finding was that when isopropyl xanthate was used, recoveries were greater than the straight chain counterpart, attributed to steric hindrance. However, this increase in alkyl chain length leads to loss of collector concentration attributed to decreased solubility of the collector (Szymula, Kozioł & Szczypa, 1996).

1.3.3.2 pK_a of collectors

As collectors are also considered surfactants, their chemical properties define their attributes and affinities at the different interfaces found in a flotation system. The frothers used widely in PGM and BMS flotation are non-ionic whereas thiol collectors are anionic. Non-ionic frothers outperform anionic collectors as surfactants at the air-water interface due to electrostatic repulsion of anionic surfactants in the solution by the surface charge of the bubble at the air-water interface (Uddin et al., 2013). Therefore, for anionic collectors, the more non-ionic character would improve their surface activity at the air-water interface, i.e. how strongly their counterions are held (Rosen, 2004).

pK_a is the measure of the tendency of the collector anion to dissociate from its counterion The collector acid-base equilibrium may be represented as:

$$XH \rightleftharpoons X^- + H^+$$

From which the dissociation constant (K_a) is calculated using their respective concentrations:

$$K_a \approx \frac{[X^-][H^+]}{[XH]}$$

And $pK_a$is simply the negative logarithm of K_a:

$$pK_a = -\log(K_a)$$

Table 1: Dissociation constants of thiol collectors: dithiophosphate (DTP), xanthate and dithiocarbamate (DTC)

Reagent	pK_a	**Reference**
Dialkyl DTP	~0	Leja, (1982); Hayashi et al., (1986)
Methyl Xanthate	2.07	Hayashi et al., (1984)
Ethyl Xanthate	2.20	
Propyl Xanthate	2.22	
Butyl Xanthate	2.23	
Dimethyl DTC	4.25	Hayashi et al., (1986)
Diethyl DTC	4.62	
Dipropyl DTC	4.72	
Dibutyl DTC	4.80	

Table 1 indicates the dissociation constants of various thiol collectors at different alkyl-group chain length. Between the different types of collectors there was a large difference in pK_a in the order DTP<xanthate<DTC, regardless of carbon chain length. Although there was an increase in pK_a with increasing carbon chain length for both xanthate and DTC, the collector type had a more pronounced effect. Therefore the electron donating effect of the collector headgroup has a more pronounced effect on the pK_a than than the positively inductive effect of the stable carbon chain tail. With the lowest pK_a, DTP is expected to be most stable at low pH and also perform as a better surfactant at the air-water interface, as described above.

This can be related back to the strength and selectivity of the collectors; a higher pK_a value would indicate an increase in strength and a decrease in selectivity

1.3.4 pH effects

pH is an important condition in flotation. It affects several factors in the flotation system including: reactivity of the mineral surface to changes in pH, leading to some minerals being depressed at certain pH's; reagent stability and activity (e.g. xanthates are most stable in alkaline solutions), and species that form on the mineral surface (CuO on chalcopyrite surfaces).

1.3.4.1 pH effects on frothers

Gupta et al. (2007) showed that the foam stability tends to improve with increasing pH at constant concentrations of various PPG frothers. This is shown in Figure 7. Alcohol frothers at constant concentrations exhibit an increasing trend of foam stability with increasing pH values across the whole range of pH studied. For this study, the PPG frother showed higher foam stability across the pH range than the alcohol frothers.

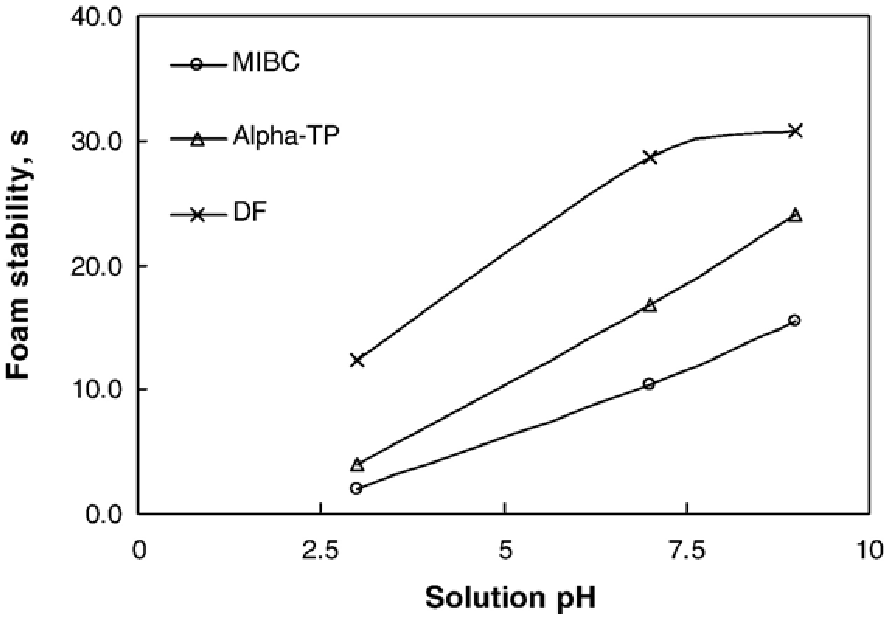


Figure 7: Effect of pH on foam stability of MIBC, Alpha-terpineol and DF-1012 (Gupta et al., 2007)

1.3.4.2 pH effects on collectors

pH can be used as a tool to separate minerals e.g. pyrite and sphalerite can be separated using ethyl xanthate at high pH values: pH change has no perceivable or a small effect on copper-activated sphalerite, exhibiting strong flotation between pH 5.5 and 12. However, pyrite does show sensitivity to pH change in the same range with recoveries and rates of flotation decreasing with increasing pH values (Shen, Fornasiero & Ralston, 1998).

In DRIFT spectra studies done by Güler et al. (2006) on the dithiophosphate-chalcopyrite system showed that at pH 6.79 and 4.67 dithiophosphate adsorbs onto chalcopyrite and forms metal thiolates (CuDTP) and dithiolates $(DTP)_2$. These species both improve hydrophobicity. However, when the pH was increased to 9.2 and 11, there was no evidence to suggest that the metal thiolates and dithiolates formed on the chalcopyrite surfaces. This absence of dithiophosphate adsorption occurred in tandem with the initiation of copper oxide and iron oxyhydroxide species formation on the chalcopyrite surface, therefore they are thought to be the reason behind the inhibition of dithiophosphate adsorption (Güler et al., 2006). This is in agreement with Finkelstein & Goold, (1972)who found that at pH 6 $(DTP)_2$ was adsorbing onto cupric ions, at a pH value of 8 less $(DTP)_2$ was measured and eventually at pH 10 no $(DTP)_2$ was found to be adsorbing onto the mineral surface. Here it is ascribed to the instability of DTP at high pH.

1.3.5 Collector-collector interaction

In flotation plants, reagent mixtures are used to ensure the maximum recovery of valuable minerals of certain ore types. Synergism occurs when these collector mixtures improve the flotation performance above that of the sum of their individual effects. Other benefits of using synergistic reagent suites include: lower frother dosages, higher rates of flotation and better coarse particle recoveries.

Synergistic effects of mixtures are usually indicated by a marked increase in flotation performance over the expected performance based on the additive effects of the pure collectors. If a collector mixture shows such behaviour, it is said to show synergistic behaviour (Bradshaw, Harris & Connor, 1998). The improved flotation performance when using collector mixtures is summarised by Lotter & Bradshaw (2010):

1. Improvement in the rate of flotation (Plaksin & Zaitseva, 1960; Adkins & Pearse, 1992)
2. Improvement in coarse particle recovery (Plaksin & Glembockii, 1954)
3. Reduced collector dosage required (Plaksin & Zaitseva, 1960; Bradshaw, 1997)
4. Optimum flotation performance at specific ratios collectors (Mingione, 1984; Critchley & Riaz, 1991; Valdiviezo & Oliveira, 1993; Bradshaw, 1997; Deng et al., 2010)

Synergy between collectors leading to improved flotation recovery shown in studies is usually ascribed to greater extent of adsorption onto the mineral surface through strong and weak collector interaction (Critchley & Riaz, 1991; Bagci, Ekmekci & Bradshaw, 2007). Either the mineral surface has a higher hydrophobicity or the surface is more suitable for collector-frother interactions (Bradshaw, Harris & Connor, 1998).

Synergism between collectors has been proposed to occur via two theories. The first proposes that the weaker, more selective collector binds onto the stronger sites with a higher surface area (thus finer size fraction) and less oxidised surfaces. Subsequently the stronger, less selective collector binds to the residual sites with lower surface areas (thus the coarser size fraction) and more oxidised surfaces. This is shown in Figure 8.

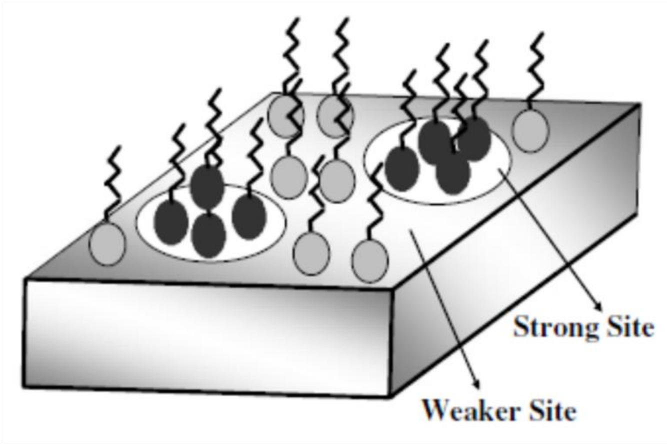


Figure 8: Synergy mechanism - strong/weak adsorption sites (Bagci, Ekmekci & Bradshaw, 2007)

The second mechanism suggests that an adsorbed species would undergo catalytic oxidation to form a dithiolate which provides an anchor for dimers to bind on, shown in Figure 9.

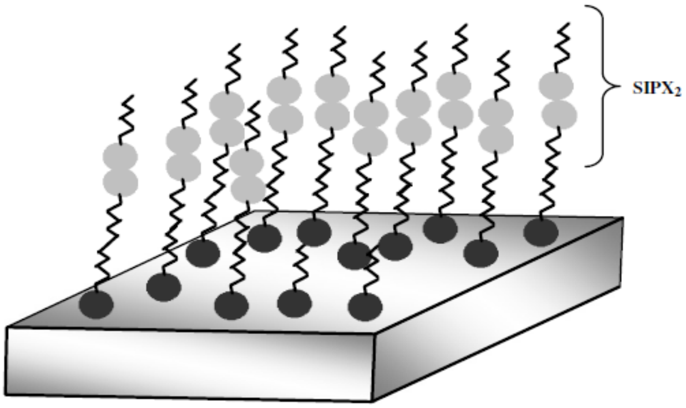


Figure 9: Synergy mechanism - anchor site with dimers. From Bagci et al. (2007)

These two mechanisms are not contradictory to one another as both can occur at the mineral interface. The sequence of addition is also known to affect the extent of synergism (Bradshaw, Harris & Connor, 1998). Generally, the weaker collector is added first, then the stronger collector. The reasoning behind this is that, when added first or simultaneously, the stronger collector will hinder weaker collector adsorption.

1.3.5.1 Xanthate-DTP interaction

DTP is commonly used as a co-collector in conjunction with xanthate in a reagent mixture. These collector mixtures, in some cases, improve flotation of sulphide minerals. However, the cases where their mixtures show little or no improvement of flotation recovery must also be considered. The improvement in recovery for the mixture has been related to synergistic effects between the collectors.

Table 2: Summary of studies concluding synergistic effects between DTP and xanthate

Collectors and ores	Study type	Findings	Authors
SEX + SEDTP; SIBX + SEDTP; galena and pyrite	Batch flotation and microflotation. pH9	Mixtures increased recovery of pyrite & galena, respectively	McFadzean et al. 2012; McFadzean et al. 2013
SIBX + SIBDTP for galena	Adsorption bubble pick up	Preferential DTP adsorption, no increased solids recovery	Wakamatsu & Numata, 1979
SIBDTP + SIBX for PGM ore	Batch flotation. pH9	Mixtures improved recovery of PGM's	Mingione, 1984
Cyclo-hexane DTC + SIBDTP for St Helena ore (pyrite)	Batch flotation. pH4	Mixtures increased recovery	Bradshaw & O'Connor, 1994
Isopropyl xanthate + dicresyl DTP for mixed copper sulphide ore	Batch flotation	Mixtures enhanced Cu recovery and led to improved rate of recovery	Adkins & Pearse, 1992
SEDTP + SIBX for Bushveld Complex ore	Batch flotation. pH9	Two collectors have different, parallel effects: as a collector (SIBX) and to stabilize froth phase	Corin et al. 2012

Table 2 summarises a few of the studies done on systems relating to synergy between DTP and xanthate. These studies do not all attribute the findings to synergy between the collectors as they are viewed as a sum of parallel mechanisms contributing to a better overall performance. For example Corin, Bezuidenhout & O'Connor, (2012) did not observe any synergy between SEDTP and SIBX but the collecting property of SIBX for target minerals and the froth stabilizing effect of SEDTP allowed a mixture of these two collectors to perform better than either would individually in terms of maximizing total solids recovery and minimizing total gangue recovery and entrainment. Wakamatsu et al. (1979), by determining bubble loading on galena found that there was competitive adsorption onto galena, however this could be an indicator which would allow the mechanism depicted in Figure 8 to occur. This mechanism is mentioned by McFadzean et al. (2012) who reason that finer particles with a larger surface area would adsorb the stronger collector first, leaving the coarser particles to adsorb the weaker collector. Once again it is mentioned that this is not true synergy as this is merely a sum of the individual parts (Bradshaw, Harris & Connor, 1998). Mingione et al. 1984 suggests that the improved recovery of various sulphides in batch flotation with a mixture of DTP and xanthate is due to the combination of their properties.

The theories describing the synergy imply there is adsorption occurring between DTP and the mineral (Bradshaw, Harris & Connor, 1998), a theory where there is some disagreement. Recent thermochemical and adsorption studies (Petrus et al., 2011; McFadzean & O'Connor, 2014; Taguta, 2015) done on DTP at high pH's, show no evident adsorption of dithiophosphate onto sulphide minerals.

Petrus et al. (2011) show that the adsorption of DTP onto tennantite and chalcopyrite is highly dependent on the pH, as this affects the surface state of the minerals. In acidic conditions (pH=4), the amount of adsorbed DTP on chalcopyrite and tennantite is almost 100%, but almost 0% in alkaline conditions (pH=9). This is due to the pH changing the surface state of the minerals. Guler et al. (2006) indicated the recovery of chalcopyrite decreases with increasing pH and could not determine the presence of DTP on the mineral surface at high pH's. Grano et al. (1997) suggests that it is the presence of iron hydroxides on the mineral surface that occupies adsorption sites, thus hindering DTP adsorption. This explains the absence of evident adsorption between DTP and galena at pH 9, determined thermochemically by McFadzean et al. (2014), as well as DTP and various other sulphides, by Taguta (2015).

Although these studies indicate no adsorption of DTP onto various sulphides, there are still some studies that show improved recovery of sulphide minerals when using dithiophosphate at a pH of 9 (Wiese, Harris & Bradshaw, 2005; McFadzean, Castelyn & O'Connor, 2012; McFadzean, Mhlanga & O'Connor, 2013). Where X:DTP mixtures were used by Wiese et al. (2005), DTP increased the frothing ability in the mixture. As particle hydrophobicity and froth stability have a complex relationship it is difficult to conclude the effect DTP has on the air-water interface. Furthermore, surface tension measurements are done at concentrations far greater than those applied to general flotation conditions, it would be difficult to predict the eventual effect on frothability.

As was previously mentioned, pH plays an important role in flotation. The batch and microflotation experiments done by McFadzean et al. (2012), McFadzean et al. (2013) McFadzean & O'Connor, (2014) and Wiese et al. (2005) were done at a pH of 9 or 9.2. The DRIFT spectra study (Güler et al., 2006) on the chalcopyrite-DTP system and the UV-vis study done on chalcopyrite and tennantite were done at pH's ranging from 4-11. Therefore, it covers a range of pH conditions where the other studies are limited in this aspect. Adsorption of DTP is evident at low pH's but is absent at higher pH's in the DRIFT studies. Microflotation experiments done at lower pH levels could be conclusive in determining the behaviour of DTP and whether pH plays the perceived role. The mineral in question is also an important parameter as different minerals have different responses to DTP, as shown by the various studies (Taguta et al. 2017; Mcfadzean et al. 2013; Güler et al. 2006; Wiese et al. 2005). Furthermore, it has been shown that minerals behave differently in terms of flotation at different pH's, which also relates to the collector activity. This could be an important factor as the oxides and hydroxides forming on the mineral surface, are influenced by the chemistry of the mineral surface.

1.3.6 Collector-frother synergy

1.3.6.1 Leja-Schulman Theory

Leja & Schulman (1954) proposed a mechanism whereby molecular interactions between collector and frother molecules allow the attachment of air bubbles to solid particles.

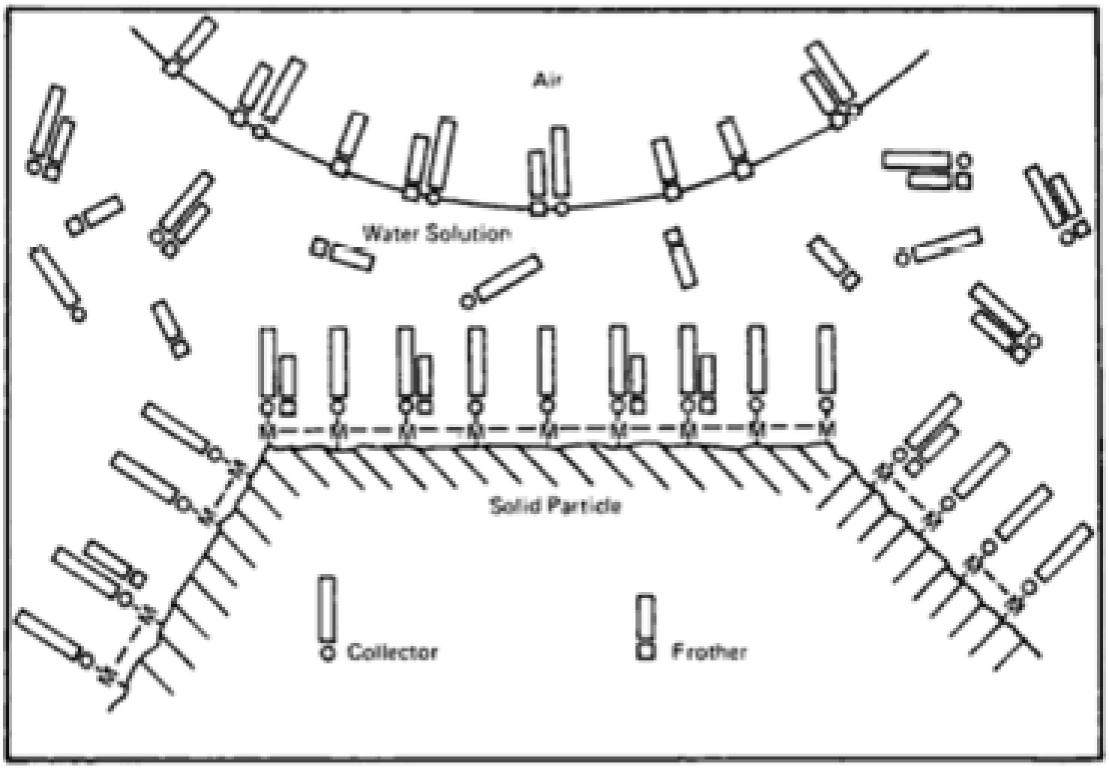


Figure 10: Formation of diffuse monolayers at both air-water interface and solid-water interface (Leja & Schulman, 1954)

Figure 10 shows the distribution of collector and frother molecules at interfaces and in solution as an air bubble and a particle approach one another. Diffuse monolayers of both associated and unassociated frother and collector molecules are present at both the air-water interface and at the solid-water interface, in equilibrium with the bulk solution. At the solid-water interface collectors are irreversibly adsorbed and frother molecules are free to adsorb and desorb.

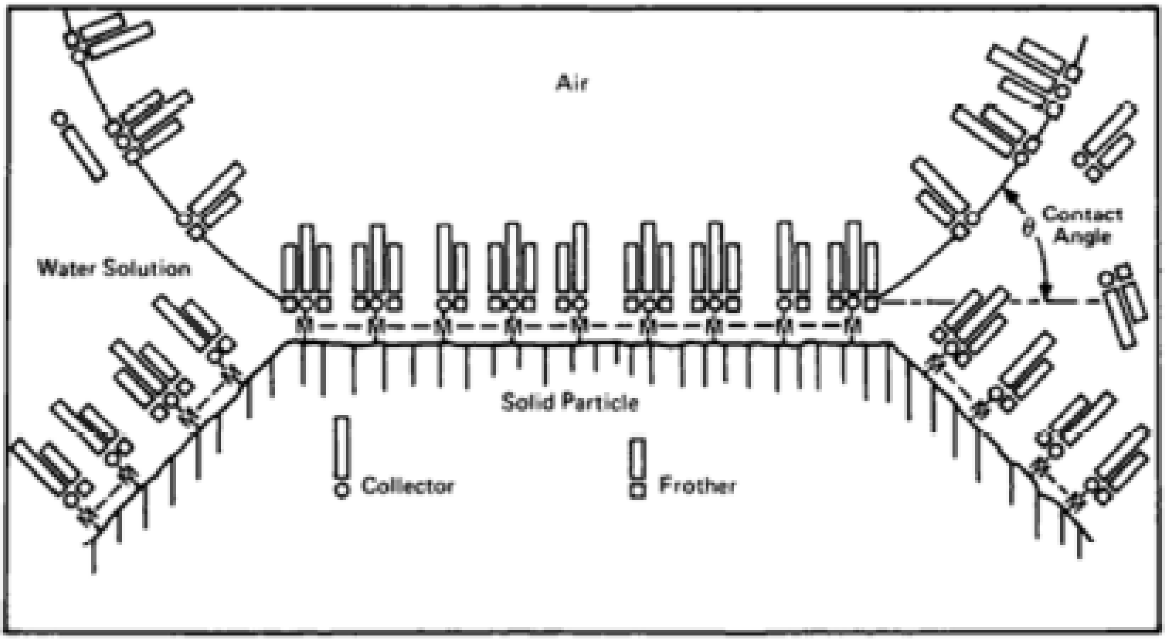


Figure 11: Formation of condensed mixed monolayers on the mineral surface, post bubble-particle collision(Leja & Schulman, 1954)

At the time of bubble particle collision, the collector-frother molecules can penetrate the diffuse monolayer at the solid and adsorb strongly at the solid-water interface. The mixed monolayer of surfactants becomes more condensed, stabilising the bubble on the surface and enhancing hydrophobicity.

Bubble adherence can be prevented if the films at the two interfaces are too highly condensed. This could be an explanation as to why overdosage of frothers and collectors lead to decreased hydrophobicities or flotation rates.

This theory supports the traditional theory that frothers attach at the air-water interface and collectors attach at the solid-water interface, which renders the particle hydrophobic and floatable. As mentioned in Section 1.4.5, the surface species on the mineral surface possibly hinders the adsorption of collectors necessary for the penetration theory, shown in Figure 10 and Figure 11, to occur.

Various authors have shown a possible synergistic effect between collectors and frothers. This is shown in Table 3, focusing on various xanthates and mostly alcohol frothers (adapted from Bradshaw, Harris & Connor (1998). Leja & Schulman (1954) indicated that there is an improvement in froth volume upon the addition of a xanthate to alcohol frothers. Lekki & Laskowski (1971) showed another xanthate – frother interaction where increasing α-terpinol concentration improved the total recovery, rate of recovery and the amount of ethyl xanthate adsorbed. Furthermore, Harris (1982) observed an increase in contact angle of butyl xanthate on galena with frother present. Crozier & Klimpel (1989) were able to reduce total collector dosage by 40% with minor addition of MIBC (sacrificing the purity of the concentrate). Hadler et al. showed that up to 20% of frother was adsorbed onto solid surfaces (PGM ore) in the presence of SIBX, but the frother remained in solution with no collector present, suggesting that the collector somehow facilitates frother adsorption onto the mineral surface.

Manev & Pugh (1993) studied the interactions of a collector and a frother in two-phase. They found that increasing SIBX concentration with alcohol frothers present reduced film thickness (which would allow better bubble-particle adherence) and reduced surface tension. This is due to the mixture of surfactants providing better electroneutrality across the bubble film and the authors also link the film thinning ability of xanthate to anti-foaming effects.

This is not supported by Leja & Schulman (1954) who found that xanthate improved froth stability upon addition to alcohol frother, with a more pronounced effect at higher alcohol carbon chain length. El-Shall, Abdel-Khalek & Svoronos, (2000) indicate that the ionization of the surfactant is important to achieve synergy. Synergistic effects between a fatty acid/fuel oil collector and a non-ionic, PPG frother were evident in column flotation of a Florida phosphate but the opposite (antagonistic) effect was achieved when the PPG frother was replaced with an anionic frother (sodium alkyl ether sulfate).

Mineral surfaces and bubbles are both charged, often negatively. Therefore, bubble-particle collision is likely to generate further electrostatic repulsion. In a natural flotation system, charges must be redistributed in overlapping electric double layers before film thinning and rupture can occur, and this requires time. In the presence of a frother with a dipole, the repulsion of identical charges can be instantaneously reversed by polarization of the dipole (Leja & He, 1984).

Table 3: Collector-frother synergy

Reagents	Study type	Findings	Authors
Ethyl xanthate + alkyl alcohols	Froth stability with chalcocite	Enhanced frothability upon the addition of xanthate to alcohols	Leja & Schulman, 1954

Ethyl xanthate + α-terpinol	Batch flotation of chalcocite	Increased recovery with increasing frother dosage with xanthate	Lekki & Laskowski, 1971
Ethyl xanthate α-terpinol	Batch flotation of chalcocite ore	Increased recovery due to joint frother-collector interactions	Lekki & Laskowski, 1975
Butyl xanthate + 41G	Contact angle on galena	Increased contact angle upon addition of frother to xanthate	Harris, 1982
Xanthogen Formate + MIBC	Batch flotation; plant practice with Chilean copper sulphide ore	Reduced collector dosage by 40% to achieve same recovery	Crozier & Klimpel, 1989
Ethyl X + alkyl alcohols	Film thickness and surface tension	Reduced film thickness and surface tension with increasing addition of X	Manev and Pugh, 1993
SIBX + PPG frother	Batch flotation on South African PGM ore	Up to 20% frother adsorbed by solids in the presence of SIBX	Hadler et al., 2005

The literature provides very little insight regarding collector-frother interaction with DTP as the collector. Recent research at UCT indicates that, in terms of foamability, DTP performed best as a foam stabilizer, better than xanthate or DTC (Nyambayo, 2014). This was also shown in 3-phase. Microflotation recovery of pyrite when only SEDTP was used (11.6%) (Taguta 2015) is very low. Castelyn (2012) used 15 ppm PPG frother throughout the microflotation experiments, thus showing an improvement in pyrite recovery from 59.1% to 67.9% when SEDTP was added.

1.4 Objectives of research

The overall objective of this research was to investigate the role which dialkyl dithiophosphates play in affecting the flotation process. In order to evaluate these effects a variety of ores and experimental procedures were used as described in Chapter 2 (Experimental Procedure) below.

The specific objectives addressed as part of this overall project were:

1. To determine the effect that DTP has on surface tension when used:
    a. As a single reagent
    b. In mixtures with other reagents
2. To determine the effect that DTP has on froth stability when used:
    a. As a single reagent with or without solids present
    b. In mixtures with other reagents, both with and without solids present
3. To determine the effect that DTP has on the recoveries of sulphide minerals in a microflotation cell. In these tests DTP was used in conjunction with xanthate and a frother.
    a. To determine the effect pH had on the floatability of pyrite at different reagent conditions
    b. To determine whether the reagent interactions observed were mineral-specific by introducing a second mineral, galena.
    c. To determine the effect of frother type, viz. PPG and alcohols with different alkyl chain lengths

1.5 Key questions

These objectives were set in order to address the following key questions:

1. Does the addition of DTP cause a decrease in bubble surface tension? This would indicate the presence of DTP at the air-water interface.
2. How do DTP-reagent interactions affect the foam and froth stability?
3. Does DTP enhance the microflotation recovery of pyrite or galena, either when used alone or in combination with other reagents?
4. How do different frother types (e.g. different alkyl chain lengths) change the effectiveness of DTP with regards to synergistic improvement in microflotation recovery, i.e. is the collector-frother interaction specific for certain frothers?
5. Are reagent effects mineral-specific?
6. Does the pH affect the performance of the reagent?

1.6 Hypothesis

SEDTP plays a role as a surfactant at both the air-water interface and at the solid-water interface and this results in improved bubble-particle attachment in the presence of a frother. Although SEDTP is an anionic collector, the very low pKa of DTP indicates that it is a better surfactant at the air-water interface than SEX. The presence of a frother and a collector reduces electrostatic repulsion between reagents at both the air-water and solid-water interface and enhances bubble-particle attachment.

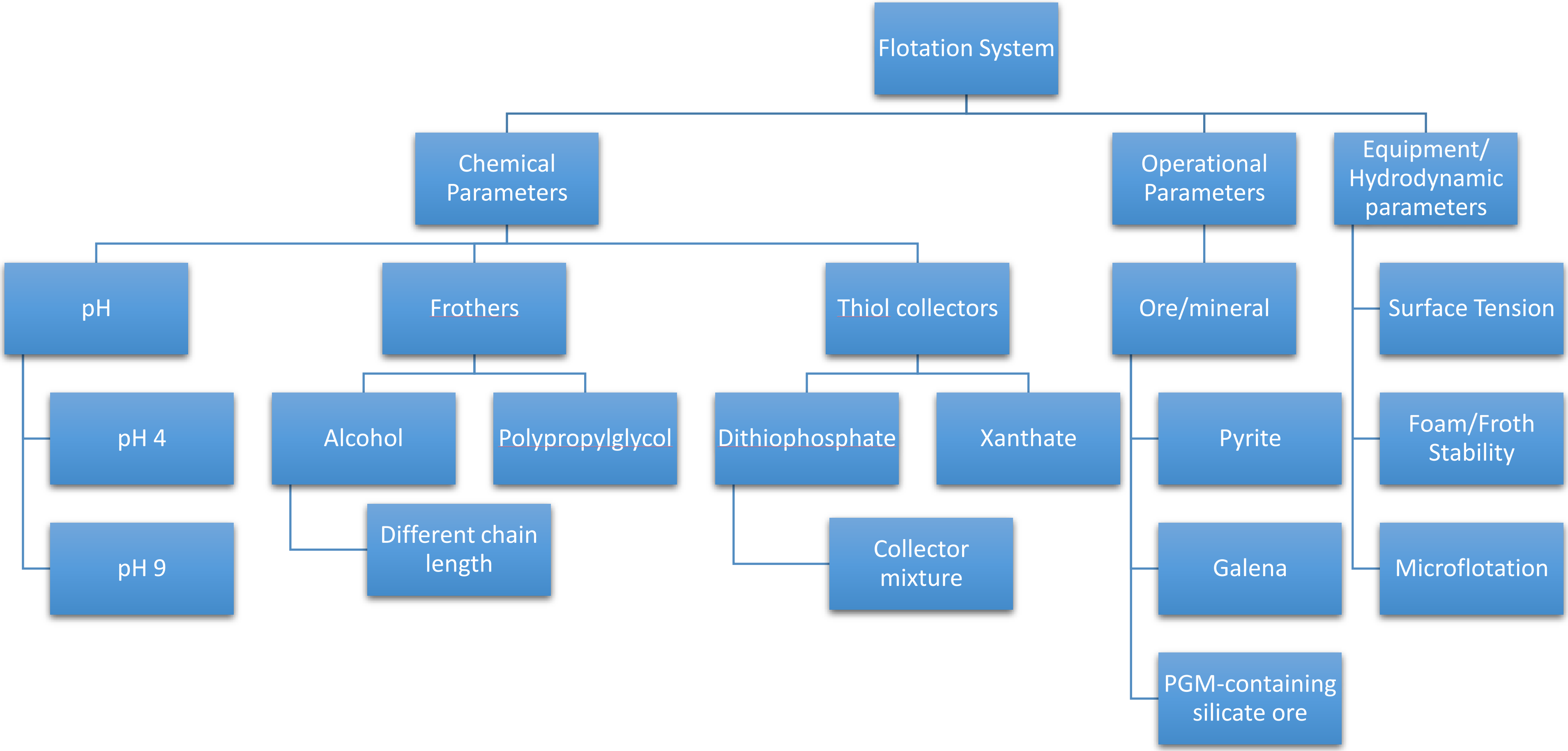
1.7 Research methodology

In order to test these questions/hypotheses a structured experimental programme was carried out. Table 4 shows the approach that was used.

Table 4: Research methodology

Key question	Experimental approach	Analysis of Results
Does the addition of SEDTP cause a drop in bubble surface tension?	Initial tests were done using a bubble pressure tensiometer (BP2). These experiments were aimed at testing the effect of the addition of SEDTP in mixtures containing SEDTP, SEX and frother in synthetic plant water and deionized water. The concentrations of the reagents varied from 5-150 mM. The pH was held constant at 9. The temperature was kept constant by a water bath.	Slight changes in the surface tension would indicate that DTP has properties similar to those of frothers. This would indicate that SEDTP is active at the air-water interface
Does the addition of SEDTP increase the froth stability?	These experiments were set up to test the effect of DTP on froth stability using a frothing column. This was done by testing mixtures of SEDTP, SEX and frother in synthetic plant water. The air flow rate, pH and concentrations were kept constant (except in mixtures containing both SEX and SEDTP). The experiments were done without solids present and with solids present in the form of a PGM-containing silicate ore.	Changes in froth stability would indicate that SEDTP has a frothing effect.
Does the addition of SEDTP increase sulphide mineral recovery?	These experiments were set up to determine the recovery of pyrite and galena using a microflotation rig. Reagent mixtures contained SEDTP, SEX and various types and chain lengths of frothers. pH was kept constant at either pH 4 or 9. Air flow rate and reagent concentrations were kept constant as well.	Changes in mineral recovery when using SEDTP would indicate that SEDTP enhances pulp mineral hydrophobicity..

1.8 Scope of thesis



2. Experimental Procedure:

This chapter describes how the behaviour of reagents at different interfaces using bubble pressure tensiometry, froth stability measurements and microflotation recoveries was investigated. Each of these experimental techniques provide valuable information on certain aspects of the different interfaces. As explained in Chapter 1 the aim of the thesis is to identify why SEDTP is able to increase the recovery of a mineral in certain cases, but does appear to adsorb to any significant extent onto various sulphide minerals (McFadzean and O'Connor, 2014; Taguta, 2015). A PGM-containing silicate ore was used for the froth stability tests and pyrite for the microflotation. Experiments were designed to elucidate the effects of single reagents as well mixtures to introduce synergistic effects.

Bubble pressure tensiometry was used to identify the effect of SEDTP and its mixtures on surface tension. Surfactants which preferentially adsorb at a gas–liquid interface reduce the interfacial surface tension, reducing bubble size and coalescence. A reduction in surface tension would indicate the reagents are attaching at the air-water interface. This would explain why SEDTP does not indicate adsorption onto certain minerals yet improves their flotation – it improves the froth stability.

As the decrease in surface tension indicates an increase in froth stability (Sweet et al., 1997), frothing column tests would be important to link the bubble pressure tensiometry results closer to a "real" flotation situation. Furthermore, the experiments were done in two-phase as well as in three-phase with ore present. The difference between two- and three-phase froth stabilities further clarified the behaviour of the different reagents at the air-water interface and solid-liquid interface.

Microflotation tests were performed to observe the pulp-phase floatability of pyrite since there is no froth phase present in such tests. The objective was to identify the difference in recoveries between different reagents and mixtures, primarily concerning those with SEDTP present. This was to give an indication of how SEDTP behaved with SEX and a frother present. Where SEDTP and SEX were both present in a mixture, a molar ratio of 90:10 was used.

2.1 Ore samples

2.1.1 Pyrite and Galena

Pyrite and galena samples were received from Wards Natural Science Establishment, Rochester NY in variably sized chunks. These chunks were manually hammered to smaller pieces (3cm), then pulverized for 20 seconds to further reduce the size fraction. The ground mineral was screened to +38 µm-106 µm. A sample of the mineral was sent for BET surface area analysis in order to determine the surface area, which is used to determine collector concentration. This size fraction was used for microflotation. These samples were stored under nitrogen in a desiccator in an attempt to prevent surface oxidation.

2.1.2 PGM-containing silicate ore

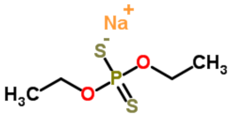
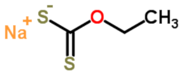
A PGM-containing silicate ore was obtained and was milled according to previous particle size distribution curves done on the same ore. Using a rod mill, 1 kg of ore was wet-milled with 2 l of water for 22 minutes to achieve 60 % of particles passing 75 microns.

2.2 Reagents

2.2.1 Collectors

The collectors used in this study were provided by Senmin (Pty) Ltd. South Africa. Xanthates were received as pellets whereas dithiophosphate was received in a high pH solution. The high pH stabilizes the dithiophosphates. Reagents were prepared in a stock solution with deionized water. The collectors used in the experiments are given in Table 5.

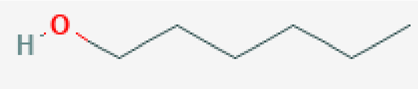
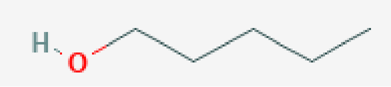
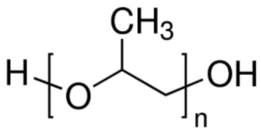
Table 5: Details of collectors used in experiments

Name	**Abbr.**	**Molecular Weight (g/mol)**	**Chemical Structure**
Sodium ethyl xanthate	SEX	144	
Sodium di-ethyl dithiophosphate	SEDTP	208	

2.2.2 Frothers

Senfroth 200 (SF 200), a polypropylene glycol was used as a frother throughout. Whenever it was used, the concentration was above the critical coalescence concentration, the concentration above which no further bubble size reduction occurs. For specific microflotation experiments, a variety of frothers were used, listed in Table 6.

Table 6: Different frother types used for microflotation experiments. Throughout all other experiments, SenFroth XP 200 was used

Frother Type	Molecular Weight (g/mol)	Chemical Structure	Purity (%)
1-hexanol	102.17 g/mol		100
1-pentanol	88.15 g/mol		100
SenFroth XP 200	205.40 g/mol		98
PPG 425	425 g/mol		100
PPG 725	725 g/mol		100%

2.3 Solution conditions

Synthetic plant water (SPW) was used in all experiments except bubble surface tensiometry where deionized water was used (DIW). The synthetic plant water was made by dissolving salts in DIW to give the ionic concentrations presented in Table 7.

Table 7: Concentration of ions in synthetic plant water

Ion	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}**	**Cr^{3+}**	**SO_4^{2-}**	**NO_3^{-}**	**NO_2^{-}**	**CO_3^{2-}**
Concentration (ppm)	80	80	35	270	250	135	40	40

The pH at which the experiments were conducted was either 4, 7, 9 or 11. This was done by adjusting the solution's pH (after reagents and solids were added) with 0.1 M HCl and 0.1 M NaOH

2.4 Bubble Pressure Tensiometry

Figure 12: Kruss BP2 surface tensiometer

Figure 12 shows the Kruss BP2 surface tensiometer used to carry out the experiments. This instrument is connected to a computer controlling the parameters and recording the data as well as a water bath to keep the temperature constant. Synthetic air is fed to the tensiometer via a gas line. For bubble pressure tensiometry experiments, a 100 ml solution was made up in a volumetric flask with reagents added from a stock solution and DIW. The experiments were run at a pH of 9 (adjusted by NaOH and HCl) as well as 4, 7 and 11 at the upper limit of the concentration ranges.

After 6 minutes of conditioning time, the solution was transferred to the vessel and put in the Kruss BP2 Tensiometer. A silanised, hydrophobic capillary was attached in its holder. Once the vessel reached the constant temperature of 25.5ºC ±0.5ºC, the vessel was lifted manually by turning a knob to get it close to the capillary. Hydrostatic pressure of the capillary depth is kept constant by detecting the surface whilst the capillary is at an uppermost position, thereby lowering it a constant amount into the solution. The instrument components are enclosed to prevent possible contamination. Using the software loaded onto the computer, a surface age over 10-1000 msec was measured and stored as Excel files for further analysis.

To get a significant surface tension response, the reagent dosages had to be increased significantly compared to that used at an industrial scale. Measurements were done over a range of concentrations: 5-100 mM.

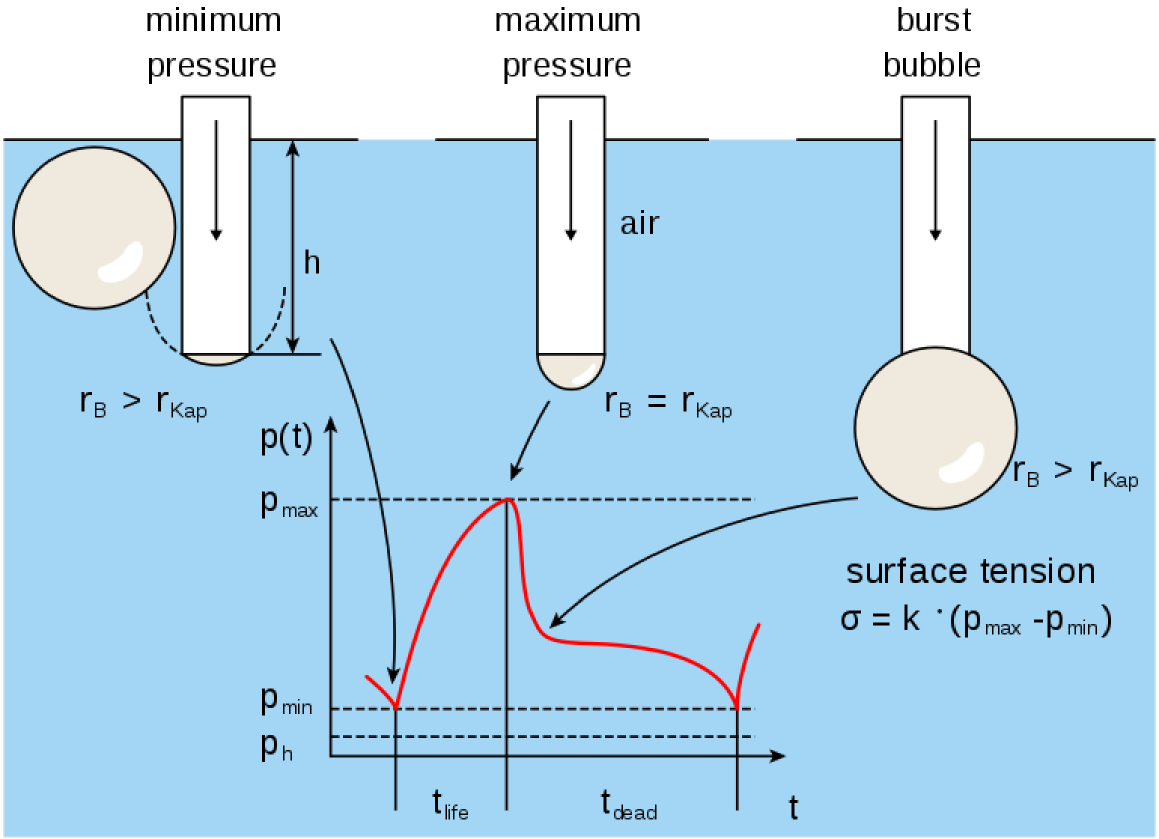


Figure 13: Schematic description of how surface tension is recorded

Figure 13 shows the way that the surface tension of a solution is recorded using bubble pressure tensiometry. The system is constantly under hydrostatic pressure, (p_h) resulting from submergence of the capillary in the liquid, which remains constant. Bubble lifetime (t_{life}) starts when bubble radius (r_B) starts to increase, resulting in increasing pressure. Maximum pressure (p_{max}) is reached when bubble radius reaches capillary radius (r_{Kap}), after which "dead" time ensues. The change in pressure during bubble growth up to $r_B = r_{Kap}$ is used to determine the surface tension, shown in Equation 1.

$$\sigma = k \cdot (p_{max} - p_{min})$$

Equation 1

2.5 Frothing Column

The effect of reagent addition on two-phase and three-phase systems was investigated using a froth stability column shown in the Figure 14. The column was made of Perspex and had a diameter of 10 cm and a height of 1 m and was fitted with a 40- 100 μm sized pore frit to ensure even gas distribution within the rig.

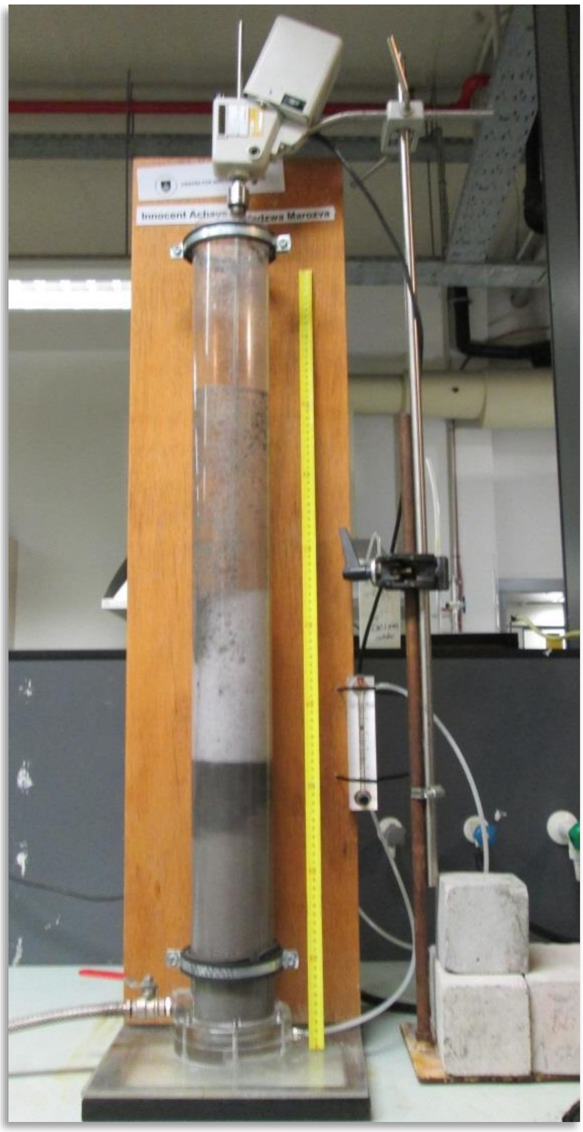


Figure 14: Frothing column setup

For each two-phase experiment the reagents were added to a 100 ml volumetric flask and conditioned for 6 minutes, except for the frother, which was only conditioned for 3 minutes (if collectors and the frother were both present in a mixture, the collector(s) would be conditioned for 3 minutes), the frother would be added, then the mixture would be conditioned for a further

3 minutes. This procedure was followed for the three-phase experiments (with the pulp in the bucket) and microflotation.

For each three-phase experiment, 1 kg of ore was wet-milled in a tumbling mill for 20 minutes to reach 60% passing 75 µm. This was quantitatively transferred to a feed tank and pulp density of the slurry was lowered to 30% solids by weight by adding more SPW. The solution was pumped from the feed tank into the frothing column using a peristaltic pump. An impeller was positioned in the solution in the frothing column and turned on.

At t_0 (time=0s) air flow was turned on at rate of 6l/min. At the times (s): 10, 20, 30, 40, 50, 60, 80, 100, 120, 150 and 180 the froth height was marked. The froth height recorded from the pulp-froth interface. After the final froth height was marked, the air was turned off and the froth collapse was measured at 2s intervals until there was no froth phase present.

The reagent dosages were calculated according to the general industrial application. For SEDTP and SEX this translates to 0.2 mM and 50 ppm for the frother. Where SEDTP and SEX were used together, their total concentration summed to 0.2mM (0.1mM each)

2.5.1 Calculating Froth Stability

Froth stability (Σ) was calculated according to Equation 2, from Bikerman, (1973):

$$\Sigma = \frac{Hmax}{Jg}$$

Equation 2

Where: $Hmax$ is foam/froth maximum equilibrium height (cm), and Jg is superficial air velocity, which is calculated by using the known dimensions of the frothing column.

2.6 Microflotation

Mass recovery of pyrite and galena was measured using a UCT microflotation rig, shown in Figure 15. Mass recovery was used as a proxy for hydrophobicity and thus contact angle.

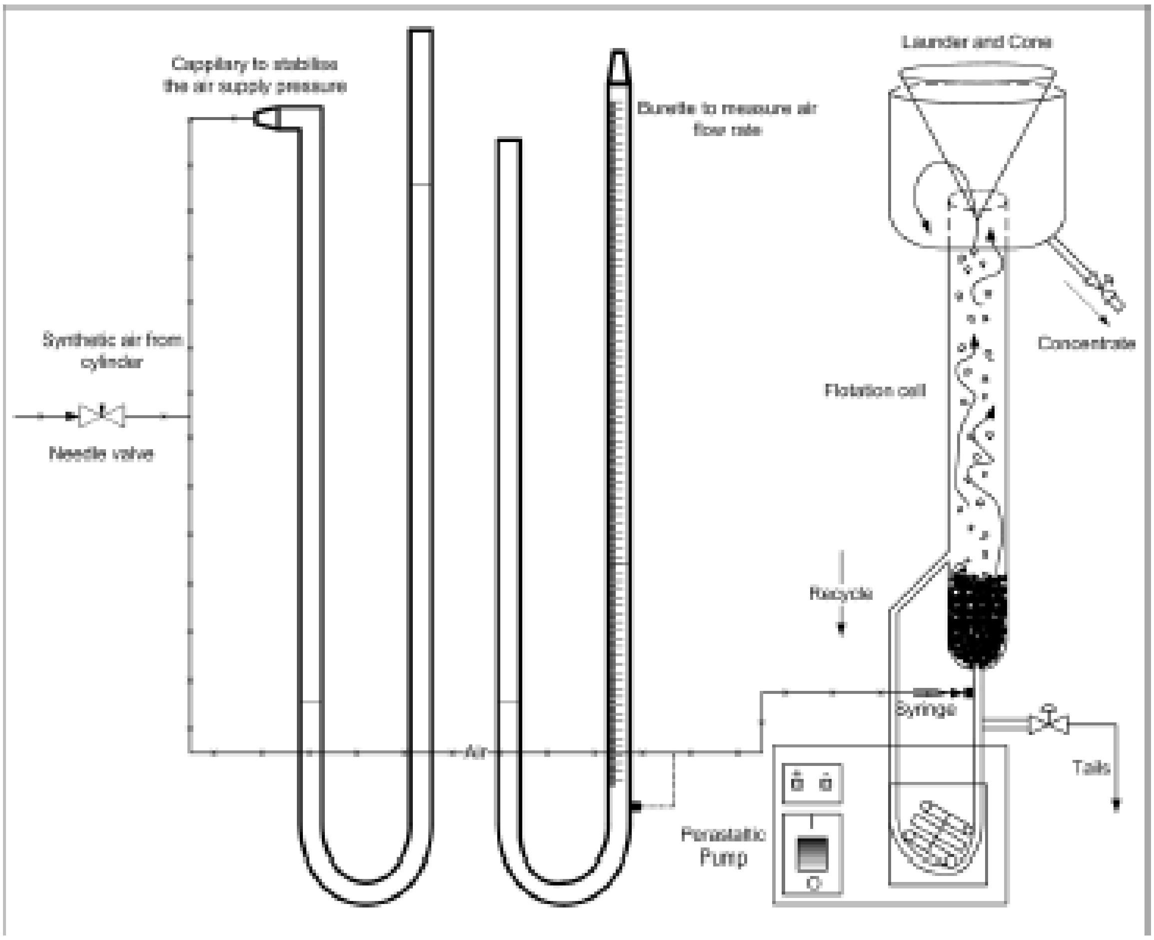


Figure 15: UCT microflotation rig used for the investigations (Bradshaw & O’Connor, 1994)

For each experiment, 2g of mineral (pyrite or galena) was weighed. The mineral contacted with 0.1M HCl for 6 minutes to remove surface oxidation. The solution was centrifuged for 6 minutes at 4000 rpm, after which the excess liquid was poured off. Water was added to the mineral and once again centrifuged for 6 minutes at 4000 rpm, after which the excess liquid was poured off. The mineral was quantitatively transferred to an Erlenmeyer flask containing the reagents. This solution was stirred for 6 minutes (frother was added after 3 minutes) to condition the reagents in the solution. To remove any agglomerates that may have formed during the preparation of the solution, the flask was placed in an ultrasonic bath for 30 seconds. This solution containing the mineral was then quantitatively transferred into the microflotation rig using SPW. The peristaltic pump was turned on and the water level was brought to the 350 ml mark with SPW. The pH was measured and adjusted to either pH 4 or 9 in the microflotation cell using 0.1 M HCl and 0.1 M NaOH.

Synthetic air was supplied from a gas cylinder. To ensure the air flow remains constant, the air flow was regularly checked, before and after experiments. After the gas was turned on, the needle supplying the air flow to the microflotation cell was allowed to rest in a beaker filled with water until there was a visible, strong and constant stream of bubbles being emitted. If the syringe was blocked, the syringe needed to be removed and sonicated for 30 minutes, after which any water still in the syringe would need to be blown out. Once a constant stream was attained, the needle was inserted into a needle valve on a burette to induce the back-pressure the system would experience during an experiment. After 10 minutes under the back-pressure, the air-flow rate was measured in a similar burette with a needle valve and a U-bend. The air flow was checked at regular intervals as well as before and after the experiments to ensure the recorded air-flow rates were constant. Q values between 6 and 7 ml/minute were accepted.

Concentrates were collected quantitatively at 2, 6, 12 and 20 minutes for pyrite and 2, 6, 12 and 24 minutes for galena. Concentrates and tails were separately filtered onto pre-weighed, dried filter paper and placed in an oven at 110 ºC for 8 hours. The weights were measured and recorded.

2.6.1 Collector dosage

Microflotation is a process where the operator is able to control the variables affecting the true flotation of solids. The dosage of reagents is highly important in this aspect, and therefore the total collector dosage is an important parameter to establish. If the concentration is too low, there will be no flotation of solids beyond that of collectorless flotation, and if it is too high, it will hinder optimal flotation. Total collector dosage was calculated based on 50% pseudo-monolayer coverage, i.e. the amount of collector molecules required to cover half of the available surface of 2 g of pyrite.

Table 8:Collector molecule surface areas

Collector	Surface area covered by one molecule head (Å^2)	Reference
SEX	28.8	Grano, Prestidge & Ralston, 1997
SEDTP	35.4	Matsuoka & Ichikoku, 1982

BET surface analysis was done by Micromeritics in the chemical analysis laboratory at UCT. Using the BET surface area the mineral, and the surface area 1 thiol collector head occupies (in Table 8), the total collector dosage was calculated as shown in Table 9

Table 9: Calculation of collector concentration according to surface area occupied by a molecule of collector (SEDTP) and available surface area of mineral

Mass of pyrite (g)	2.000
Surface area of mineral (m^2/g)	0.377
Specific surface area of mineral (m^2)	0.753
One molecule collector head (m^2)	3.54E-19
Number of molecules required for 50% coverage	1.064E+18
Number of moles for 50% coverage	1.767E-06
Molecular weight (g/mol)	144.14
Collector mass for 50% surface coverage(g)	0.000255

All collector conditions were performed with and without a frother present for the minerals. SenFroth XP 200 was added at a concentration of 20 ppm. When the other PPG's and alcohol frothers were used, they were used in the same concentration

2.6.2 Calculating R_{max}

The raw data of microflotation recovery vs flotation time was modelled according to a modified Klimpel model (1984) which states that the flotation process was divided into two regimes, viz. a rate controlled and an equilibrium, or ultimate recovery controlled regime. Two constants, R and k, are used to describe these characteristics and can be obtained from the first order model of the recovery- time data shown in Equation 3

$$R = Rmax(1 - (1/(k * t))(1 - EXP(-k * t)))$$

Equation 3

The modelled and experimentally recorded values are depicted in Figure 16 and the constants R and k are shown in Table 10

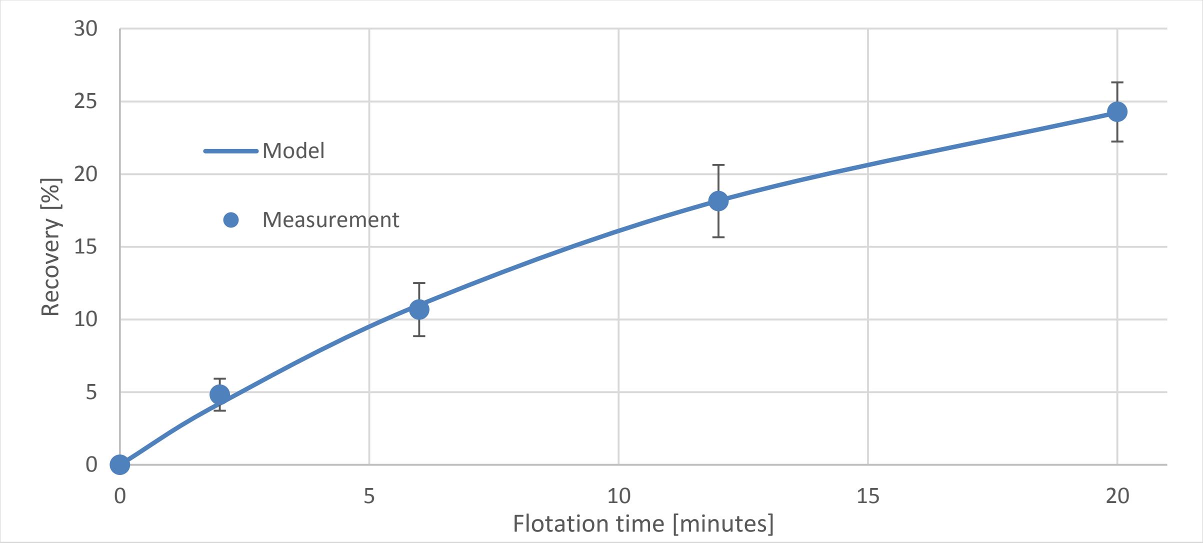


Figure 16: Depiction of the modelled data of the natural floatability of pyrite in microflotation.

Table 10: First order rate constant (k) and modelled recovery at infinite time (Rmax) for the natural floatability of pyrite

K:	0.11
Rmax:	40.12

2.7 Adsorption experiments

To test whether the collectors remained in the aqueous phase or attached at the solid-water or air-water interface, simple adsorption experiments were done. SEDTP concentration was measured using UV-vis absorption spectrophotometry.

2.7.1 Adsorption at the air-water interface

As is discussed in Section 1.4.5 and 1.4.6, there is reason to believe that SEDTP stabilizes frothability. For this to occur, SEDTP must adsorb onto bubbles which would rise into the froth phase, thus resulting in increased SEDTP concentration in concentrates compared to the pulp.

For the adsorption of SEDTP at the air-water interface, a batch flotation procedure was followed. Reagents were conditioned in SPW for 6 minutes prior to air flow being turned on, which signified t=0 min. Foam rising to the foam phase was collected into a launder every 15 seconds and different concentrates were taken at the following times: 2, 6, 12 and 20 min. the water level was kept at a consistent level and the dilution effect was accounted for. UV-vis calibration was done for SEDTP for which the characteristic wavelength was its peak around

227 nm (Petrus et al., 2011). Using this calibration at different concentrations, the concentration of SEDTP in each of the concentrates was determined.

2.7.2 Adsorption at the solid-water interface

As SEDTP is conditioned, it is free to adsorb onto the solid surface. The amount of DTP adsorbed onto solids can be quantified by measuring the residual SEDTP concentration in solution, which is the amount of SEDTP that did not adsorb onto the solid.

$$(1) SEDTP_0 = SEDTP_{ads} + SEDTP_{sol}$$

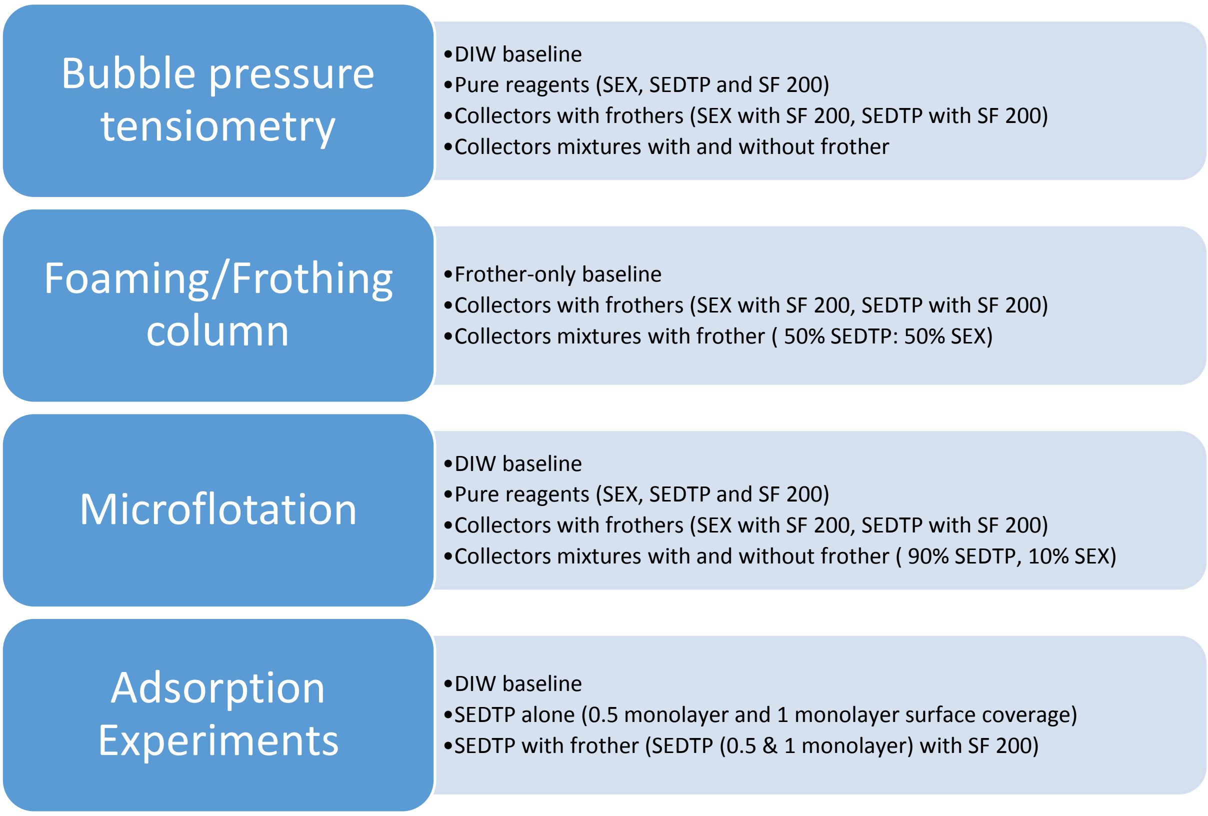
$$(2) SEDTP_{ads} = SEDTP_0 - SEDTP_{sol}$$

Equation 4

For the adsorption at the solid-water interface, the sample preparation for pyrite and reagent conditioning was the same as the microflotation experiments (Section 2.6). After 6 minutes of conditioning time for the reagents and solids, an aliquot was poured off and centrifuged. UV-vis spectroscopy of this sample would give an indication as to which collector is still in the aqueous phase and which had adsorbed, using calibration described in Section 2.7.1. The relevant concentrations are substituted in (2), Equation 4, where $SEDTP_0$ is the initial SEDTP concentration, $SEDTP_{ads}$ is the SEDTP concentration adsorbed onto the solid and $SEDTP_{sol}$is the residual SEDTP concentration in solution. As a control, a reagent-less sample of the liquid after the pyrite had been conditioned for 6 minutes was taken – this was used as a blank.

2.8 Experimental program

Figure 17 and Figure 18 explains schematically the overall experimental program used to address the key questions of the project. An initial baseline case where no response is to be expected were run; i.e experiments run with deionised water. The next step was to identify the interactions between collector and the frother, followed by collector-collector interaction with and without the presence of frother.



Bubble pressure tensiometry

- DIW baseline
- Pure reagents (SEX, SEDTP and SF 200)
- Collectors with frothers (SEX with SF 200, SEDTP with SF 200)
- Collectors mixtures with and without frother

Foaming/Frothing column

- Frother-only baseline
- Collectors with frothers (SEX with SF 200, SEDTP with SF 200)
- Collectors mixtures with frother (50% SEDTP: 50% SEX)

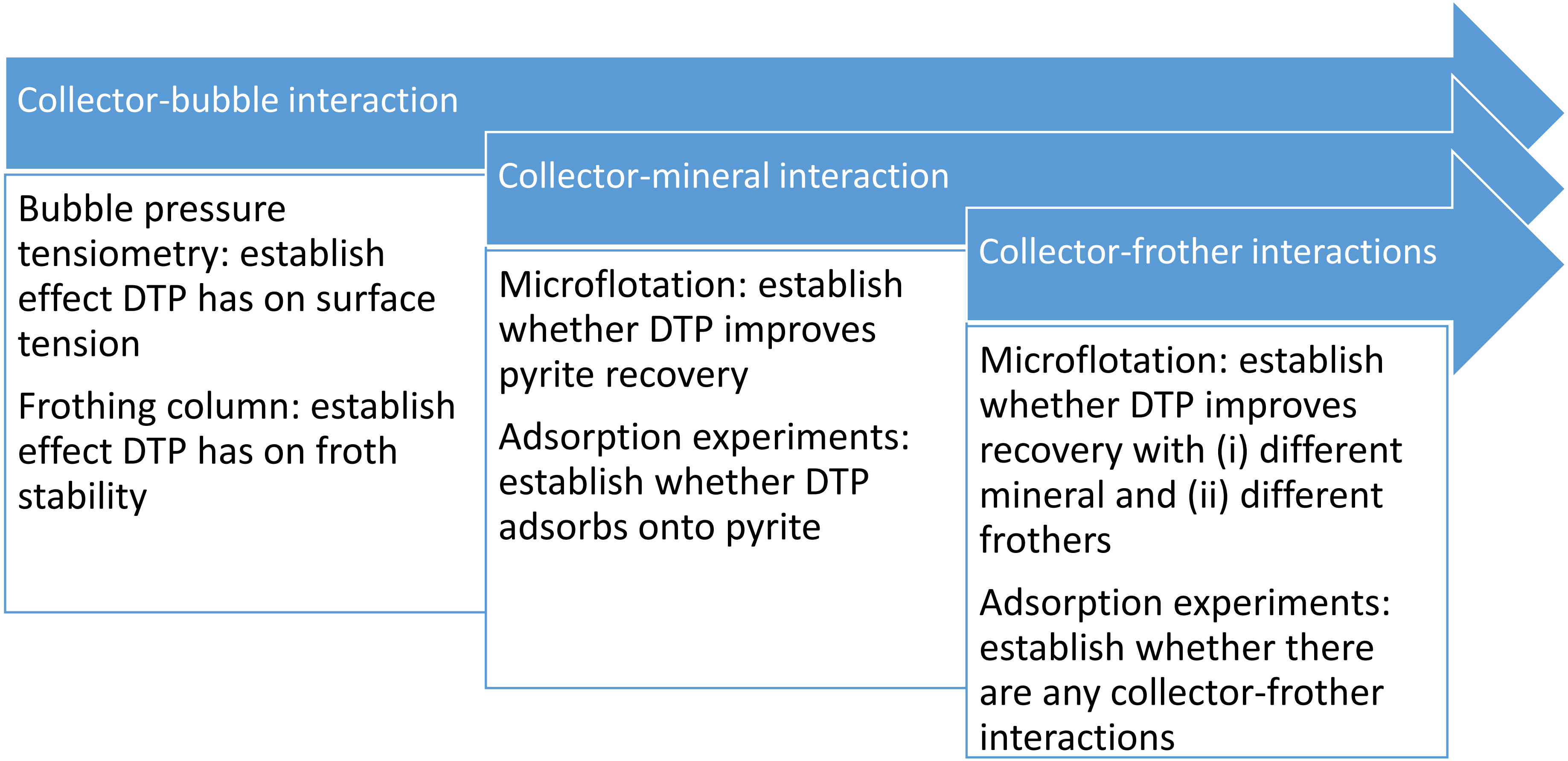
Microflotation

- DIW baseline
- Pure reagents (SEX, SEDTP and SF 200)
- Collectors with frothers (SEX with SF 200, SEDTP with SF 200)
- Collectors mixtures with and without frother (90% SEDTP, 10% SEX)

Adsorption Experiments

- DIW baseline
- SEDTP alone (0.5 monolayer and 1 monolayer surface coverage)
- SEDTP with frother (SEDTP (0.5 & 1 monolayer) with SF 200)

Figure 17: Experimental procedure



Collector-bubble interaction

Bubble pressure tensiometry: establish effect DTP has on surface tension

Frothing column: establish effect DTP has on froth stability

Collector-mineral interaction

Microflotation: establish whether DTP improves pyrite recovery

Adsorption experiments: establish whether DTP adsorbs onto pyrite

Collector-frother interactions

Microflotation: establish whether DTP improves recovery with (i) different mineral and (ii) different frothers

Adsorption experiments: establish whether there are any collector-frother interactions

Figure 18: Depiction of how the experimental results are interpreted

3. Results

3.1 Introduction

The results chapter of this thesis outlines surface tension, frothing column and microflotation studies carried out when using:

- Single reagents. These experiments served as a benchmark for assessing changes in performance when compared to reagent mixtures.
- Mixtures containing two or more reagents which could include a frother, xanthate or DTP. The xanthate was in the form of sodium ethyl xanthate (SEX) and the DTP was in the form of sodium diethyl dithiophosphate (SEDTP). Where both collector and frother was used, the collector(s) were conditioned with the solids first, followed by the addition of the frother.
- For microflotation experiments, frother type and chain length were investigated in conjunction with SEDTP.

This chapter is laid out to first focus on DTP at the air-water interface by looking at surface tension and two-phase foaming column results, thereafter also considering the solid-water interface by looking at three-phase frothing column and microflotation results.

3.2 Bubble pressure tensiometry

Surface tension experiments were done using a dynamic surface tension method – measuring the surface tension of the solution as a function of surface age. According to Kruss, the manufacturers of the BP2 tensiometer, an accurate equilibrium surface tension is established after 1000 ms surface age.

3.2.1 Bubble pressure tensiometry reproducibility

Bubble pressure tensiometry (BPT) experiments were done in triplicate, an example of the results of an experiment done in triplicate is shown in Table 11.

Table 11: Triplicate equilibrium surface tension measurements of SenFroth XP 200

Concentration [mM]	Surface Tension [dyne/cm]				Relative Standard Deviation [%]
	Run 1	Run 2	Run 3	Average	
0	72.40	72.40	72.40	72.40	0.00
5	68.61	68.54	68.50	68.55	0.08
25	63.84	63.95	63.84	63.88	0.10
50	61.56	61.53	61.53	61.54	0.03
75	59.89	59.93	59.86	59.89	0.06
100	58.94	58.91	58.87	58.91	0.06

The repeats of the BPT experiments show a high level of reproducibility. The different conditions were compared according to their standard deviations – this value determined whether the differences in results were significant or not. All the relative standard deviations for the bubble pressure tensiometry results are very low (≤ 0.10 %) and error bars are not visible on the graphs.

Further test work was done to ensure the pH did not affect the activity of the reagents. The highest concentrations tested in the BPT experiments were tested at three different pH's. The results of these experiments are shown in Table 12, which shows no variation of surface tension at the tested pH's.

Table 12: Equilibrium surface tension of DIW, frother, SEDTP and SEX at pH 7, 9 and 11. Each reagent concentration was 100 mM

pH	DIW	SF 200	SEDTP	SEX
7	72.96	58.50	68.94	72.68
9	72.97	58.70	69.00	72.68
11	72.98	58.71	69.01	72.70

3.2.2 Bubble pressure tensiometry results

Figure 19 shows the effect that increasing concentration of single reagents has on equilibrium surface tension. The frother reduces the equilibrium surface tension to a greater extent than that obtained for the two collectors. Increasing the SEX concentration showed no decrease in surface tension – the surface tension remained similar to that of deionized water (72.40 dyne/cm). Increasing SEDTP concentrations only slightly decreased the surface tension, which is more evident at higher concentrations (72.38 dyne/cm at 5 mM decreases to 68.42 dyne/cm at 100 mM). The reduction in surface tension is not as significant as in the case of the frother (58.91 dyne/cm at 100 mM), but more significant than that of SEX (72.68 dyne/cm at 100 mM).

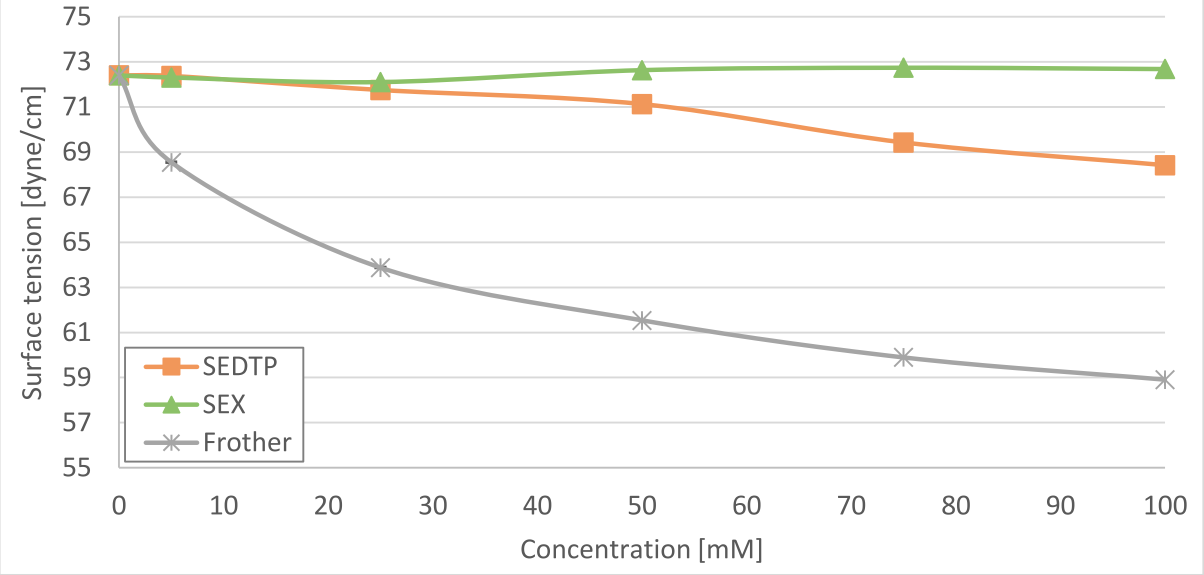


Figure 19: Equilibrium surface tension measurements at increasing concentrations of single reagents. Error bars are present but not visible due to high reproducibility

Figure 20 shows the effect that varying SEDTP concentration had on the surface tension of a mixture of reagents. SEX and frother concentrations are kept constant at 50 mM and 25 mM, respectively. As a baseline reference, the surface tension of 25mM frother is shown for comparison. At higher concentrations, both the mixtures shown in the figure decrease the surface tension slightly. The surface tension of SEDTP with frother is consistently lower than that of SEDTP with SEX and frother. This difference remains constant from 25-100 mM SEDTP. In addition, the surface tension of DTP with frother is lower than in the case of frother alone.

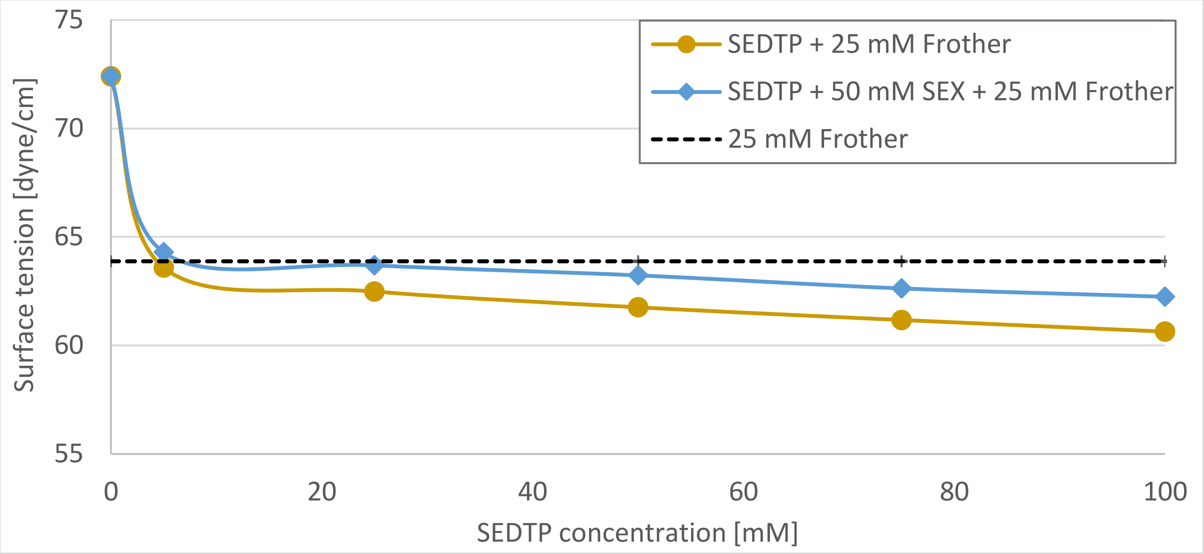


Figure 20: Equilibrium surface tension measurements of reagent mixtures at increasing SEDTP concentrations. Error bars are present but not visible due to high reproducibility

However, when considering the total surfactant concentration, the surface tension of the mixtures was consistently higher than that of any of the single reagents, apart from frother, shown in Figure 21. The mixtures (SEDTP + 25 mM Frother and SEDTP + 50 mM SEX + 25 mM Frother) lowered the surface tension across the concentration range greater than SEDTP or SEX, however the total surfactant concentration is higher than single reagents. Neither of the mixtures reduce the surface tension more than frother alone, even at the increased total concentration

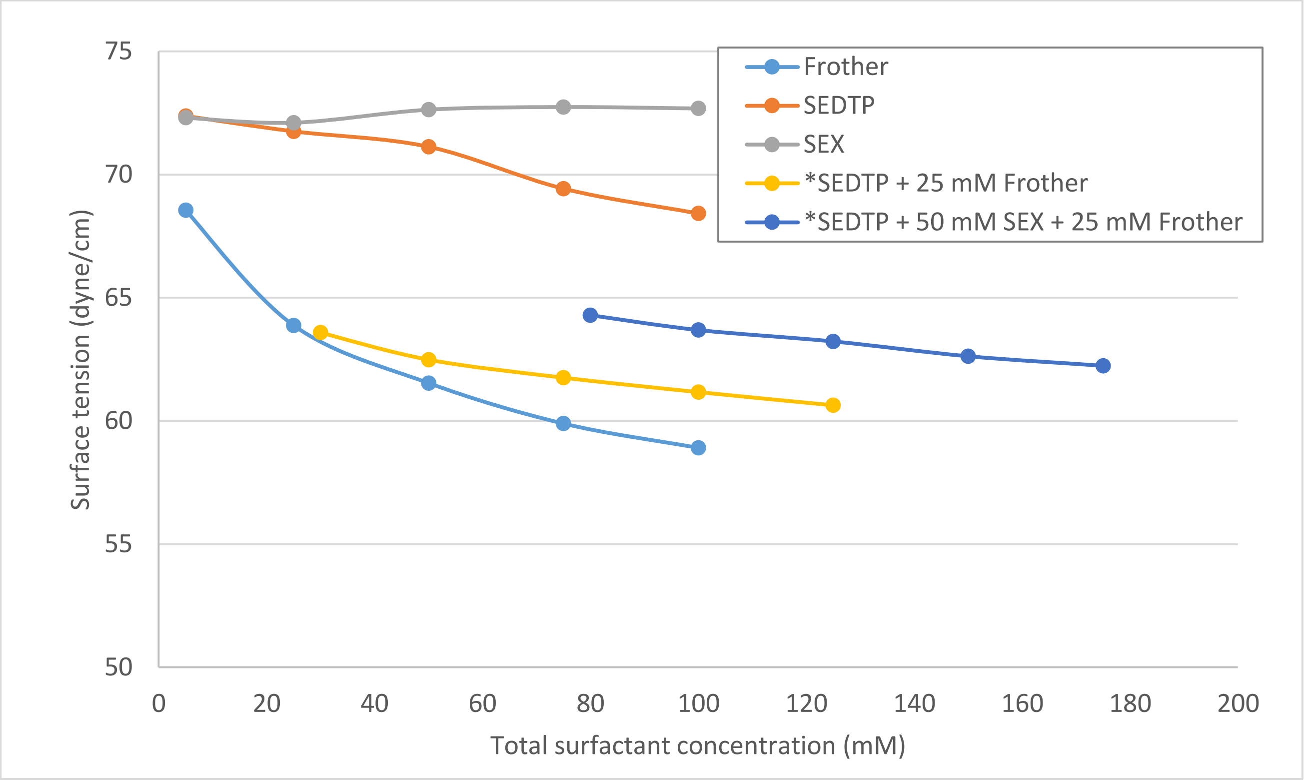


Figure 21: Surface tension of single reagents and their mixtures. For the mixtures, the total concentration was made up by *SEDTP component

3.3 Foaming/Frothing Column

3.3.1 Foam/Froth height measurements reproducibility

The frothing column was used to measure froth heights over time, i.e. the growth of the froth phase. The experiments were done in duplicate to ensure accuracy. An example of such an experiment is shown in Table 13.

Table 13: Froth height measurements of 100 g/t SEDTP with 50 ppm frother with an ore present up to 180 s (froth heights were measured up to 300 s)

Time [s]	**Froth Height [cm]**				**Standard Deviation**	**Relative Standard Deviation [%]**	**Relative standard error [%]**
	Run 1	**Run 2**	**Run 3**	**Average**			
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	18.3	19.4	20.0	19.2	0.9	4.5	0.5
20	29.4	30.5	30.7	30.2	0.7	2.3	0.4
30	35.9	37.0	36.7	36.5	0.6	1.6	0.3
40	39.0	41.5	42.3	40.9	1.7	4.2	1.0
50	43.2	45.4	45.8	44.8	1.4	3.1	0.8
60	46.4	48.0	46.0	46.8	1.1	2.3	0.6
70	48.7	49.6	48.6	49.0	0.6	1.1	0.3
80	50.5	50.4	49.4	50.1	0.6	1.2	0.4
90	52.6	50.4	51.0	51.3	1.1	2.2	0.7
105	53.5	51.6	52.0	52.4	1.0	1.9	0.6
120	54.2	53.0	52.9	53.4	0.7	1.4	0.4
140	56.3	54.6	52.9	54.6	1.7	3.1	1.0
160	56.3	55.3	54.2	55.3	1.1	1.9	0.6
180	56.3	56.0	54.8	55.7	0.8	1.4	0.5

Once again the difference in results in conditions was interpreted according to standard error: the error bars in the graphs show this value. If two different values fall within the error range of one another, the difference is deemed insignificant.

3.3.2 Foam/Froth stability calculations

Bikerman (1973) determined a dynamic stability factor of the foam/froth phase as a ratio of the equilibrium volume of foam generated to the gas flowrate. This is shown in Equation 5

$$\Sigma = \frac{V_f}{Q} = \frac{H_{max} * A}{Q}$$

Equation 5

Where:

V_f is the volume of the foam of froth,

Q is the gas flowrate,

H_{max} is the experimentally derived maximum equilibrium height and

A is the cross-sectional area of the column.

The equation describes the average bubble lifetime in the froth.

3.3.3 Foam stability results

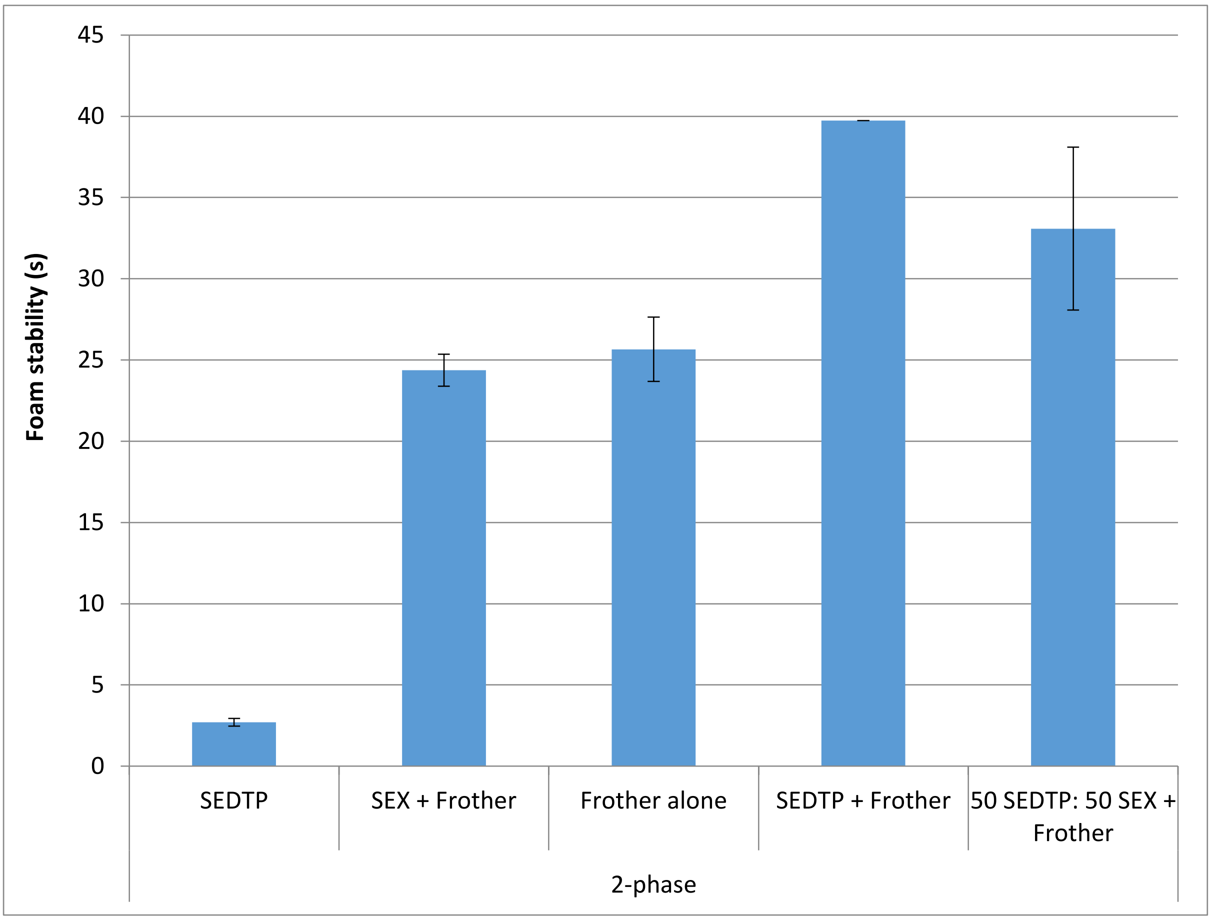


Figure 22: Foam stability of various reagents and mixtures in two-phase at 0.2 mM total collector and 50 ppm frother dosage

Figure 22 shows the measured foam stability values of mixtures containing frother with different collectors without solids present. SEDTP alone exhibited little foaming response, as shown by its low foam stability value (2.7 s). When a frother was introduced to the solution containing SEDTP, the foam stability increased beyond that of frother alone from 25.66 s to 39.73 s, i.e the result was greater that what would be expected from the individual contributions of each reagent. However, the foam stability of a mixture containing SEX and frother (24.37 s), did not improve upon the foam stability of frother alone (25.66 s). When both collectors were present with frother, there was still an increase in foam stability beyond that of frother alone but not to the same extent as SEDTP + frother.

3.3.4 Froth stability results

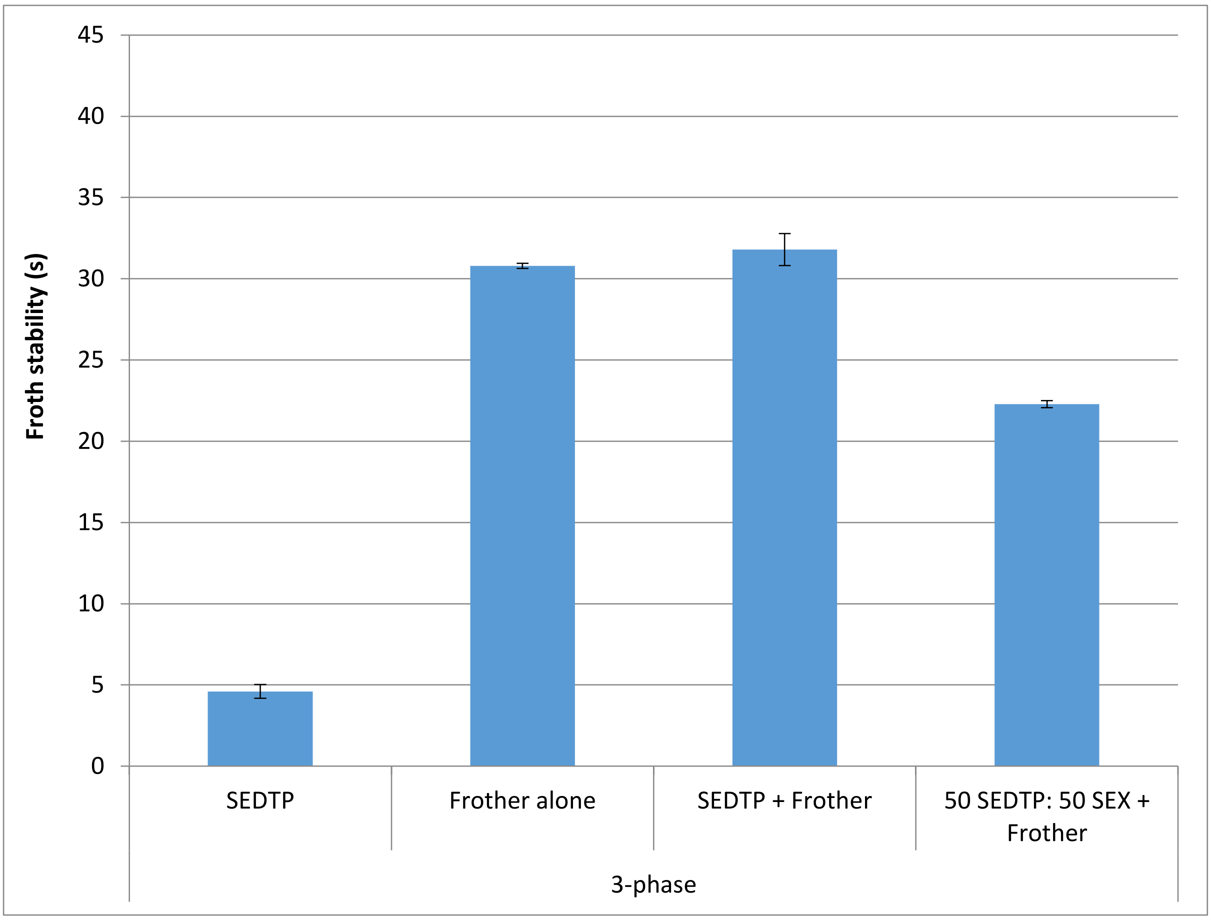


Figure 23: Froth stability of various reagents and mixtures in three-phase (using a PGM-containing silicate ore) at 0.2 mM total collector and 50 ppm frother dosage

Figure 23 shows the froth stability of various reagents and mixtures with solids present which in this case was a sample of a PGM-containing silicate ore. These are presented on the same graph as the 2-phase froth stability results, for comparison. As a single reagent, SEDTP showed little to no frothing ability, similar to its behaviour in 2-phase. However, unlike the 2-phase system, when frother was added to the solution containing SEDTP, there was no significant increase in froth stability beyond the froth stability of frother alone. When both SEDTP and SEX were combined with frother, there was a decrease in froth stability compared to the froth stability of frother alone.

3.4 Microflotation

The purpose of these experiments was to assess the pulp phase microflotation recovery of pyrite and galena, at pH 4 and 9 using synthetic plant water (SPW). All other conditions being constant, the mineral recovery is a reflection of the particle hydrophobicity when doing microflotation tests since there is no froth phase. In addition, bubble size is not dependent on frother addition in order to inhibit bubble coalescence, since there is a single stream of bubbles and not a bubble swarm. This has been shown in the work of Cho and Laskowski (2002). Reagent-less floatability of the respective minerals was used as the initial benchmark against which the single reagents were compared. When adding frother to solutions containing collectors, the flotation performance was compared to the flotation performance when using the single components. The collector dosages were calculated according to the surface area of the mineral, determined as described in Section 2.6.1.

3.4.1 Microflotation reproducibility

Microflotation experiments were carried out in duplicate and in some cases triplicate if the reproducibility was deemed insufficient (where the RSD>15%). Table 14 shows the cumulative recovery of three experimental runs when using 50% SEX surface coverage and the statistical evaluation thereof.

Table 14: Microflotation recoveries of pyrite in triplicate without any reagents.

Time [min]	**Cumulative Recovery [%]**				**Standard Error**	**Relative Standard Error [%]**
	Run 1	**Run 2**	**Run 3**	**Average**		
0	0	0	0	0	0	0
2	8.78	8.27	9.26	8.77	1.66	8.91
6	17.45	17.69	18.82	17.99	1.14	3.84
12	27.22	29.50	28.96	28.56	0.80	1.97
20	36.58	33.23	35.09	34.97	0.91	1.88

Throughout the experiments the standard error remained below 10% and thus indicated good reproducibility, with a few exceptions. Where the relative standard error was above 15%, the air flow rate had dropped during an experiment. In such cases the experiments were repeated in triplicates and in some cases even quadruplicates until the relative standard deviation dropped below 15%.

The error bars shown in the graphs indicate the standard error. This helps interpret the level of significance of differences in recovery. If the standard error of two results overlapped, their difference is not deemed significant.

3.4.2 Microflotation of pyrite

3.4.2.1 Microflotation of pyrite at pH 9

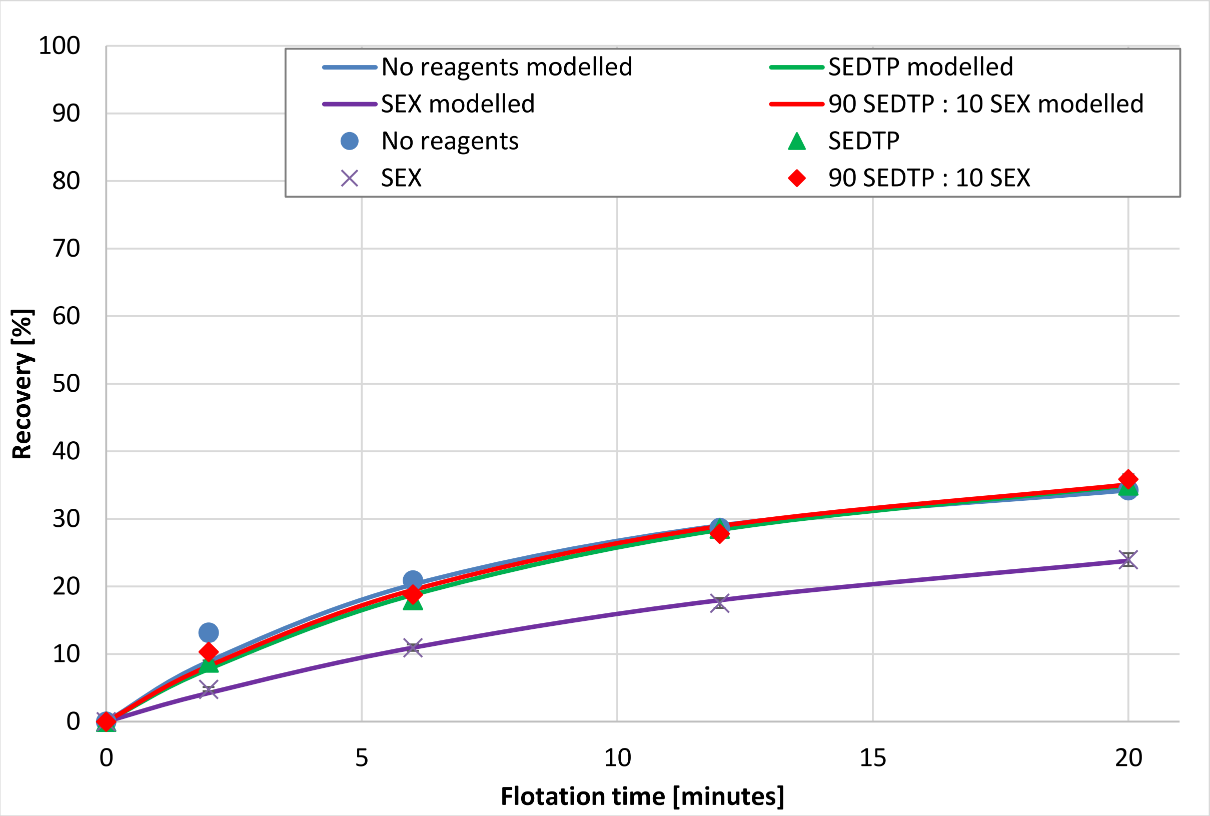


Figure 24: Microflotation recoveries of pyrite with two single collectors and their mixture, pH 9. Reproducibility was high, making the error bars invisible.

Table 15: Total mass recovery of pyrite and 1st order rate constants for given reagent condition, pH 9

Condition	Final Mass Recovery [%]	1st order rate constant [min^{-1}]
No reagents	34.27	0.24
SEX	23.98	0.12
SEDTP	34.97	0.18
90 SEDTP: 10 SEX	35.86	0.20

Figure 24 shows the recovery of pyrite using the two collectors and their collector mixture only, at pH 9. It is clear that SEDTP (34.97%) did not increase the recovery of pyrite beyond its natural floatability (34.27% reagent-less recovery). There is also very little increase observed when SEX is combined with SEDTP (35.86%). The 90 SEDTP:10 SEX nomenclature refers, throughout this dissertation, to a mixture of a mole ratio of 90% SEDTP mixed with 10% SEX. Furthermore, in the case of SEX, the recovery (23.98%) was lower than that of the reagent-less recovery (34.27%).

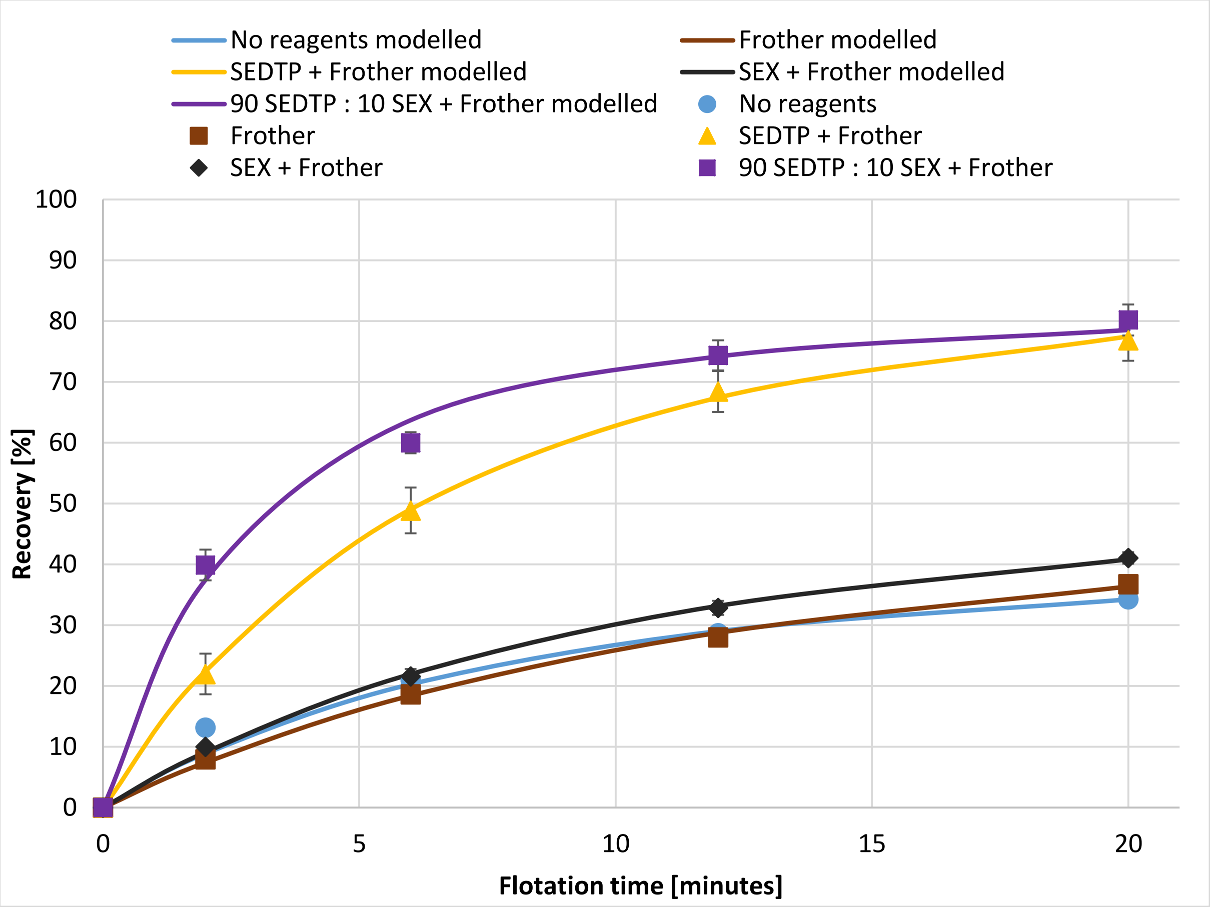


Figure 25: Microflotation recoveries of pyrite with two collectors and their mixture, each combined with a frother, pH 9

Table 16: Total mass recovery of pyrite and 1st order rate constants for given reagent condition, pH 9

Condition	Final Mass Recovery [%]	1st order rate constant [min^{-1}]
No reagents	43.15	0.24
Frother	36.72	0.16
SEDTP + Frother	76.87	0.29
SEX + Frother	41.07	0.18
90 SEDTP: 10 SEX + Frother	80.22	0.65

Figure 25 shows the recovery of pyrite at pH 9 when adding a frother to the collectors and their mixture, with the single reagents depicted for comparison. Frother as a single reagent, with a total mass recovery of 36.72%, does not significantly increase the recovery beyond the reagent-less recovery of 34.27%. However, when combining SEDTP and frother in a solution, there is a substantial increase in recovery from 34.27% with no reagents, 36.72% with frother only, 34.97% with SEDTP only and ultimately 76.87 % with SEDTP and frother. Furthermore, when the 90 SEDTP:10 SEX mixture was combined with frother, it increased the recovery of SEDTP + frother further to 80.22%. It is also important to note the rate of flotation, as indicated by the first order rate constant k, is faster for 90 SEDTP:10 SEX with frother (k=0.65) than for only SEDTP with frother (k=0.29). This is shown in Table 16 and observable in Figure 25 by comparing their curves.

3.4.2.2 Microflotation of pyrite at pH 4

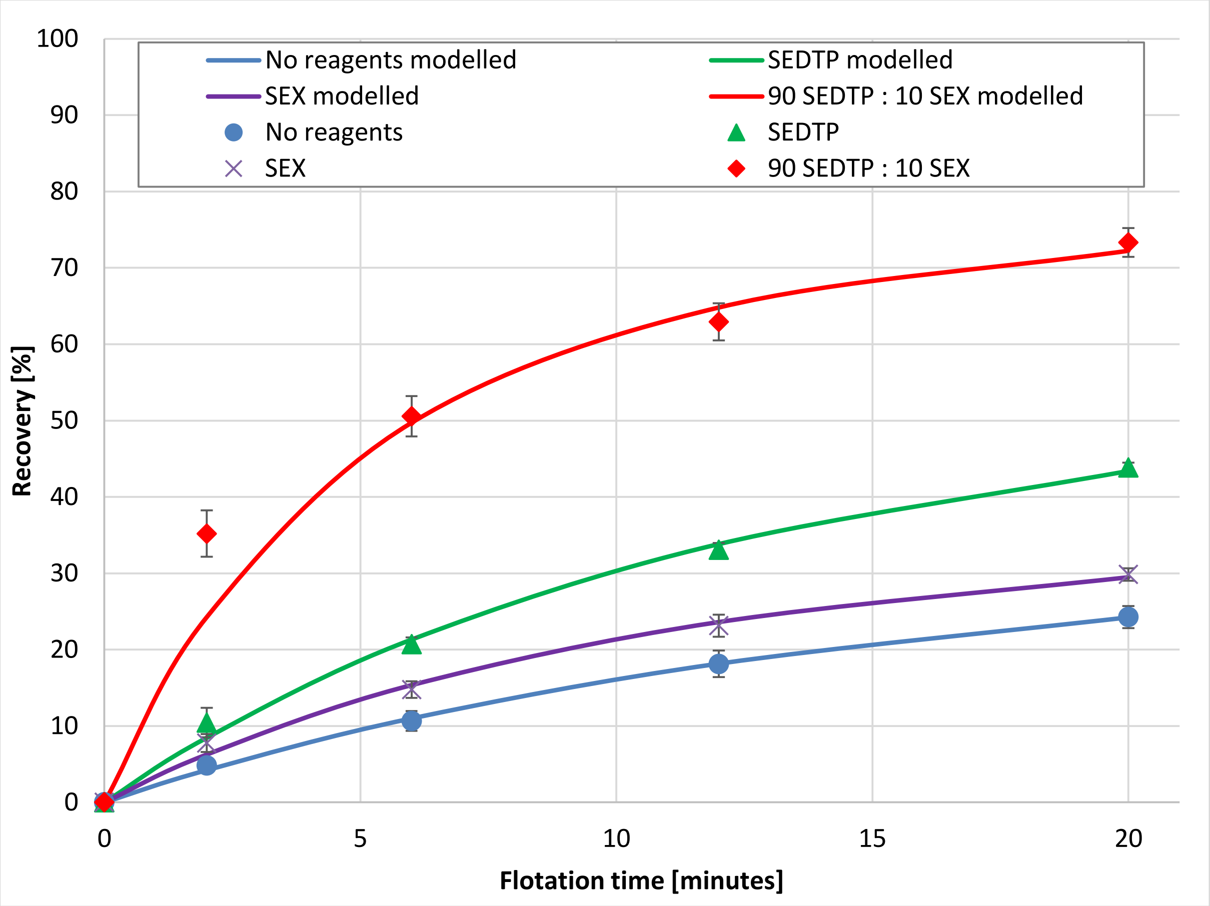


Figure 26: Microflotation recoveries of pyrite with two single collectors and their mixture, pH 4

Table 17: Total mass recovery of pyrite and 1st order rate constants for given reagent condition, pH 4

Condition	Final Mass Recovery [%] (at t=20 min)	1st order rate constant (min^{-1})
No reagents	24.28	0.11
SEX	29.84	0.17
SEDTP	43.87	0.14
90 SEDTP: 10 SEX	73.33	0.36

Figure 26 shows the recovery of pyrite at pH 4 using the two collectors and their collector mixture. SEX only slightly increased the reagent-less recovery from 24.28 % total recovery to 29.84%. Pyrite recovery when using SEDTP as a single reagent increases the reagent-less recovery from a final recovery of 24.28% to 43.87%. When 90 SEDTP: 10 SEX is used, there is a significant improvement in flotation recovery compared to their individual recoveries from 43.87% (SEDTP) to 73.33%. Table 17 also shows that the rate of recovery for the 90 SEDTP: 10 SEX mixture (k=0.59) is far higher than the rates for SEX (k=0.17) and SEDTP (k=0.14).

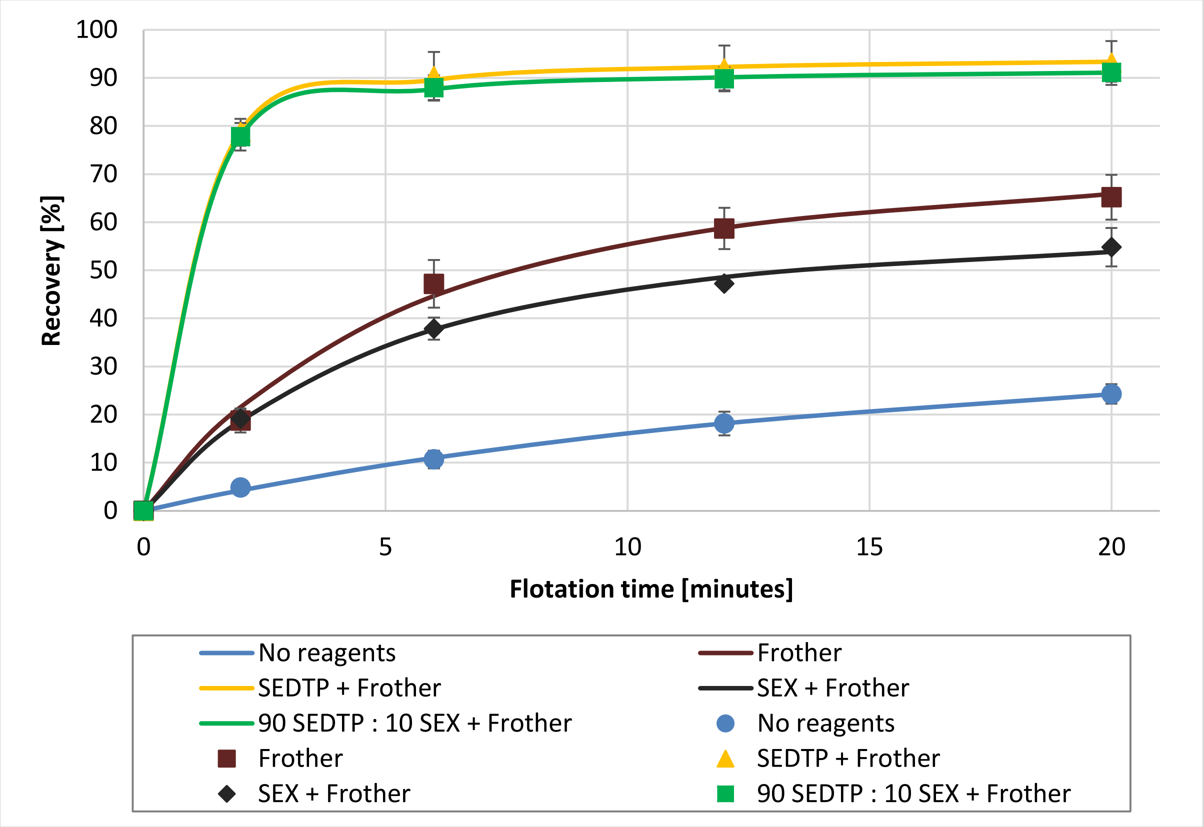


Figure 27: Microflotation recoveries of pyrite with two collectors, each combined with a frother, pH 4

Table 18 Total mass recovery of pyrite and 1st order rate constants for given reagent condition, pH 4

Condition	**Final Mass Recovery [%] (at t=20 min)**	**1st order rate constant (min^{-1})**
No reagents	24.28	0.11
Frother	65.19	0.35
SEDTP + Frother	93.11	2.93
SEX + Frother	54.79	0.38
90 SEDTP: 10 SEX + Frother	91.15	3.13

Figure 27 shows the recovery of pyrite at pH 4, using different single collectors and collector mixtures in the presence of a frother. Frother, as a single reagent, increases the recovery significantly above the reagent-less recovery from a total recovery of 24.28% to 65.19%. This improvement in recovery is not observed to such an extent at pH 9 where using frother resulted in a total recovery of 36.72% compared to reagent-less conditions at 34.27%. SEDTP with frother again significantly increased the recovery beyond that of frother or DTP alone from 65.19% to 93.11% total recovery. 90 SEDTP:10 SEX with frother shows very similar recoveries to SEDTP with frother (91.15% and 93.11% total recovery respectively). This is not observed when SEX is used with frother as the recovery is lower than that of frother alone. Table 18 shows the rate of recovery of 90 SEDTP:10 SEX with frother (k=3.13) is slightly higher than SEDTP with frother (k=2.93). This is not as significant as the difference in their rate of recoveries at pH 9 (Table 16: k=0.65 and 0.29 respectively)

3.4.3 Microflotation using different frothers

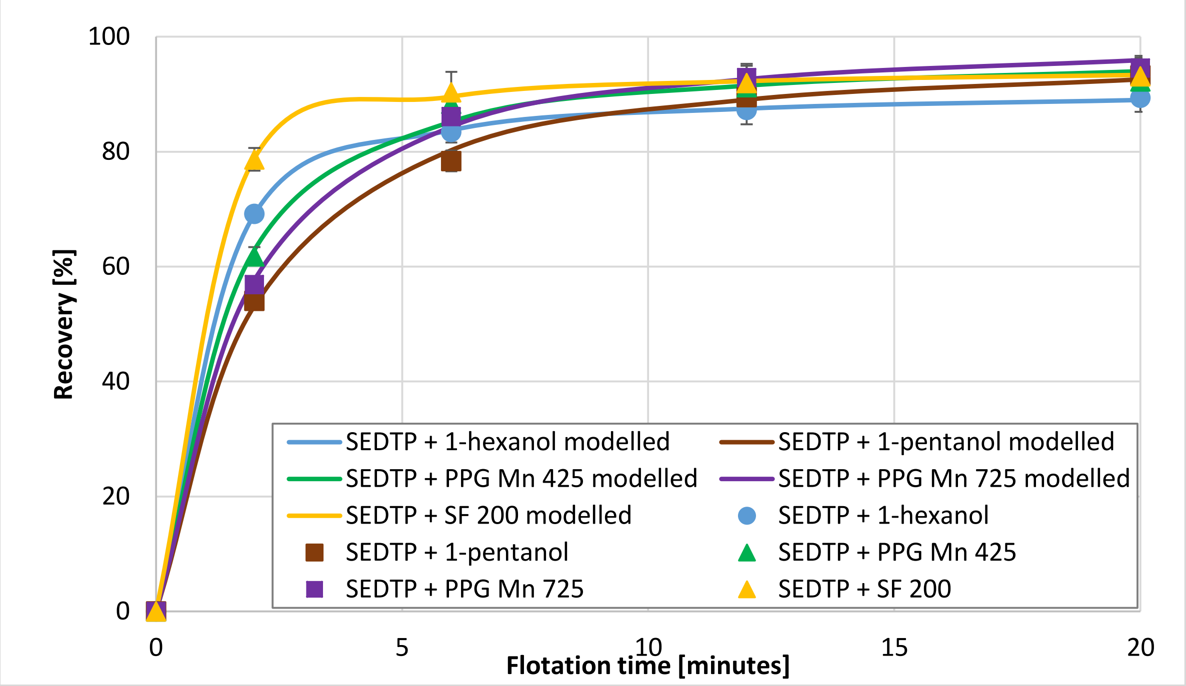


Figure 28: Microflotation recoveries of pyrite using SEDTP with various different frothers, pH 4

Table 19: Total mass recovery of pyrite and 1st order rate constants for SEDTP with different frothers, pH 4

Condition	Total mass recovery [%]	1st order rate constant (min^{-1})
SEDTP + 1-hexanol	89.39	2.02
SEDTP + 1-pentanol	93.30	0.92
SEDTP + PPG Mn 425	92.21	1.30
SEDTP + PPG Mn 725	94.59	1.01
SEDTP + SF 200	93.11	2.93

Figure 28 shows the microflotation recoveries of pyrite when using different frother types and molecular weights in conjunction with SEDTP. The polypropyleneglycol (PPG) frothers used had variable molecular weights: approximately 206 g/mol for SenFroth XP 200, which was used for all other experiments, 425 g/mol for Mn 425 and 725 g/mol for PPG 725. Alcohol frothers were used in the form of 1-hexanol (102.17 g/mol) and 1-pentanol (88.15 g/mol). All the different frothers had the same positive effect on the flotation recovery as shown by the initial SenFroth XP 200 frother, with only slight differences in rates and recoveries. Table 19 indicates that SEDTP with SenFroth XP 200 (frother used throughout all other microflotation, frothing column and surface tension tests) had the highest rate of recovery (k=2.93) of all the frothers tested with SEDTP.

3.4.4 Microflotation of galena

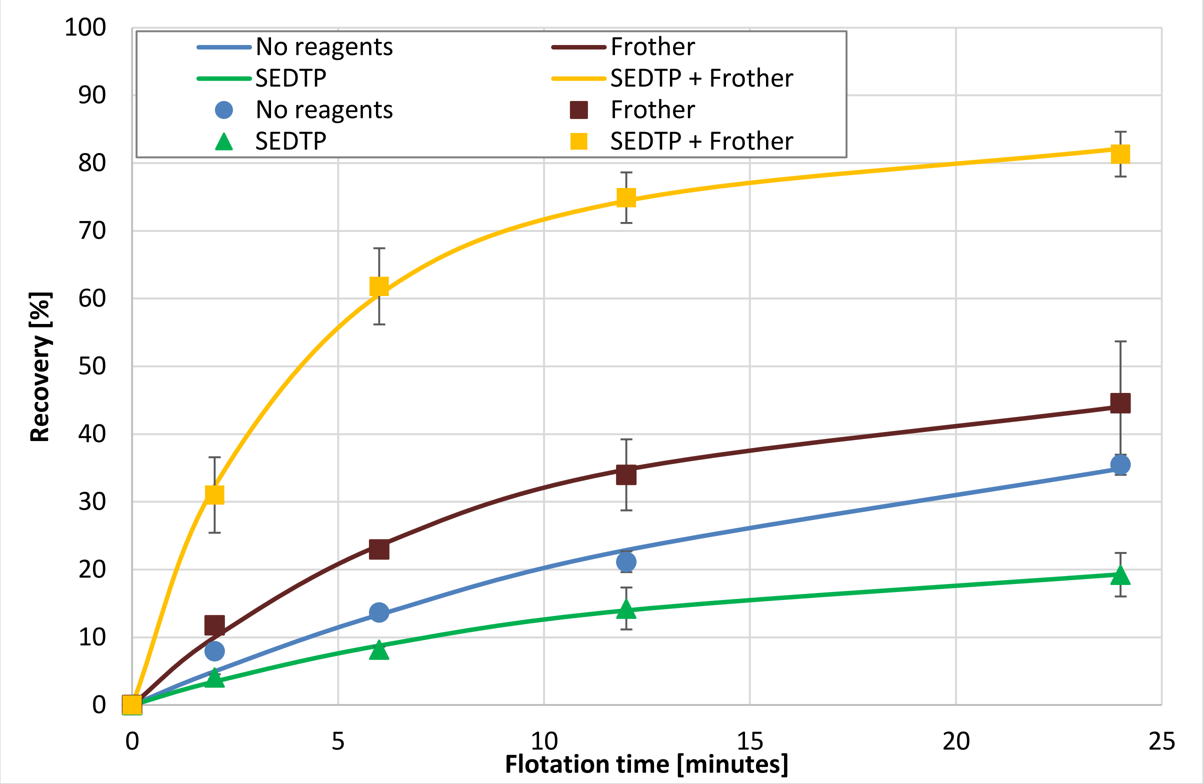


Figure 29: Microflotation recoveries of galena with frother, SEDTP and a frother-SEDTP mixtures, pH 4

Table 20: Total mass recovery of galena and 1st order rate constants for given reagent condition, pH 4

Condition	Total mass recovery [%]	1st order rate constant [min^{-1}]
No reagents	35.47	0.09
Frother	44.55	0.21
SEDTP	19.25	0.14
SEDTP + Frother	81.32	0.48

The effects of collector-frother mixtures were tested on a different sulphide mineral to ascertain whether the results were mineral-specific. Figure 29 shows the recovery of galena using SEDTP and frother as single reagents and combined as a mixture of their single components at pH 4.

SEDTP as a single reagent did not show any improvement in galena recovery. Indeed, reagent-less conditions yielded higher recoveries. Frother alone slightly increased the rate of recovery and total recovery of galena. Once again, SEDTP in the presence of frother showed synergistic effects by increasing the rate and recovery significantly, from 19.25% for DTP alone to 81.25% in the presence of frother. Galena also had slower flotation kinetics than pyrite, requiring a longer flotation time for the total recovery to reach a value close to Rmax.

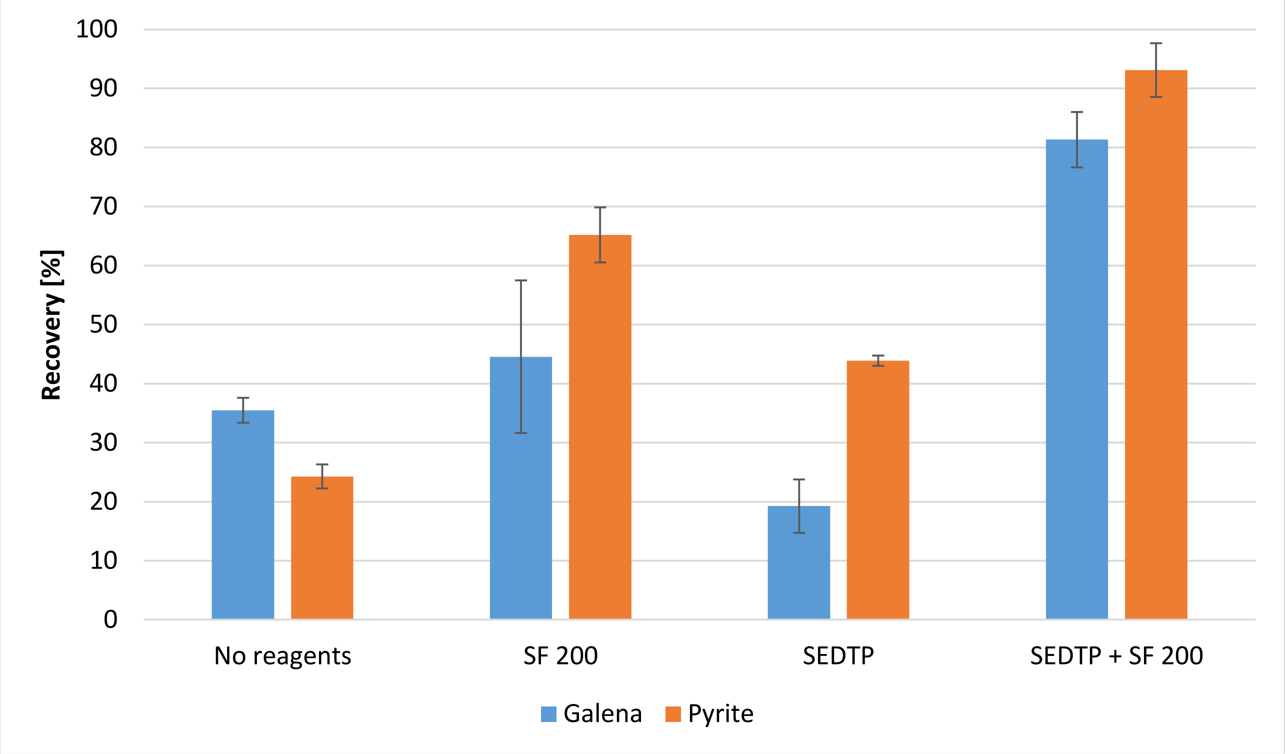


Figure 30: Comparison of the total microflotation recoveries of galena and pyrite, pH 4

Figure 30 compares the total recoveries of pyrite and galena at pH 4 for reagent-less flotation, SEDTP and frother and a mixture containing both. With the exception of the natural flotation of galena being higher than pyrite, pyrite showed better floatability where reagents were used. The same trends were followed by galena in terms of response to SEDTP and frother, where SEDTP with frother had a synergistic effect.

3.5 Adsorption experiments

These experiments were performed to investigate the presence of SEDTP at the air-water interface and/or the mineral surface. The adsorption experiments done in air-water systems were part of the validation experiments done at the start of the thesis and the adsorption experiments for the solid-water interface done with pyrite is part of the concluding experiments to confirm findings throughout the thesis.

3.5.1 Adsorption at the air-water interface

Standard batch flotation experiments were performed in a 2-phase system, excluding solids. The aim of the tests was to determine the DTP concentration in the feed, tails and concentrates by UV-Vis spectrophotometry and determine whether the DTP was selectively reporting to the concentrate. This would confirm that the DTP was attaching at the air-water interface. Standard batch flotation procedure was followed where concentrates were collected at t = 2, 6, 12 and 20 min (C1, C2, C3 and C4 respectively). The results in Figure 31 show that the concentration of the SEDTP in the froth and in the pulp is exactly the same, showing that there is no fractionation of the SEDTP into the froth phase.

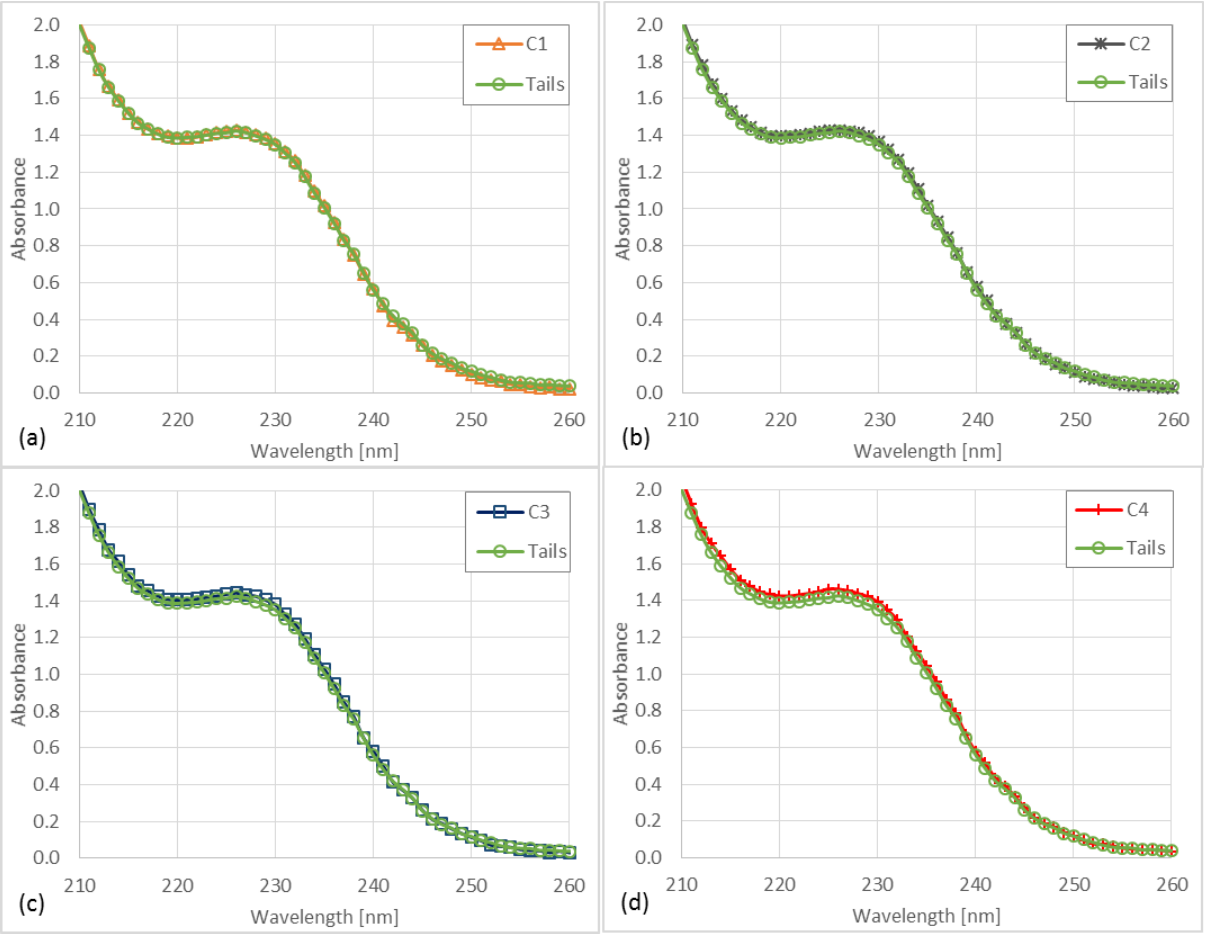


Figure 31: UV-vis absorbance spectra of SEDTP at 2-phase batch flotation collection times (a): 2 min; (b): 6 min; (c): 12 min; (d): 20 min

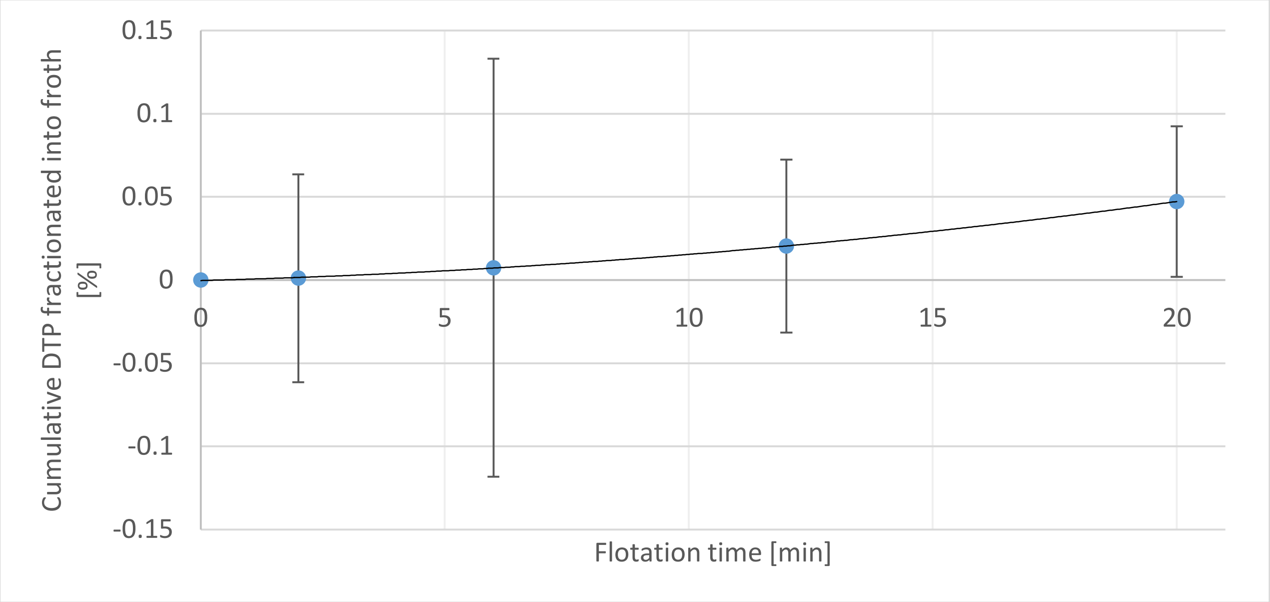


Figure 32: Percentage of SEDTP fractionating into froth phase (concentrates)

Figure 32 shows the cumulative percentage of SEDTP that has fractionated into the respective concentrates (t (min) =2, 6, 12, 20), i.e. the froth phase, during a batch flotation experiment. This is the difference in SEDTP concentration between the feed and the concentrate. The results indicate that any deviation from the pulp concentration cannot be deemed significant as the error bars overlap.

3.5.2 Adsorption at the solid-water interface

Adsorption experiments measured the SEDTP concentration before and after adsorption onto pyrite under the same conditions as the microflotation experiments.

Table 21: Absorbance of SEDTP onto pyrite at different monolayer dosages. Initial absorbance values are defined as the absorbance of SEDTP in DIW

	1/2 monolayer eq. SEDTP	**1 monolayer eq. SEDTP**	**1/2 monolayer eq. SEDTP + frother**	**1 monolayer eq. SEDTP + frother**
Absorbance at 225 nm before contact with pyrite	0.623	1.134	0.623	1.134
Absorbance at 225 nm after contact with pyrite	0.416	0.549	0.409	0.645

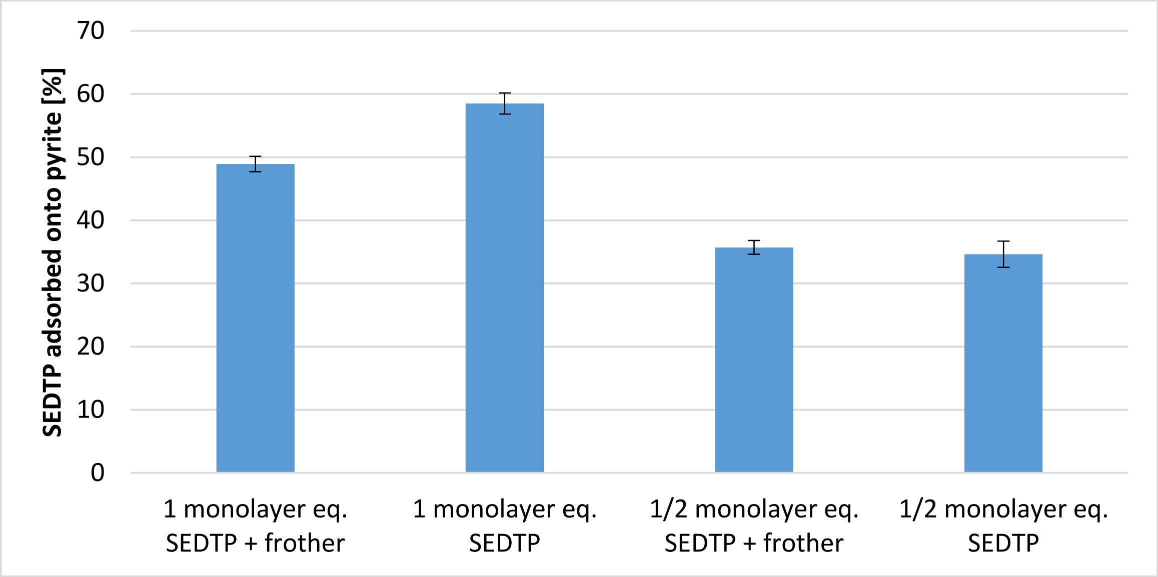


Figure 33: Adsorption experiments depicting the percentage of SEDTP adsorbing onto pyrite surfaces, pH 4

Figure 33 and Table 21 shows the percentage of SEDTP that adsorbed onto the pyrite surface; i.e. the fraction of SEDTP that did not remain in solution. It is shown that there is adsorption of SEDTP onto the pyrite surface. The total percentage of SEDTP that is adsorbed onto pyrite is 58.5% at 1 monolayer equivalent of SEDTP and 34.6% at half a monolayer equivalent. At the highest concentration of SEDTP, the presence of a frother reduces the adsorption of SEDTP onto pyrite by about 10%. This is not evident at half a monolayer equivalent surface coverage of SEDTP where the presence of frother has no effect on the amount of SEDTP adsorbed.

4. Discussion

This section discusses the findings in the experiments and relates them to the key questions, objectives and hypothesis. The experiments were designed to elucidate what effect SEDTP had at the different interfaces, alone, or in the presence of SEX and/or a frother. SEX was chosen to assess the performance of a common thiol collector as a comparison to SEDTP. Previous studies have tested the effects of different collectors on the microflotation of pyrite and galena, but did not investigate the role of frother (Castelyn, 2012; Taguta, 2015).

Flotation systems containing DTP often improve flotation recovery in a synergistic manner. That is, the flotation recoveries of a reagent suite containing SEDTP exceed the expected recoveries from the additive recoveries of the single reagents (Adkins & Pearse, 1992; Hangone, Bradshaw & Ekmekci, 2005; Corin, Bezuidenhout & O'Connor, 2012; McFadzean, Mhlanga & O'Connor, 2013; Roy, Datta & Rehani, 2015) . It has been shown in literature that pyrite is floatable with xanthate and DTP, where xanthate performs better than DTP as a collector (Fuerstenau, Huiatt & Kuhn, 1971). However this is an oversimplification as chain length and branching plays an important role in the strength/selectivity of the collectors, as discussed in Section 1.4.3. The flotation of pyrite is also highly dependent on the pH, electrochemistry and presence of Fe ions in the solution. These factors contribute greatly to the oxidation products that form on the pyrite surfaces. It has been shown that at higher pH, the flotation of pyrite is depressed.

The pyrite used in this study was not readily floatable with a standard collector (SEX). The galena also had a low floatability compared to a previous study done with the same mineral sample (Taguta, 2015). Thus the minerals were likely oxidized to some extent, although various measures described in Section 2.6 were taken to prevent and remove sulphide oxidation species. Pyrite is a relatively easily oxidized mineral, thus alkaline conditions will result in surface oxidation: oxygen promotes the anodic dissolution of minerals and also allows the formation and precipitation of metal hydroxides on the mineral surface (Feng & Aldrich, 1999). The oxidation at a higher pH is not limited to pyrite, it has been observed on other sulphide minerals as well. The adsorption of DTP onto chalcopyrite is hindered by the formation of iron hydroxides on chalcopyrite surfaces (Grano et al., 1997) and xanthate adsorption onto galena and chalcopyrite is lower when the minerals have been exposed to air for 24 hours than when they were freshly abraded. Taking this into account, the fact that the mineral floatability improved significantly in the presence of certain reagent mixtures, lends more significance to the findings. In addition, it may indicate a route towards the processing of oxidised BMS and PGM, something for which there is increasing demand.

The collectors used in the studies were the ethyl chain length variants of DTP and xanthate, i.e. SEDTP and SEX. SEDTP was chosen for reasons previously stated – it was suspected in previous studies that it did not absorb onto mineral surfaces yet improves flotation recovery (McFadzean, Castelyn & O’Connor, 2012; McFadzean, Mhlanga & O’Connor, 2013; McFadzean & O’Connor, 2014). In previous studies researching the synergistic interactions between collectors, SEX had synergistic interactions with SEDTP, therefore it was chosen with the hope to initiate a synergistic response in the various experiments and identify the sub-processes which drive the synergistic response. It was also necessary to compare the SEDTP results to a more standard collector response, which was given by SEX. Xanthate and DTP oxidation to their more hydrophobic dithiolates is also dependent on the pH of the solution and the presence of ferric and cupric ions in solution (Fuerstenau, Huiatt & Kuhn, 1971) where it is shown that the two collectors behave differently in terms of oxidation to their dithiolates and their flotation performance with pyrite and chalcocite.

The frother that was used in the experiments was SenFroth XP 200, a polypropylene glycol. Frothers prevent bubble coalescence in the pulp and promote froth stability. They also potentially form weak Van Der Waals bonds with collectors when there is a mineral present to which the collector adsorbs (Bradshaw, Harris & Connor, 1998). Initially, the presence of a frother in microflotation experiments was not expected to have a significant impact on the flotation performance since a single bubble stream will exhibit no bubble coalescence and therefore frother would not reduce bubble size in the pulp (Cho & Laskowski, 2002). Furthermore, due to the absence of a froth phase, there would be no increase in froth stability. However it was discovered, with the development of the thesis, that the presence of a frother was an important factor in initiating a synergistic microflotation response.

4.1 Interactions at the air-water interface

The experiments performed in the absence of solids need to be examined separately from the experiments that were performed in the presence of solids – the presence of a solid presents the surfactant with another interface at which to adsorb. However, the two-phase system for the surface tension and foam stability results provide vital information as to how the collectors and frothers may interact without a solid surface present.

4.1.1 Effect on surface tension

Surface tension results showed that SEDTP decreased the surface tension as a single reagent when reaching higher concentrations (100mM), but not as significantly as a frother. It did, however, reduce the surface tension more than SEX, which did not decrease the surface tension beyond that of deionized water.

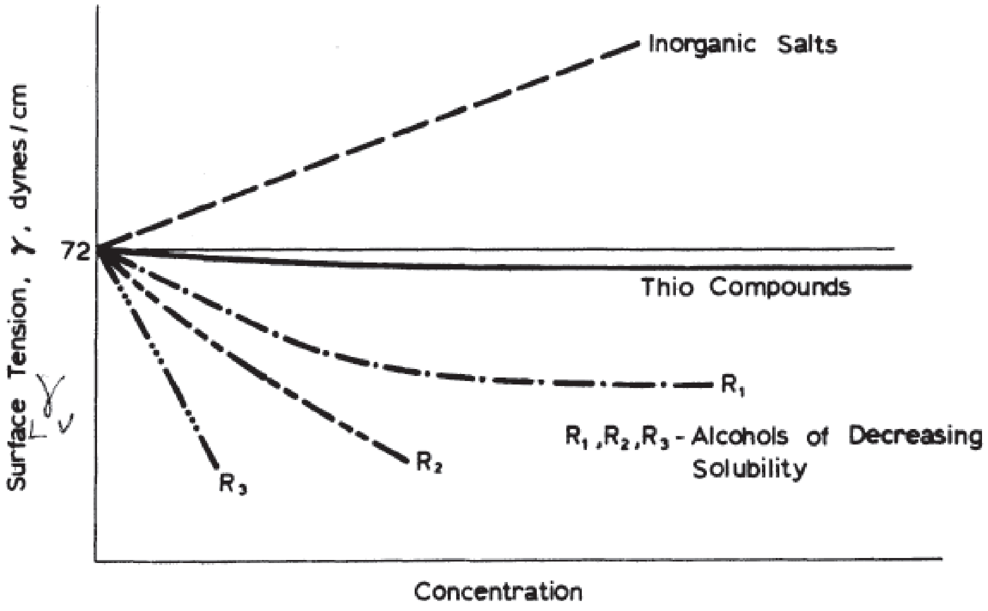


Figure 34: Schematic representation of the effect of the increasing concentration of different surfactants used in flotation on surface tension (Leja, 1982)

Figure 34 shows simplified surface tension approximations for inorganic salts, thio compounds (both SEX and SEDTP fall into this category) and alcohol frothers with decreasing solubility/increasing chain length (Leja, 1982).

As a single reagent, the frother behaved in a typical fashion by reducing the surface tension across the concentration range, similarly to other surface tension studies done on frothers (Marozva, 2015). At higher concentrations, the surface tension values reach a steady value – a sign that the frother is nearing its critical micellar concentration (a concentration at which the surfactants start micellization and become less available at the air-water interface (Eastoe & Dalton, 2000)). SEX, on the other hand, behaved as a typical thiol collector. It did not reduce the surface tension at increasing concentrations, with surface tensions remaining similar to that of deionised water.

However, SEDTP did show a slight decrease in surface tension at increasing concentration. The concentration of SEDTP necessary to cause a decrease in surface tension equivalent to 5 mM frother is 100 mM SEDTP. Therefore, the SEDTP is not a strong surfactant. However, it was shown to be stronger than the ethyl xanthate. As thiol collectors are similar in structure to frothers; with a polar, hydrophobic headgroup and a hydrophilic carbon chain, it is speculated that they behave similarly at the air-water interface. The packing of surfactants at the air-water interface is reliant on their size, length and branching (Laskowski & Woodburn, 1998; Zhang & Somasundaran, 2006). For anionic surfactants Rosen (2004) shows that adsorption at the air-water interface increased with a decrease in the effective charge of the hydrophilic group. This might occur by having a more tightly bound, less hydrated counterion (the sodium ion) or an increase in the ionic strength in the aqueous phase. As the aqueous phase remains constant throughout the respective experiments, the difference in air-water interface activity between the SEX and SEDTP arises from the SEDTP molecules' ability to bind more tightly to their counterion, described by their pK_a in Section 1.4.3.2. SEDTP (pK_a≈0) has a far lower pK_a than SEX (pK_a=2.20), indicating the strength of the bond between anion and cation, and thus greater adsorption at the air-water interface.

Surface tension experiments of the mixtures were designed to test the effect of SEDTP concentration on surface tension in mixtures with other reagents. The other reagent concentrations were kept constant as follows: frother = 25 mM; SEX = 50 mM. Preliminary experiments were done to test the effect of varying frother and SEX concentrations, with their constant concentrations chosen to best represent the effect of increasing SEDTP concentration. In mixtures with increasing SEDTP concentration and a constant frother concentration, the surface tension was reduced compared to the constant frother concentration as a single component. However, this was attributed to the additive effect of the SEDTP that was introduced.

A similar result was obtained when combining SEDTP with SEX and frother at constant concentrations for the latter two reagents. However, in this case the additive effect caused a slight increase in surface tension across the concentration range compared to the SEDTP + frother mixture. This is attributed to the contribution by the higher SEX surface tension.

Synergistic effects in mixtures of surfactants, especially where cationic and anionic surfactants are used in equimolar concentrations are common (Lucassen-Reynders, Lucassen & Giles, 1981; Jia et al., 2017) due to the surfactant mixtures arranging at the surface to achieve electroneutrality. Synergistic effects between anionic (sodium dodecyl sulfate) and non-ionic (PPG) surfactants, which is the case in these surface tension measurements, are also observed (Trawí, Hallmann & Edrzycka, 2016). However, the synergistic reduction of surface tension with two surfactants allow a given surface tension to be attained at a total molar concentration lower than that required by either surfactant, i.e surface tension of a mixture of surfactants A and B at concentration [C] is lower than that of the surface tension of A or B at concentration [C] (Rosen, 2004). Figure 21 shows that at total molar concentrations, the addition of SEDTP to frother showed no reduction in surface tension. Therefore, no synergy in surface tension reduction was observed between the surfactants.

Figure 34 indicates that inorganic salts will increase the surface tension: SEX and SEDTP both have Na^+ as a cation. However, surface tension measurements of the maximum concentration of the surfactants at different pH levels showed no significant effect on the surface tensions, therefore the effect of Na^+ is deemed negligible.

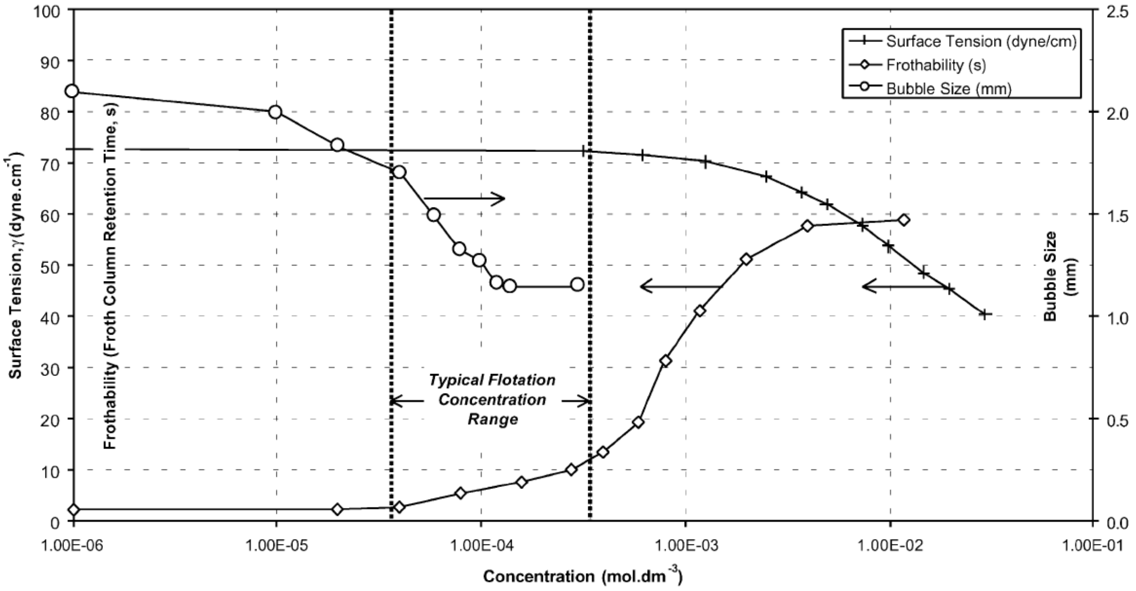


Figure 35: Effect of n-hexanol on froth stability, surface tension and bubble size

Figure 35 shows the effect of n-hexanol on surface tension, frothability and bubble size (Sweet et al. 1997). The different experiments put the difference in concentrations in the different experiments into context. The experimental data of both bubble size and frothability show pronounced changes in a concentration range where the change in equilibrium surface tension is virtually undetectable. The experiments applicable to this thesis (froth stability and surface tension) only have similar concentrations at the upper and lower limits of their experiments. Therefore, the observations for surface tensiometry and froth stability are not always relatable.

4.1.2 Adsorption at the air-water interface

UV-vis data from the batch flotation experiments showed no fractionation of SEDTP into the froth phase throughout the experiment. This indicates that the SEDTP molecules are not hydrophobic enough to adhere to the air-water interface to an extent that would be identifiable by UV-vis spectrometry.

4.1.3 Effect on foam stability

Foam stability data allows us to look at a more applicable situation in terms of reagent concentration and flotation dynamics to plant conditions. As is mentioned in the literature review, surfactants are surface active agents, i.e. molecules that attach at the air-water interface and subsequently reduce surface tension. There is a correlation between the reduction in surface tension due to surfactants and foam stability (two-phase: gas and liquid). This is often used to assess different types of surfactants or the effect of different molecular weights of the same surfactant type (Cohen et al., 1981; Jachimska, Lunkenheimer & Małysa, 1995; Tan et al., 2006). Therefore if SEDTP is behaving as a surfactant, it should stabilize the foam through a similar mechanism through which a frother would.

SEDTP as a single reagent showed very little foamability, with only very high concentrations creating a significant foam phase. To achieve a significant foaming response, the presence of a frother was necessary. When SEDTP was used with a frother, there was a large increase in foam stability compared to frother alone. This is an important finding as it signifies that SEDTP may require a frother present to increase its activity at the air-water interface at these concentrations. Nyambayo (2014) found that collectors improved the water recovery in a two-phase system with frother present. The order in which the collectors improved the water recovery is in the following order: SEDTP>SEDTC>SEX/SIBX mixture>SEX. The author reasons that the water recovery, which is related to foam stability, is related to the size and steric properties of SEDTP compared to the other thiol collectors as well as the less electronegative P atom, which is mentioned in the discussion of the surface tension results in this section. As a frother is non-ionic and thiol collectors are ionic, a mixture containing both surfactants would allow the surfactants to arrange themselves at the air-water interface to reduce intermolecular repulsion. The synergistic increase in foam stability when both SEDTP and frother are present infers that both reagents are present at the air-water interface. The intermolecular repulsion is greater between ionic surfactants, thus a mixture containing anionic and cationic surfactants would have a better arrangement at the interfaces than a mixture containing non-ionic and ionic surfactants.

Furthermore, surfactants can have additional effects on other surfactants in a mixture, for instance the presence of a nonionic alkyl polyglycoside improved the compatibility of other ionic/zwitterionic surfactants at higher, alkaline pH by increasing mixed micelle solubilizing capability (Marinova et al., 2017). Thus, it is possible that the PPG frother used (SenFroth XP 200) enhances the compatibility of SEDTP at pH 9.

When including SEX as 50% of the collector component (SEDTP being the other 50%) with frother, the foam stability remained greater than the case where only frother was used but less than when SEDTP was used with frother. Therefore, in this case, it seems that SEX does not have the same activity as SEDTP – it does not have the ability to attach at the air-water interface thereby increasing the foam stability. This is shown when only SEX is used with frother: the foam stability is very similar to the case where only frother is used. A thin film and surface tension study shows that an increase in concentration of KEX (potassium ethyl xanthate) increases the negative charge on the bubble film, reducing film thickness and thus making it more likely to rupture. To counteract this anti-foaming effect, increased concentration of frother was necessary to stabilise the film (Manev & Pugh, 1993). Therefore the two thiol collectors (SEX and SEDTP) are acting differently at the air-water interface and gives further insight as to what is occurring when interpreting the surface tension results: the slight decrease in surface tension at increasing concentrations signifies that SEDTP does have surface activity. This surface activity of SEDTP, along with that of the frother stabilizes the foam phase.

4.2 Interactions at the solid-water interface

The presence of a solid can greatly affect the activity of surfactants since certain of the surfactants may adsorb at the solid-water interface and no longer be available to stabilise the air-water interface. Therefore comparative (two-phase and three-phase) studies provide an indication of where the surfactants are attaching, if at all. Froth stability data is important for this part of the study as it was obtained for two-phase and three-phase.

4.2.1 Effect on froth stability

A PGM ore was used that typically uses SEDTP in the on-site reagent suite. During the conditioning of the ore, collectors were added first followed by the frother after 5 minutes. According to the Leja-Schulman penetration theory this is necessary so that the collector molecules can arrange themselves at the solid-water interface. When the frother is added, the molecules arrange themselves in between the collector molecules at the solid-water interface.

Once again SEDTP as a single reagent showed very low froth stability and a frother was necessary to induce a significant frothing response. When SEDTP was used with frother, it did not show the same increase in froth stability observed when no solids were present – the froth stability was similar to that of frother alone. A possible explanation is that the DTP has adsorbed onto the particles and is, therefore, no longer available in the solution to stabilise the air-water interface. If that were so, then it is quite probable that the particle properties (hydrophobicity) have also been altered, which will change the froth structure (see Figure 36).

Furthermore when a 50:50 mixture of SEDTP and SEX is used in combination with a frother, the froth stability is lower than when only frother is used. This is thought to be due to an increase in the hydrophobicity of the solids. As is depicted in Figure 36, increasing hydrophobicity (i.e. contact angle) increases froth stability up to a certain point after which the high hydrophobicity has an adverse effect on the froth stability. The increasing hydrophobicity of pyrite in the SEDTP-SEX-frother system is corroborated by the microflotation results, which showed a large increase in recovery under these conditions. This will be discussed in more detail in the following section.

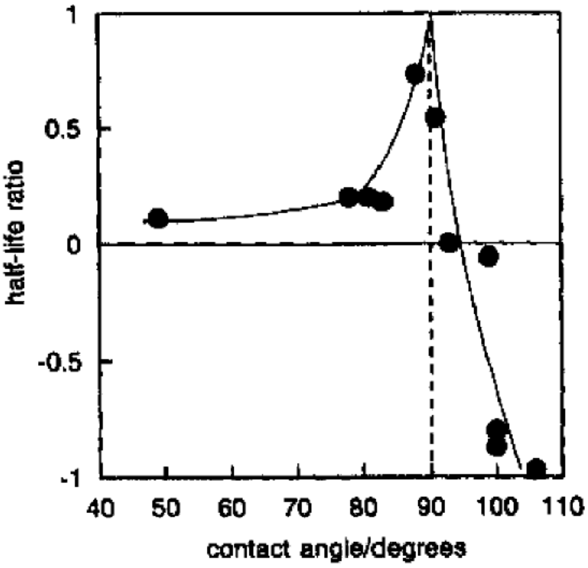


Figure 36: Bubble half-life ratio as a function of contact angle (Aveyard et al., 1994)

4.2.2 Effect on pulp-phase hydrophobicity

Microflotation experiments comprise a very important part of this thesis. This focuses on the pulp phase sub-processes and excludes the froth phase and the effect of changing pulp bubble size, since there is a single stream of bubbles and therefore no bubble coalescence. Microflotation recoveries give an indication of the hydrophobicity of the minerals, which is determined by the reagent conditions. It was necessary to keep air flow rate and pH constant (at different levels) as this affects the microflotation recovery results.

No compositional analysis was done but it is assumed that the mineral samples were partially oxidized (even though efforts were taken to prevent oxidation) as other studies have shown that pyrite (Fuerstenau, Huiatt & Kuhn, 1971) and galena (Taguta, 2015) are floatable with ethyl xanthate – which was not the case here. The two pH levels tested with pyrite were chosen to promote an oxidizing and reducing environment at pH 9 and 4, respectively. pH 9 is much closer to the pH level one would find on a plant and therefore the results are more applicable to a real world situation. pH 4 does not promote surface oxidation of pyrite/galena, in turn allowing collectors to adsorb onto the mineral surface; making the potential interactions between collector and mineral more likely to occur. The DTP – chalcopyrite system illustrates the effect of pH in several studies: the adsorption of DTP is highly dependent on the state of the chalcopyrite surface. The state of the chalcopyrite surface, in turn, is highly dependent on pH (Grano et al., 1997; Güler et al., 2005, 2006) in a similar manner to pyrite.

4.2.2.1 Effect of single reagents

At pH 9, pyrite had low natural floatability and none of the single reagents (frother, SEDTP or SEX) improved microflotation recovery. As the microflotation recovery is a measure of mineral hydrophobicity, it implies that the pyrite is not hydrophobic enough to attach to the bubbles rising through the cell. However it does not rule out adsorption of collectors at the solid-water interface. For example, xanthate alone does not increase the hydrophobicity of pyrite in these microflotation studies but has been shown to produce significant energies of adsorption in thermochemical studies on pyrite (Taguta, 2015).

At pH 4, the recovery of pyrite was improved upon the addition of all reagents, with the frother improving recovery the most, followed by SEDTP, and SEX with the lowest recovery. This suggests that a lower pH accommodates the adsorption of the reagents onto the mineral surface. The effect of pH on the DTP-chalcopyrite system has shown that a high pH inhibits the adsorption of DTP onto chalcopyrite surfaces due to the surface oxidation and subsequent precipitation of iron hydroxides (Grano, Prestidge & Ralston, 1997; Güler et al., 2005). Furthermore, the dithiolates of SEDTP and SEX, which are responsible for the flotation of pyrite, occur at pH 4 and not at pH 9 (Fuerstenau, Huiatt & Kuhn, 1971)

4.2.2.2 Effect of collector mixtures

There was no significant improvement in recovery when SEDTP and SEX were combined at pH 9. The mineral hydrophobicity is too low to induce flotation, whether the collector-mineral adsorption occurs or not. In the case of pH 4, there is a significant improvement in the recovery of pyrite when using the collector mixture. McFadzean et al. (2012) showed for such a mixture, SEX showed an improvement in recovery of fine particles, whereas SEDTP improved the recovery of coarser size fractions, thus, improving overall flotation performance when combined as a mixture dominated by the stronger collector (90% SEDTP, 10% SEX). This is attributed to the strong-weak collector interaction, which is indicated by their recoveries as single reagents at pH 4.

4.2.2.3 Effect of frother addition

The addition of a frother to the single reagents and the collector mixture changed the recovery significantly where SEDTP was used. At pH 9, the addition of a frother to SEDTP, improved the recovery of pyrite from 34.97% (SEDTP alone) to 76.87% (SEDTP+frother). This shows that SEDTP and frother have a synergistic effect when combined. However, this synergistic increase is not observed for SEX: when SEX is used with frother, the recoveries are lower than when frother is used alone.

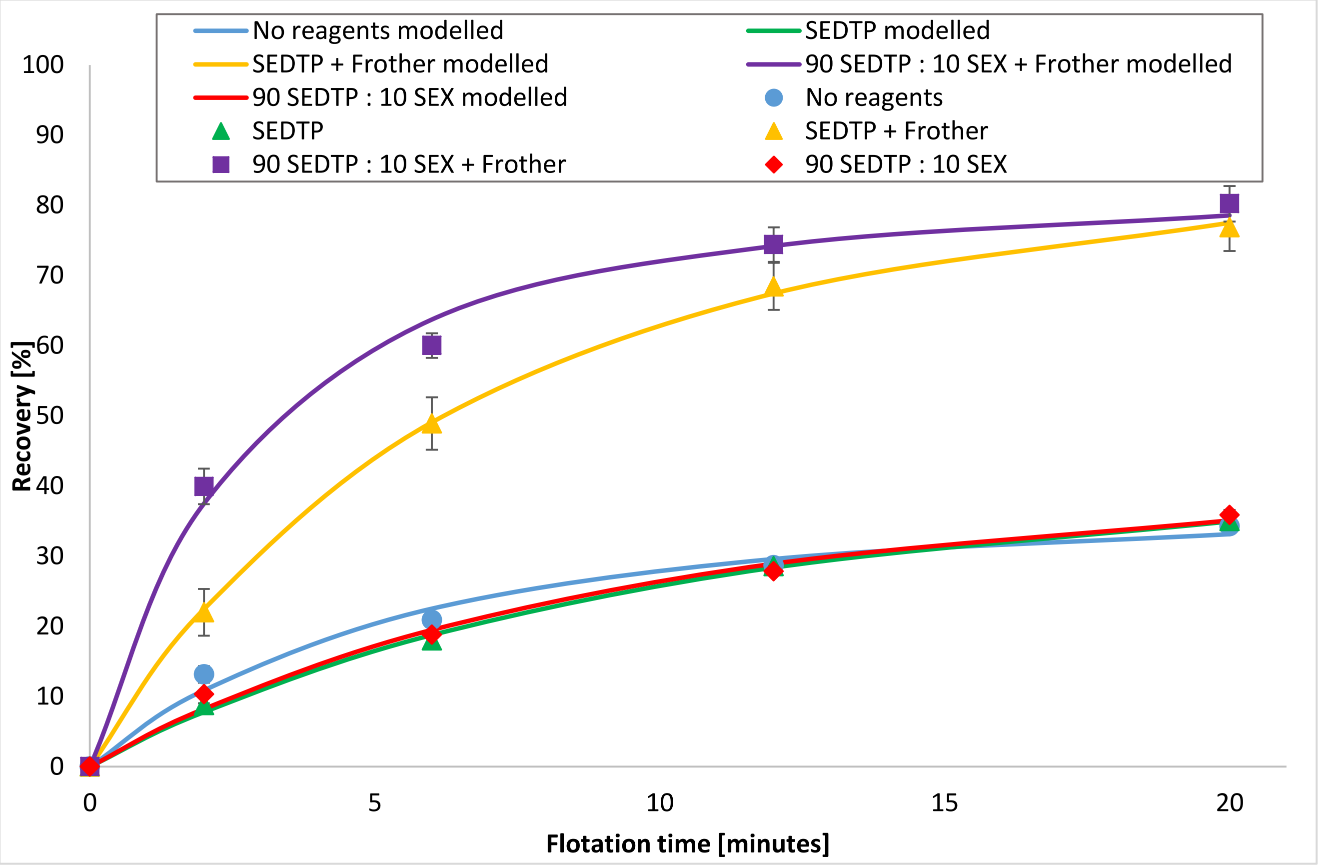


Figure 37: Microflotation recoveries of pyrite at pH 9 showing the synergistic effects between SEDTP and frother, and SEDTP, SEX and frother.

When frother is added to the collector mixture, the total recoveries reach the same total recovery of SEDTP with frother (Figure 37). This is to be expected because the majority of the collector component in the mixture is still SEDTP. Interestingly, the main difference between SEDTP + frother and 90 SEDTP: 10 SEX + frother in Figure 37 is the change in kinetics: the rate of flotation is higher for the collector mixture with frother. This is calculated using the Klimpel flotation model (Equation 3), presented in Table 22. This improvement in kinetics when using the collector mixture with frother at pH 9 could be related to the improved flotation response when using the collector mixture (without frother) at pH 4, but there is no further data to support this.

Table 22: Flotation rate constants for 90 SEDTP: 10 SEX + frother and SEDTP + frother on pyrite, pH 9

Reagents	k (rate of flotation)
90 SEDTP: 10 SEX + frother	0.65
100 SEDTP + frother	0.29

The addition of frother to the collectors and their mixture at pH 4 shows similar behaviour compared to pH 9. Once again, the addition of frother to SEDTP and the collector mixture improves the recovery of pyrite significantly. Relating this to the flotation response of pyrite at pH 4, it is expected that the collector mixture with frother would improve the flotation rate of SEDTP with frother. However, there is no significant difference between the two results. This has been observed when particle hydrophobicity reached an optimum point beyond which no further improvement in hydrophobicity was attained (Wakamatsu, Numata & Park, 1979; Bradshaw & O’Connor, 1994).

At both pH’s, SEX with frother does not enhance the recovery of pyrite. Therefore, it can be assumed that SEX does not have a synergistic effect with a frother and is a poor collector for pyrite.

To determine whether the synergy is mineral specific, experiments were performed on galena. SEDTP alone did not improve the recovery of galena beyond its natural floatability. When adding frother to SEDTP, the recovery once again improved significantly beyond that of frother or SEDTP alone. This tells us that the same synergistic effect is found where SEDTP and frother are combined in a mixture. This indicates the synergistic effect is not limited to pyrite, but also applicable to galena.

The frother-collector synergy observed for SEDTP and SF 200 (the frother discussed up to this point) was further explored by attempting to elucidate what characteristics were necessary for a frother to exhibit synergy with SEDTP. Literature shows that the properties of surfactants are dependent on their chain length/ molecular weights (Tan et al., 2006). Two different types of frothers were tested at different chain lengths: alcohol frothers and PPG frothers. The experiments were done at pH 4 to ensure a reducing environment to promote flotation. Although there are slight differences in the rate of recoveries for the different frothers, the total recoveries all fell in a similar range; i.e. neither chain length nor frother type changed the synergistic interaction. If the collector-frother synergy is attributed to the surfactants arranging in a more favourable fashion at the different interfaces in order to achieve electroneutrality, then an antagonistic effect is to be expected when an anionic frother is used and a stronger synergistic effect when a cationic frother is used. This is a recommendation for future studies.

4.2.2.4 Effect of pH

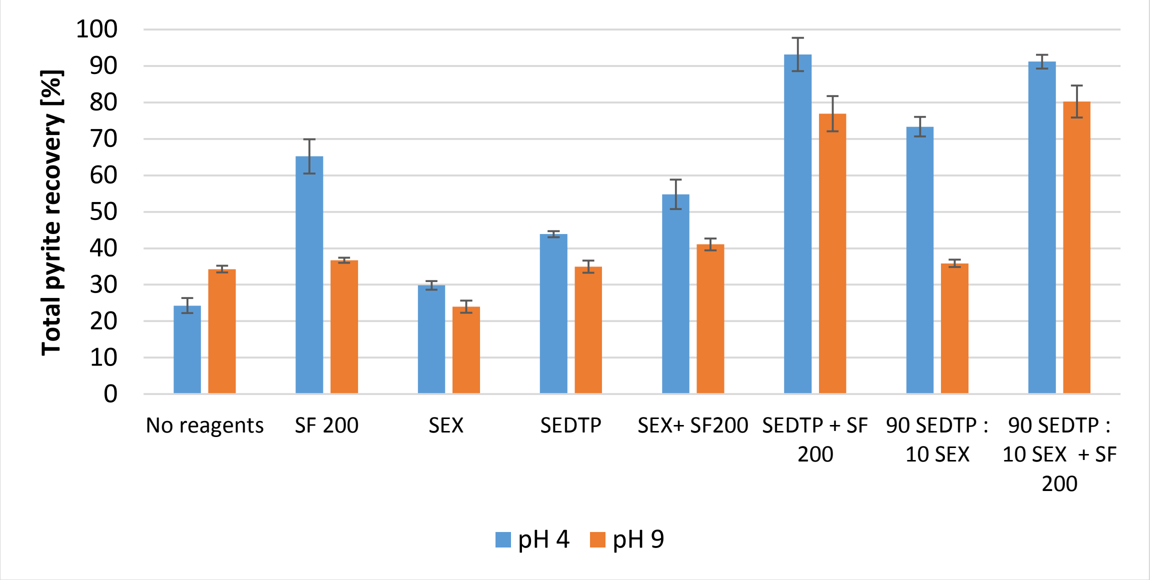


Figure 38: Comparison of total microflotation recoveries of pyrite at pH 4 and pH 9

The recoveries of pyrite were higher at pH 4 than pH 9 when reagents were present shown in Figure 38. This was expected as previously discussed: the lower pH promotes a cleaner mineral surface which is more susceptible to collector adsorption. The overall trends were similar with the exception of frother alone and 90 SEDTP: 10 SEX at pH 4 showing significantly higher recoveries. The collector mixture is thought to behave synergistically. Frother activity can change with pH (Gupta et al., 2007) and this is seen here where the frother has a higher recovery at pH 4 than at pH 9. However, it was shown in Table 12 that the surface tension of the frother does not change with pH. Therefore, it is some other mechanism, such as frother adsorption onto the solid particles or better bubble-particle attachment due to thinning of the 3-phase contact line in the presence of frother that promotes enhanced recovery.

As the Leja-Schulman penetration theory suggests, the synergy between frother and collector relies on both reagents adsorbing at both the solid-water interface and air-water interface (Leja & Schulman, 1954). The SEDTP-pyrite adsorption tests showed that SEDTP does in fact adsorb onto the surface of pyrite at pH 4, both in the presence and absence of a frother. However, not all the SEDTP adsorbed to the pyrite surface, contrary to literature findings for xanthate (KEX) on pyrite by Shen, Fornasiero & Ralston, (1998) which indicated complete adsorption onto pyrite. The recovery of pyrite using KEX and adsorption of KEX onto pyrite surface increased with decreasing the pH, which prevented surface oxidation. The interaction of SEX with pyrite does not always correlate with flotation recovery, as Taguta (2015) showed that SEX had a similar enthalpy of adsorption with pyrite as PAX (potassium amyl xanthate) with pyrite but SEX did not improve the flotation of pyrite whereas PAX did. Therefore, if only 55% or less of the available SEDTP molecules are adsorbing at the solid-water interface, the rest of the SEDTP component is available to adsorb at the air-water interface. In the case of SEX, the reagent would be adsorbed onto the solid surface and unavailable to interact at the air-water interface.

4.2.3 SEDTP-frother interaction

The strength of anionic thiol collectors as surfactants at the air-water interface is related to the ability of the molecule to hold its counterion. The stronger the bond between the anionic collector and its cation, the stronger surfactant it will be (Rosen, 2004). This is described by the pKa of the collector; a lower pKa indicates a stronger bond and thus a better surfactant. Compared to two other thiol collectors, DTP has the lowest pKa and thus should be the best surfactant at the air-water interface (see Section 1.4.3.2). The two-phase experiments indicate that SEDTP does attach at the air-water interface, reducing surface tension and synergistically improving foam stability with frother.

SEDTP does indicate some adsorption on pyrite surface at pH 4, with or without frother present. Approximately half of the SEDTP remains in solution and is available to attach at the air-water interface. This is thought to be what is occurring during the microflotation experiments. However adsorption of SEDTP onto the mineral surfaces alone is not sufficient to improve recovery significantly, yet the addition of a frother greatly improves the recovery.

The foam stabilizing effect of SEDTP indicates that it will attach at the air-water interface as well, thus creating a mixed monolayer of surfactants with frother molecules so as to reduce electrostatic repulsion. On the solid surface, the frother molecules are thought to adsorb along with SEDTP, as Hadler et al. (2005) indicated that up to 20% of frother is removed from solution, only in the presence of xanthate and a PGM ore. Figure 39 shows how collectors and frothers attach at both the air-water interface and the solid-water interface prior to bubble-particle collision. During bubble-particle collision, the bubble film thins, allowing the surfactants to interact with one another as only SEDTP is irreversibly adsorbed at the solid-water interface. This allows for better packing and stronger adsorption of the surfactants (Figure 40), thus increasing the local hydrophobic character.

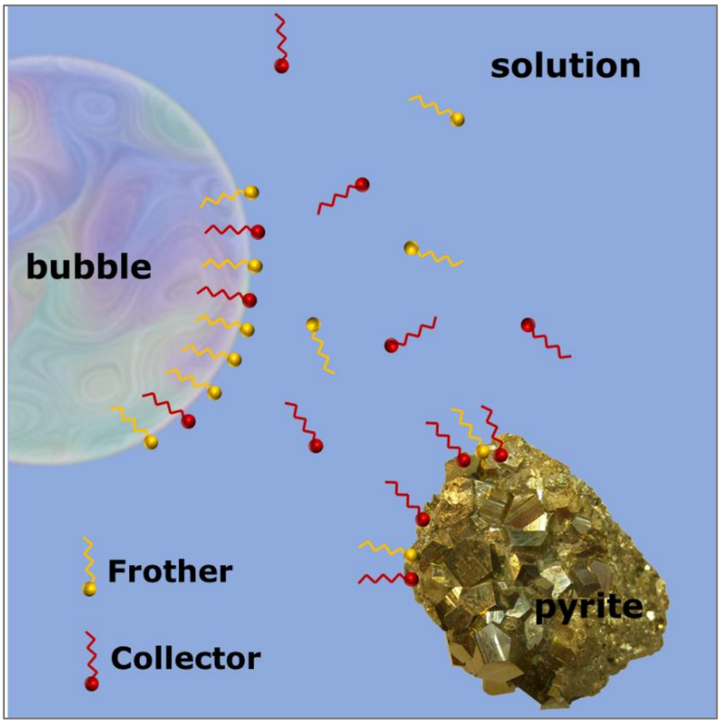


Figure 39: Interaction of collectors and frothers at the solid-water interface of pyrite and the air-water interface of a bubble film prior to bubble-particle contact.

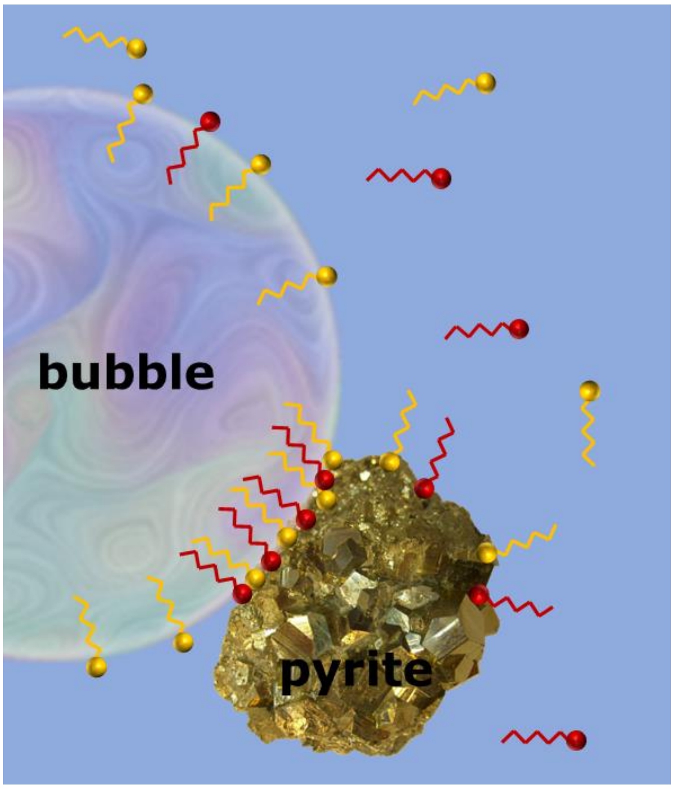


Figure 40: Interaction of frothers and collectors at the bubble-pyrite interface after bubble-particle collision and attachment

Furthermore, the presence of a frother molecules allows electrostatic repulsion to be satisfied as they possesses the ability to reorientate their dipole nearly instantaneously (Leja & He, 1984). For this to occur during bubble-particle attachment, the contact time between bubble and particle contact must be longer than the time the frother molecule requires for reorientation of its dipole (relaxation time). When the film becomes too condensed, relaxation time increases and this reduces bubble particle attachment. Of the anionic collectors, SEDTP has a more electroneutral character as its counterion is more tightly bound, therefore it would reduce the relaxation time and improve bubble-particle attachment.

Considering the interaction between SEDTP and frother leads to speculation as to why SEX does not behave similarly. Although pyrite has been proven to be floatable with ethyl xanthate in various studies (Fuerstenau, Huiatt & Kuhn, 1971; Shen, Fornasiero & Ralston, 1998), the mineral sample used in this study is more than likely somewhat oxidized. Adsorption of SEX onto pyrite is still likely to occur, SEX shows no indication of being present at the air-water interface from the surface tension and foam stability data. In fact, in the froth stability experiments there is an indication that SEX has a destructive effect on the froth phase. Furthermore, Taguta (2015) showed that SEX does adsorb onto the same sample of pyrite. Therefore if SEX is not present at both the air-water interface and solid-water interface, the addition of a frother does not improve foam/froth stability or the recovery of pyrite.

5. Conclusion

The mechanism through which SEDTP improves flotation performance has been clarified. It is proposed that SEDTP has properties which allow it to adsorb at the air-water interface. This is determined by comparing surface tension and foam/froth stability results of SEDTP with another collector, SEX, and a frother. Furthermore, the ability of SEDTP to interact at air-water and the solid-water interface suggests that it would improve bubble-particle attachment and thus bubble-particle hydrophobicity. For this, microflotation recoveries of pyrite and galena are a measure of particle hydrophobicity and bubble-particle attachment.

A combination of SEDTP and a frother improved the pulp hydrophobicity of pyrite and galena synergistically in terms of microflotation recovery. This synergy was observed at both acidic and alkaline pH, and at variable frother molecular weights and types, indicating that the same mechanism was responsible for all recovery improvements. In comparison, SEX displayed no synergy with a frother in the microflotation of pyrite at both pH levels. The ability of SEDTP to improve recovery in the presence of frother, while SEX did not, is attributed to the ability of SEDTP to adsorb at both the air-water and solid-water interfaces.

Although SEDTP possesses little foaming ability as a single reagent, a mixture of SEDTP and frother increased foam stability synergistically, thus indicating the presence of SEDTP on bubble films. Enhanced foam stability of this mixture is thought to be a result of better packing of the surfactants at the air-water interface. SEDTP-frother synergy for 3-phase froth stability is not exhibited: SEDTP is thought to adsorb onto the PGM-containing ore and thus become partially unavailable to adsorb at the air-water interface. SEDTP does not display the ability to reduce surface tension (thus be more surface active) to the same extent as a frother, however it is a better surfactant at the air-water interface than SEX due to the molecule having a stronger bond with its cation. UV-vis adsorption shows that SEDTP only partially adsorbs onto pyrite, with the remaining SEDTP in solution, available to attach at the air-water interface. The presence of both SEDTP and frother at both the air-water interface and solid-water interface allows better bubble-particle attachment and enhanced particle hydrophobicity

Neither SEDTP nor SEX improved the flotation of pyrite at pH 9 and only a slight improvement in recovery was achieved at pH 4. Thus, although various measures were taken to prevent and remove surface oxidation, it is safe to assume that the pyrite (and galena) was oxidized. Therefore, the SEDTP-frother synergy could have a major application in the flotation of oxidized PGM ores.

5.1 Recommendations for future work

The recommended future work to expand on the findings in this thesis is given below:

1. Dynamic surface tension and bubble sizing experiments on mixtures with DTP would give further insight to the behaviour of DTP at the air-water interface, inferred by improved rate of adsorption and bubble size reduction.
2. The effects of frother of different ionic character may give insights into co-adsorption at interfaces. It is assumed that the performance of a cationic frother would be significantly improved by the addition of the anionic SEDTP molecule.
3. Batch flotation and microflotation experiments at controlled redox environment would give further insight to the collector and mineral speciation required to initiate the synergistic DTP response. Furthermore, colourimetric determination of frother concentration in solution would give an indication of their adsorption behaviour.
4. Initial mineral oxidation and its effect on the downstream processes in terms of its effect on the pulp conditions and collector adsorption needs to be investigated.

6. References

Ackerman, P.K., Harris, G.H., Klimpel, R.R. & Aplan, F.F. 1987. Evaluation of flotation collectors for copper sulfides and pyrite, III. Effect of xanthate chain length and branching. *International Journal of Mineral Processing*. 21(1–2):141–156. DOI: 10.1016/0301-7516(87)90011-1.

Adkins, S.J. & Pearse, M.J. 1992. The Influences of Collector Chemistry on Kinetics and Selectivity in Base-Metal Sulphide Flotation. *Minerals Engineering*. 5(3–5):295–310.

Allan, G.C. & Woodcock, J.T. 2001. A review of the flotation of native gold and electrum. *Minerals Engineering*. 14(9):931–962. DOI: 10.1016/S0892-6875(01)00103-0.

Aveyard, R., Binks, B.P., Rutherford, C.. & Fletcher, P.D.. 1994. Measurement of contact angles of spherical monodisperse particles with surfactant solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 83(1):89–98.

Bagci, E., Ekmekci, Z. & Bradshaw, D. 2007. Adsorption behaviour of xanthate and dithiophosphinate from their mixtures on chalcopyrite. *Minerals Engineering*. 20(10):1047–1053. DOI: 10.1016/j.mineng.2007.04.011.

Bikerman. 1973. Foams. In *Applied Physics and Engineering*. Berlin: Springer-Verlag.

Booth, R.B. & Freyberger, W.L. 1962. Froths and frothing agents. *Froth Flotation, 50th Anniversary Volume*.

Bradshaw, D.J. 1997. Synergistic effects between thiol collectors used in the flotation of pyrite. University of Cape Town.

Bradshaw, D. & O’Connor, C. 1994. The flotation of pyrite using mixtures of dithiocarbamates and other thiol collectors. *Minerals Engineering*. 7(5–6):681–690.

Bradshaw, D.J., Harris, P.J. & Connor, C.T.O. 1998. Synergistic interactions between reagents in sulphide flotation. *The Journal of The South African Institute of Mining and Metallurgy*. 98(4):189–194.

Bradshaw, D.J., Buswell, A.M., Harris, P.J. & Ekmekci, Z. 2006. Interactive effects of the type of milling media and copper sulphate addition on the flotation performance of sulphide minerals from Merensky ore Part I: Pulp chemistry. *International Journal of Mineral*

Processing. 78(3):153–163. DOI: 10.1016/j.minpro.2005.10.004.

Buckley, A.N. & Woods, R. 1997. Chemisorption—the thermodynamically favoured process in the interaction of thiol collectors with sulphide minerals. *International Journal of Mineral Processing*. 51:15–26. DOI: 10.1016/S0301-7516(97)00016-1.

Bulatovic, S.M. 2010. *Handbook of Flotation Reagents: Chemistry, Theory and Practice*. DOI: 10.1016/B978-0-444-53082-0.00023-8.

Castelyn, D.G. 2012. The effect of mixing thiol collectors in the flotation of pure sulphide ores. University of Cape Town.

Chander, S. 1999. Fundamentals of Sulfide Mineral Flotation. In *Advances in Flotation Technology*. B.K. Parekh & J.D. Miller, Eds. Littleton, CO: SME. 129–146.

Cho, Y.. & Laskowski, J.S. 2002. Effect of Frothers on Foamability, Foam Stability, and Bubble Size. *International Journal of Mineral Processing*. 64(1–3):69–80. DOI: 10.1080/07349340701249794.

Cohen, R., Vazharova, M., Sokolowski, A., Burcyzk, B. & Exerova, D. 1981. Foam stabilizing properties of linear acetals containing oxyethylene units in their molecules. *Tenside Detergents*. 18(4):202.

Cooper, H., Fuerstenau, M.C., Harris, C.C., Kuhn, M.C., Miller, J.D. & Yap, R.F. 1985. Flotation. In *SME Mineral Processing Handbook*. N.L. Weis, Ed. New York: Society of Mining Engineers. 1–110.

Corin, K.C., Bezuidenhout, J.C. & O'Connor, C.T. 2012. The role of dithiophosphate as a co-collector in the flotation of a platinum group mineral ore. *Minerals Engineering*. 36–38:100–104. DOI: 10.1016/j.mineng.2012.02.019.

Critchley, J. & Riaz, M. 1991. Study of synergism between xanthate and dithiocarbamate collectors in flotation of heazlewoodite. *Transactions of the Institution of Mining and Metallurgy*. 100:55–57.

Crozier, R.D. & Klimpel, R.R. 1989. Frothers: Plant Practice. *Mineral Processing and Extractive Metallurgy Review*. 5(1–4):257–279. DOI: 10.1080/08827508908952652.

Cytec. 2002. *Mining Chemicals Handbook*. 3rd ed. A. Day, Ed. Cytec.

Deng, T., Yu, S., Lotter, N. & Feo, A. Di. 2010. *Laboratory testwork of mixed xanthates for the raglan ore*. Ottawa.

Eastoe, J. & Dalton, J.. 2000. Dynamic surface tension and adsorption mechanisms of surfactants at the air–water interface. *Advances in Colloid and Interface Science*. 85(2–3):103–144. DOI: 10.1016/S0001-8686(99)00017-2.

Ekmekci, Z. & Demirel, H. 1997. Effects of galvanic interaction on collectorless flotation behaviour of chalcopyrite and pyrite. *International Journal of Mineral Processing*. 52:31–48.

El-Shall, H., Abdel-Khalek, N.A. & Svoronos, S. 2000. Collector-frother interaction in column flotation of Florida phosphate. *International Journal of Mineral Processing*. 58(1–4):187–199. DOI: 10.1016/S0301-7516(99)00054-X.

Farrokhpay, S. & Zanin, M. 2012. Synergic Effect of Collector and Frother on Froth Stability and Flotation Recovery – An Industrial Case. In *11th Mill Operators' Conference*. Hobart: Australasian Institute of Mining and Metallurgy. 29–31.

Feng, D. & Aldrich, C. 1999. Effect of particle size on flotation performance of complex sulphide ores. *Minerals Engineering*. 12(7):721–731. DOI: 10.1016/S0892-6875(99)00059-X.

Finkelstein, N.P. & Goold, L.A. 1972. *The reaction of sulphide minerals with thiol compounds*. Johannesburg.

Finkelstein, N.P. & Poling, G.. 1977. Role of Dithiolates in the Flotation of Sulphide minerals. *Minerals Science Engineering*. 9(4):177–197.

Fuerstenau, D.W. & Wayman, C.H. 1958. Effect Of Chemical Reagents On The Motion Of Single Air Bubbles In Water. In *Transactions of the Institute of Mining and Metallurgy 211*. 694–699.

Fuerstenau, M.C., Kuhn, M.C. & Elgillani, D.A. 1968. The role of dixanthogen in xanthate flotation of pyrite. *Trans. AIME*. 241:148–156.

Fuerstenau, M.C., Huiatt, J.L. & Kuhn, M.C. 1971. Dithiophosphate vs . Xanthate Flotation of Chalcocite and Pyrite. *Trans. AIME*. 250:227–231.

Fuerstenau, M.C., Chander, S. & Woods, R. 2007. Sulfide Mineral Flotation. In *Froth Flotation: A Century of Innovation*. M.C. Fuerstenau, R.H. Yoon, & G.J. Jameson, Eds. Littleton, CO:

Society for Mining, Metallurgy and Exploration Inc. 425–464.

Grano, S.R., Cnossen, H., Skinner, W., Prestidge, C.A. & Ralston, J. 1997. Surface modifications in the chalcopyrite-sulphite ion system, II. Dithiophosphate collector adsorption study. *International Journal of Mineral Processing*. 50:27–45. DOI: 10.1016/S0301-7516(97)00003-3.

Grano, S.R., Prestidge, C.A. & Ralston, J. 1997. Solution interaction of ethyl xanthate and sulphite and its effect on galena flotation and xanthate adsorption. *Int. J. Miner. Process*. 52:161–186.

Grau, R.A., Laskowski, J.S. & Heiskanen, K. 2005. Effect of frothers on bubble size. *International Journal of Mineral Processing*. 76(4):225–233. DOI: 10.1016/j.minpro.2005.01.004.

Güler, T., Hiçyilmaz, C., Gökağaç, G. & Ekmekçi, Z. 2005. Electrochemical behaviour of chalcopyrite in the absence and presence of dithiophosphate. *International Journal of Mineral Processing*. 75(3–4):217–228. DOI: 10.1016/j.minpro.2004.08.009.

Güler, T., Hiçyilmaz, C., Gökağaç, G. & Ekmeçi, Z. 2006. Adsorption of dithiophosphate and dithiophosphinate on chalcopyrite. *Minerals Engineering*. 19:62–71. DOI: 10.1016/j.mineng.2005.06.007.

Gupta, A.K., Banerjee, P.K., Mishra, A., Satish, P. & Pradip. 2007. Effect of alcohol and polyglycol ether frothers on foam stability, bubble size and coal flotation. *International Journal of Mineral Processing*. 82(3):126–137. DOI: 10.1016/j.minpro.2006.09.002.

Hadler, K., Aktas, Z. & Cilliers, J.J. 2005. The effects of frother and collector distribution on flotation performance. *Minerals Engineering*. 18(2 SPEC. ISS.):171–177. DOI: 10.1016/j.mineng.2004.09.014.

Hangone, G., Bradshaw, D. & Ekmekci, Z. 2005. Flotation of a copper sulphide ore from Okiep using thiol collectors and their mixtures. *The Journal of The South African Institute of Mining and Metallurgy*. 105:199–206.

Harris, P.J. 1982. Frothing phenomena and frothers. In *The Principles of Flotation*. 237–248.

Hayashi, K., Sasaki, Y., Inomata, S. & Yanagidani, T. 1984. Acid Dissociation Constants of Alkyl Xanthic Acids and Formations Constant of Cadmium (II) and Zinc (II) Complexes in 1:1

v/v H20-DMF Medium. *Bulletin of the Chemical Society of Japan*. 57(11):3074–3076.

Hayashi, K., Sasaki, Y., Tagashira, S. & Yanagidani, T. 1986. Acid Dissociation Constants of Dialkyldithiocarbamic Acids and O, O′-Dialkyl S-Hydrogen Dithiophosphates and Formation Constants of Their Complexes with Cadmium(II), Zinc(II), and Lead(II) in 1:1 v/v Water-DMF Medium. *Bulletin of the Chemical Society of Japan*. 59(4):1255–1256. DOI: 10.1246/bcsj.59.1255.

Jachimska, B., Lunkenheimer, K. & Małysa, K. 1995. Effect of Position of the Functional Group on the Equilibrium and Dynamic Surface Properties of Butyl Alcohols. *Journal of Colloid and Interface Science*. 176:31–38.

Jia, H., Leng, X., Hu, M., Song, Y., Wu, H., Lian, P., Liang, Y., Zhu, Y., et al. 2017. Systematic investigation of the effects of mixed cationic/anionic surfactants on the interfacial tension of a water/model oil system and their application to enhance crude oil recovery. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 529:621–627. DOI: 10.1016/j.colsurfa.2017.06.055.

Kelebek, S. & Yoruk, S. 2002. Bubble contact angle variation of sulphide minerals in relation to their self-induced flotation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 196:111–119.

Klimpel, R.R. 1984. The Effect of Chemical Reagents on the Flotation Recovery of Minerals," C. *Chemical Engineering*. 21(18):75–79.

Klimpel, R.R. 1994. A review of sulfide mineral collector practice. In *Advances in Flotation Technology*. B.K. Parekh & J.D. Miller, Eds. Littleton, CO: Society for Mining, Metallurgy, and Exploration. 115–127.

Klimpel, R. & Hansen, R. 1988. Frothers. *Marcel Dekker, Inc., Reagents in Mineral Technology,*.

Laskowski, J. & Woodburn, E. 1998. *Frothing in Flotation II: Recent Advances in Coal Processing*. 2nd ed. CRC Press.

Leja, J. 1982. Flotation surfactants. In *Surface Chemistry of Froth Flotation*. 1st ed. New York: Plenum Press. 205–339.

Leja, J. & He, B.Q. 1984. The role of flotation frothers in the particle-bubble attachment process. In *Principles of Mineral Flotation*. M.H. Jones & J.T. Woodcock, Eds. Australasian Institute of Mining and Metallurgy. 73–89.

Leja, J. & Schulman, J.H. 1954.

Lekki, J. & Laskowski, J. 1971. On the dynamic effect of frother-collector joint action in flotation. *Transactions of the Institute of Mining and Metallurgy, Section C*. 80(June):174–180.

Lekki, J. & Laskowski, J. 1975. A new concept of frothing in flotation systems... - Google Scholar. *Proceedings of 11th International Minerals Processing Congress*.

Leppinen, J.O., Basilio, C.I. & Yoon, R.H. 1989. In-situ FTIR study of ethyl xanthate adsorption on sulfide minerals under conditions of controlled potential. *International Journal of Mineral Processing*. 26(3–4):259–274. DOI: 10.1016/0301-7516(89)90032-X.

Lotter, N.O. & Bradshaw, D.J. 2010. The formulation and use of mixed collectors in sulphide flotation. *Minerals Engineering*. 23(11–13):945–951. DOI: 10.1016/j.mineng.2010.03.011.

Lucassen-Reynders, E.H., Lucassen, J. & Giles, D. 1981. Surface and Bulk Properties of Mixed Anionic/Cationic Surfactant Systems I. Equilibrium Surface Tensions. *Journal of Colloid and Interface Science*. 81(1):150–157.

Manev, E. & Pugh, R.J. 1993. Frother/collector interactions in thin froth films and flotation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 70(3):289–295. DOI: 10.1016/0927-7757(93)80302-U.

Marinova, K.G., Naydenova, K.T., Basheva, E.S., Bauer, F., Tropsch, J. & Franke, J. 2017. New surfactant mixtures for fine foams with slowed drainage. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 523:54–61. DOI: 10.1016/j.colsurfa.2017.03.050.

Marozva, T. 2015. Investigating the effect of frother type on froth stability , froth recovery and entrainment Tafadzwa Marozva. University of Cape Town.

Martin, C.J., Rao, S.R., Finch, J.A. & Le Roux, M. 1989. Complex Sulphide Ore Processing with Pyrite Flotation by Nitrogen. *International Journal of Mineral Processing*. 26:95–110.

Matsuoka, I. & Ichikoku, T. 1982. Study on Collection of Galena by Dithiophosphates. *J. Min. Metall. Inst. Jpn*. 98(1131):423–428.

McFadzean, B. & O’Connor, C.T. 2014. A thermochemical study of thiol collector surface reactions on galena. *Minerals Engineering*. 65:54–60. DOI: 10.1016/j.mineng.2014.04.010.

McFadzean, B., Castelyn, D.G. & O'Connor, C.T. 2012. The effect of mixed thiol collectors on the flotation of galena. *Minerals Engineering*. 36–38:211–218. DOI: 10.1016/j.mineng.2012.03.027.

McFadzean, B., Mhlanga, S.S. & O'Connor, C.T. 2013. The effect of thiol collector mixtures on the flotation of pyrite and galena. *Minerals Engineering*. 50–51:121–129. DOI: 10.1016/j.mineng.2013.06.018.

Mingione, P.A. 1984. Use of dialkyl and diaryl dithiophosphate promoters as mineral flotation agents. In *Reagents in the Minerals Industry*. London: Institute for Mining and Metallurgy. 19–24.

Mu, Y., Peng, Y. & Lauten, R.A. 2016. The depression of pyrite in selective flotation by different reagent systems – A Literature review. *Minerals Engineering*. 96–97:143–156.

Nagaraj, D.R. 2005. Reagent selection and optimization—the case for a holistic approach. *Minerals Engineering*. 18(2):151–158. DOI: 10.1016/j.mineng.2004.10.017.

Nagaraj, D.R. & Brinen, J.S. 2001. SIMS study of adsorption of collectors on pyrite. *International Journal of Mineral Processing*. 63(1):45–57. DOI: 10.1016/S0301-7516(01)00043-6.

Nagaraj, D.R. & Ravishankar, S.A. 2007. Flotation reagents - A critical overview from an industry perspective. In *Froth Flotation: A Century of Innovation*. M.C. Fuerstenau, G. Jameson, & R.-H. Yoon, Eds. Littleton, CO: Society for Mining, Metallurgy and Exploration Inc. 375–424.

Nyambayo, C.K. 2014. The use of mixed thiol collectors in the flotation of Nkomati sulphide ore. University of Cape Town.

Petrus, T.B.M., Hirajima, T., Sasaki, K., Okamoto, H. & Petrus, H.T.B.M. 2011. Study of Diethyl Dithiophosphate Adsorption on Chalcopyrite and Tennantite at Varied pHs. *ISSN Journal of Mining Science*. 47(5):1062–7391.

Plaksin, I. & Glembockii, V. 1954. Investigations of the possible intensification of the flotation process using combinations of collectors. *Tr. Inst. Gorn. Akad. Nauk SSSR,*. 1:213–214.

Plaksin, I. & Zaitseva, S. 1960. Effect of the combined action of certain collectors on their distribution between galena particles in a flotation pulp. *Nauchn. Soobshch.,*. 15–20.

Ralston, J. 1991. Eh and its Consequences in Sulphide Mineral Flotation. *Minerals Engineering*. 4(7–11):859–878.

Rao, C.R.M. & Reddi, G.S. 2000. Platinum group metals (PGM); occurrence, use and recent trends in their determination. *TrAC - Trends in Analytical Chemistry*. 19(9):565–586. DOI: 10.1016/S0165-9936(00)00031-5.

Rosen, M.J. 2004. *Surfactants and interfacial phenomena*. V. 40. DOI: 10.1016/0166-6622(89)80030-7.

Roy, S., Datta, A. & Rehani, S. 2015. Flotation of copper sulphide from copper smelter slag using multiple collectors and their mixtures. *International Journal of Mineral Processing*. 143:43–49. DOI: 10.1016/j.minpro.2015.08.008.

Schumann, R. 1942. Flotation Kinetics. I. Methods for steady-state study of flotation problems. *The Journal of Physical Chemistry*. 8:891–902.

Shen, W.Z., Fornasiero, D. & Ralston, J. 1998. Effect of collectors, conditioning pH and gases in the separation of Sphalerite from Pyrite. *Minerals Engineering*. 11(2):145–158.

Shortridge, P.G., Harris, P.J., Bradshaw, D.J. & Koopal, L.K. 2000. The effect of chemical composition and molecular weight of polysaccharide depressants on the flotation of talc. *International Journal of Mineral Processing*. 59(3):215–224. DOI: 10.1016/S0301-7516(99)00077-0.

Smar, V.D., Klimpel, R.R. & Aplan, F.F. 1994. Evaluation of chemical and operational variables for the flotation of a copper ore Part I - Collector concentration, frother concentration, and air flow rate. *International Journal of Mineral Processing*. 42(3–4):225–240. DOI: 10.1016/0301-7516(94)00029-8.

Stowe, K.., Chryssoulis, S.. & Kim, J.. 1995. Mapping of composition of mineral surfaces by TOF-SIMS. *Minerals Engineering*. 8(4/5):421–430.

Sweet, C., van Hoogstraten, J., Harris, M.C. & Laskowski, J.S. 1997. The effect of frothers on bubble size and frothability of aqueous solutions. In *2nd UBC-McGill Symposium: Processing of Complex Ores*. J.A. Finch & I. Holubec, Eds. Montreal: Canadian Institute of Mining, Metallurgy and Petroleum. 235–246.

Szymula, M., Kozioł, A.E. & Szczypa, J. 1996. Effect of xanthate chain length on decrease of xanthate concentration in solutions in contact with copper sulphides. *International Journal of Mineral Processing*. 46(1–2):123–135. DOI: 10.1016/0301-7516(95)00012-7.

Taggart, A.F. 1951. *Elements of Ore Processing*.

Taggart, A.F., del Guidice, G.R.M. & Ziehl, O.A. 1934. The case for the chemical theory of flotation. *Trans. AIME*. 112:348–381.

Taguta, J. 2015. Thermochemical behaviour of thiol collectors and collector mixtures with sulphide minerals. University of Cape Town. DOI: 10.1017/CBO9781107415324.004.

Tan, S.N., Fornasiero, D., Sedev, R. & Ralston, J. 2006. The interfacial conformation of polypropylene glycols and their foam properties. *Minerals Engineering*. 19(6):703–712. DOI: 10.1016/j.mineng.2005.09.018.

Tolun, R. & Kitchener, J. 1964. Electrochemical study of the galena-xanthate-oxygen flotation system. *Trans. 2001*. 73:313–322.

Trawí, A., Hallmann, E. & Edrzycka, K.M. 2016. The effect of alkyl chain length on synergistic effects in micellization and surface tension reduction in nonionic gemini (S-10) and anionic surfactants mixtures. *Aspects*. 506:114–126. DOI: 10.1016/j.colsurfa.2016.06.001.

Uddin, S., Jin, L., Mirnezami, M. & Finch, J.A. 2013. An apparatus to measure electrical charge of bubble swarms. *Journal of Colloid and Interface Science*. 389(1):298–305. DOI: 10.1016/J.JCIS.2012.08.056.

Valdiviezo, E. & Oliveira, J.F. 1993. Synergism in Aqueous Solutions of Surfactant Mixtures and its effect on the Hydrophobicity of Mineral Surfaces. *Minerals Engineering*. 6(6):655–661.

Valli, M., Malmensten, B. & Persson, I. 1994. A vibration spectroscopic study of the interaction between some sulphide minerals and 0, O-diethyl dithiophosphate ions in aqueous solution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 83:227–236.

Wakamatsu, T., Numata, Y. & Park, C. 1979. Fundamental study on the flotation of minerals using two kinds of collectors. In *Fine Particle Processing,*. New York: American Institute of Mining, Metallurgical and Petroleum Engineers. 787.

Wark, E.E. & Wark, I. a N.W. 1933. The Physical Chemistry of Flotation III. The Relationship Between Contact Angle and the Constitution of the Collector. *American Institute of Mining & Metallurgical Engineers*. 37(6):805–814.

Wiese, J., Harris, P. & Bradshaw, D. 2005. Investigation of the role and interactions of a dithiophosphate collector in the flotation of sulphides from the Merensky reef. *Minerals Engineering*. 18:791–800. DOI: 10.1016/j.mineng.2005.01.032.

Wiese, J., Harris, P. & Bradshaw, D. 2006. The role of the reagent suite in optimising pentlandite recoveries from the Merensky reef. *Minerals Engineering*. 19(12):1290–1300. DOI: 10.1016/j.mineng.2006.04.003.

Zhang, R. & Somasundaran, P. 2006. Advances in adsorption of surfactants and their mixtures at solid/solution interfaces. DOI: 10.1016/j.cis.2006.07.004.

Appendix A: Bubble Pressure Tensiometry

Reagent conditions	pH	average	RSD (%)
DIW	7	72.97	0.02
	9	72.97	0.05
	11	72.98	0.07
100 mM Frother	7	58.50	0.03
	9	58.70	0.03
	11	58.68	0.00
100 mM SEDTP	7	68.93	0.08
	9	69.02	0.14
	11	69.15	0.06
100 mM SEX	7	72.67	0.04
	9	72.68	0.03
	11	72.70	0.01

Concentration (mM)	Frother	RSD (%)	SEDTP	RSD (%)	SEX	RSD (%)
0	72.40	0.00	72.40	0.00	72.40	0.00
5	68.55	0.08	72.38	0.03	72.31	0.07
25	63.88	0.10	71.75	0.05	72.10	0.03
50	61.54	0.03	71.13	0.03	72.63	0.03
75	59.89	0.06	69.43	0.07	72.74	0.03
100	58.91	0.06	68.42	0.03	72.68	0.03

SEDTP Concentration (mM)	SEDTP + 25 mM Frother	RSD (%)	SEDTP + 50 mM SEX + 25 mM Frother	RSD (%)
0	72.40	0.00	72.40	0.00
5	63.58	0.03	64.29	0.03
25	62.48	0.06	63.69	0.00
50	61.76	0.03	63.23	0.08
75	61.17	0.03	62.63	0.03
100	60.64	0.06	62.24	0.03

Appendix B: Foam heights

t(s)	Frother with:							
	No collectors		SEX		50 SEDTP: 50 SEX		SEDTP	
	Foam height (cm)	RSD (%)	Foam height (cm)	RSD (%)	Foam height (cm)	RSD (%)	Foam height (cm)	RSD (%)
5	8.40	0.00	9.20	6.15	9.75	2.18	10.20	1.39
10	14.60	0.00	14.85	11.90	16.20	3.49	16.75	2.96
15	19.47	3.10	18.80	4.51	21.40	1.32	23.20	4.27
20	23.83	7.46	22.10	3.20	24.90	2.84	27.90	6.08
25	28.03	5.29	25.20	0.56	29.70	1.90	34.30	0.41
30	31.93	5.37	27.60	1.02	33.40	3.39	38.60	0.37
35	35.70	5.41	29.90	0.47	36.70	2.70	42.80	0.66
40	38.30	7.21	31.65	1.12	39.20	3.97	46.75	0.76
45	41.05	7.75	33.55	1.05	41.30	5.14	50.00	0.57
50	43.10	7.55	35.15	1.01	43.55	4.06	53.45	0.93
55	44.10	6.09	36.15	0.98	45.35	5.77	55.60	0.51
60	44.90	5.67	37.55	0.19	46.90	5.13	57.70	0.74
65	45.35	4.21	38.45	0.55	48.50	6.71	59.35	1.55
70	44.85	3.63	39.15	0.18	50.05	6.08	61.15	1.97
75	44.65	3.01	39.60	0.36	50.75	6.55	62.55	3.05
80	44.10	2.89	40.25	0.88	51.85	7.77	63.60	3.11
85	43.45	2.12	40.55	0.17	52.35	7.70	64.10	1.99
90	42.70	0.33	40.55	0.17	52.95	7.08	64.25	1.65
95	41.80	0.34	40.55	0.17	53.60	7.12	64.50	1.10
100	41.40	0.68	40.55	0.17	54.15	7.18	65.00	0.00
105	41.20	0.00	40.55	0.17	54.65	6.60	65.00	0.00
110	40.25	0.88	40.80	0.69	54.65	6.60	65.00	0.00
115	39.90	2.13	41.35	0.86	55.05	7.58	65.00	0.00
120	39.90	2.13	41.10	1.72	55.05	7.58	65.00	0.00
135	41.40	3.07	41.10	1.72	55.55	6.24	65.00	0.00
150	42.95	5.43	40.90	2.42	55.05	7.58	65.00	0.00
165	44.20	4.48	40.10	3.53	54.45	9.22	65.00	0.00
180	44.45	5.25	40.05	1.59	53.75	11.18	65.00	0.00
210	45.80	4.01	38.20	2.96	51.20	13.81	63.50	3.34
240	46.15	2.91	36.80	3.84	49.25	11.92	61.85	3.77
270	43.80	2.91	35.10	5.24	47.70	7.71	60.95	4.76
300	41.00	2.41	33.95	4.79	46.20	3.37	58.30	5.09

Appendix C: Froth heights

t (s)	Frother with:					
	No collector		SEDTP		50 SEDTP: 50 SEX	
	Froth height (cm)	RSD (%)	Froth height (cm)	RSD (%)	Froth height (cm)	RSD (%)
0	0	0	0	0	0	0
10	17.80	7.80	19.23	4.48	17.73	3.26
20	28.27	3.78	30.20	2.32	23.40	1.97
30	34.37	5.45	36.53	1.56	27.43	1.87
40	38.57	2.49	40.93	4.21	30.13	2.87
50	41.17	1.58	44.80	3.13	32.17	1.77
60	44.03	2.61	46.80	2.26	33.63	2.31
70	46.23	1.65	48.97	1.12	34.47	3.10
80	47.87	2.72	50.10	1.21	35.53	1.14
90	49.40	3.71	51.33	2.22	36.53	1.90
105	50.47	1.60	52.37	1.91	37.77	3.37
120	51.97	0.68	53.37	1.36	38.23	4.61
140	52.57	1.15	54.60	3.11	39.03	6.97
160	53.33	1.36	55.27	1.90	39.03	4.40
180	53.83	0.28	55.70	1.43	40.00	5.50

Appendix D: Microflotation

Pyrite, pH 9

No Reagents

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	
2	13.15	1.66	1.17
6	20.91	1.14	0.80
12	28.68	0.80	0.57
20	34.27	0.91	0.65

SenFroth XP 200

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	
2	7.95	0.28	0.20
6	18.61	0.50	0.35
12	28.03	0.59	0.42
20	36.72	0.71	0.50

SEDTP

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	
2	8.77	0.50	0.29
6	17.99	0.73	0.42
12	28.56	1.19	0.69
20	34.97	1.68	0.97

SEX

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	
2	4.79	0.53	0.31
6	10.94	0.80	0.46
12	17.55	1.24	0.71
20	23.99	1.65	0.95

SEDTP + SenFroth XP 200

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	
2	21.97	4.70	3.33
6	48.88	5.29	3.74
12	68.43	4.76	3.36
20	76.87	4.81	3.40

SEX + SenFroth XP 200

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	
2	9.98	0.97	0.56
6	21.60	2.05	1.18
12	32.87	2.01	1.16
20	41.07	1.63	0.94

90 SEDTP : 10 SEX + SenFroth XP 200

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	
2	39.92	4.39	2.53
6	60.02	3.05	1.76
12	74.37	4.27	2.46
20	80.22	4.40	2.54

90 SEDTP : 10 SEX

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	
2	10.32	0.52	0.37
6	18.81	0.66	0.46
12	27.83	0.71	0.50
20	35.86	1.02	0.72

Pyrite, pH 4

No Reagents

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	0
2	4.81	1.10	0.78
6	10.68	1.83	1.29
12	18.14	2.48	1.76
20	24.28	2.041	1.44

SenFroth XP 200

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	0
2	18.74	2.50	1.77
6	47.17	4.95	3.50
12	58.69	4.28	3.02
20	65.19	4.67	3.30

SEDTP

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	0
2	10.46	2.73	1.93
6	20.73	1.24	0.88
12	33.07	1.27	0.90
20	43.87	0.86	0.60

SEX

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	0
2	7.77	1.68	1.19
6	14.77	1.53	1.08
12	23.14	2.04	1.44
20	29.84	1.17	0.83

SEDTP + SenFroth XP 200

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	0
2	78.66	2.79	1.97
6	90.32	5.04	3.57
12	91.95	4.75	3.36
20	93.11	4.58	3.24

SEX + SenFroth XP 200

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	0
2	19.13	1.84	1.30
6	37.84	2.30	1.63
12	47.20	0.68	0.48
20	54.79	4.00	2.83

90 SEDTP : 10 SEX + SenFroth XP 200

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	0
2	77.77	2.86	2.02
6	87.95	2.57	1.81
12	89.80	2.42	1.71
20	91.15	1.92	1.36

90 SEDTP : 10 SEX

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	0
2	35.19	4.30	3.04
6	50.57	3.74	2.64
12	62.93	3.41	2.41
20	73.33	2.65	1.87

SEDTP + 1-hexanol

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	0
2	69.19	0.41	0.29
6	83.44	2.59	1.83
12	87.29	3.56	2.52
20	89.39	3.48	2.46

SEDTP + 1-pentanol

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	0
2	54.02	0.57	0.41
6	78.39	2.54	1.80
12	89.48	0.69	0.49
20	93.30	2.03	1.44

SEDTP + PPG Mn 425

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	0
2	61.80	2.23	1.58
6	88.33	1.04	0.73
12	91.20	2.66	1.88
20	92.21	2.60	1.84

SEDTP + PPG Mn 725

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	0
2	56.86	1.03	0.73
6	86.10	1.71	1.21
12	92.92	2.88	2.04
20	94.59	2.92	2.07

Galena, pH 4

No reagents

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	0
2	7.94	1.19	0.84
6	13.66	0.31	0.22
12	21.15	2.16	1.53
24	35.47	2.11	1.49

SenFroth XP 200

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	0
2	11.79	1.33	0.94
6	23.00	0.32	0.23
12	33.97	7.41	5.24
24	44.55	12.94	9.15

SEDTP

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	0
2	4.09	0.66	0.46
6	8.18	0.59	0.42
12	14.25	4.38	3.10
24	19.25	4.53	3.20

SEDTP + SenFroth XP 200

Time	Average Cumulative Recovery [%]	Standard deviation	Standard error
0	0	0	0
2	31.01	7.86	5.56
6	61.79	7.95	5.62
12	74.92	5.27	3.73
24	81.32	4.70	3.32