The use of mixed thiol collectors in the flotation of Nkomati sulfide ore

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A thesis submitted to the faculty of Engineering and the Built Environment, University of Cape Town in fulfilment of the requirements for the degree of Master of Science in Engineering.

March 2014

Mwari mubatsiri wangu……..

Declaration

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

Constance Kudakwashe Nyambayo

Acknowledgements

I would like to acknowledge the following people who made it possible for me to complete this thesis:

- My supervisors: Dr Belinda McFadzean, Dr Kirsten Corin and Professor Cyril O’Connor for their input. Belinda McFadzean for her guidance, encouragement and patience as my main supervisor, Kirsten Corin for always being available for discussion throughout the course of this thesis and her invaluable input in the final days. Cyril O’Connor for the guidance and technical input.

- The UCT Centre for Minerals Research for the financial support

- Members of the CMR unit who were always willing to lend a helping hand especially Moegsien Southgate for the practical advice.

- My colleagues in CMR with whom I shared this journey, especially Margreth Tadie, Tanaka Shumba, Motena Takalamani , Monica Kalichini and Tafadzwa Marozva.

- Finally my family who have been with me from the beginning and laid the foundations on which my dream and goals are built on.

Synopsis

Mixtures of collectors are widely used in sulfide and platinum group mineral (PGM) flotation, and a range of performance benefits have been reported for many different systems. An increase in paymetal recovery and grade as well as increased rates of recovery at lower collector dosages has been observed when single collectors are replaced with multi-collector suites. These benefits have been attributed to increased carrying capacity of the froth phase, faster kinetics and increased recovery of middling or course particles. However, the mechanism of action of such collector suites is not clearly understood. Candidate selection of mixed collector suites is currently based on experience and contextual knowledge. The overall objective of this study was to experimentally identify a three component collector suite consisting of conventional collectors which could enhance the metallurgical performance of Nkomati nickel-copper sulfide ore. A three component collector suite consisting of sodium isobutyl xanthate (SIBX), sodium ethyl xanthate (SEX) and either sodium ethyl dithiophosphate (DTP) or sodium ethyl dithiocarbamate (DTC) was used.

The scope of this work was confined to the use of xanthates, DTC's and DTP's since they are in common use in industry, are supplied over a relatively low price range and have shown potential performance enhancements when used as mixtures. The standard University of Cape Town (UCT) batch flotation procedure was used in this investigation and changes in electrochemical potential were monitored as collector was added to the flotation cell. It is hypothesised that the benefits of collector mixtures are only evident at low dosages, thus, dosages were carefully controlled. The study aimed to determine whether benefits of collector mixtures were dominant in the pulp or froth phase and suggest a possible mechanism of action.

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1 Introduction

1.1 Background

Froth flotation is a physicochemical separation process which exploits the differences in surface properties of the valuable minerals and the gangue. This involves introduction of air bubbles to the ore slurry, the selective attachment of hydrophobic particles to air bubbles and the subsequent transfer of these particle-bearing bubbles to the froth layer. The froth, which is concentrated with hydrophobic mineral particles, is then removed to concentrate. The hydrophilic particles (the gangue) remain suspended in the aqueous phase and are removed to tailings (Whelan and Brown, 1956). Of particular interest to this study are collectors, these are chemicals that induce selective hydrophobicity onto the mineral of interest, allowing it to attach to the air bubbles.

The purpose of this study was to determine the effect of collector mixtures on the metallurgical performance of Nkomati sulfide ore and attempt to establish the mechanism by which performance is enhanced. General practice employs a two component collector system, however, in this study; three component collector suites will be investigated. Theory proposes that a suite of these collectors could synergistically be combined to give an optimal formula to improve grade and recovery. Synergism is defined by the Oxford dictionary as “the combined effect that exceeds the sum of the parts”. Investigations were carried out using the standard UCT batch flotation tests. The scope of this work was deliberately confined to the use of xanthates, dithiocarbamates and dithiophosphates since they are in common use are supplied at a relatively low price range and have potential performance enhancement when used as mixtures. If sustainable paymetal recovery gains can be made and proven from a reagent suite change, these gains represent high rates of return for any project concentrators since they do not require capital funds to implement (Woods, 2004) . This warrants the need for on-going research which addresses the need to further develop and advance the beneficiation process of nickel, copper and other minerals.

1.2 Project scope

The current study focuses on the evaluation of the metallurgical performance of collector suites as opposed to single collectors by chemically analysing for copper, nickel and sulphur recovery as well as particle size distribution of the concentrates recovered from batch flotation tests. Further tests were carried out in an attempt to understand how collector suites enhance flotation. These are size by size analysis, measurement of pulp potential during flotation and the investigating the effect of sequential addition of collector during batch flotation.

Two phase batch flotation tests were also carried out to investigate the frothing properties of the collectors used in this study. The collectors used were limited to collectors and frothers i.e. no depressants, activators or modifiers were used. The primary collectors used were; sodium isobutyl xanthate (SIBX), sodium ethyl xanthate (SEX), co-collectors used were; sodium ethyl dithiophosphate (DTP) and sodium ethyl dithiocarbamate (DTC) and the frother was DOW 200. Statistical analyses of results obtained are shown as error bars on relevant figures. These error bars represent the standard error between duplicate tests.

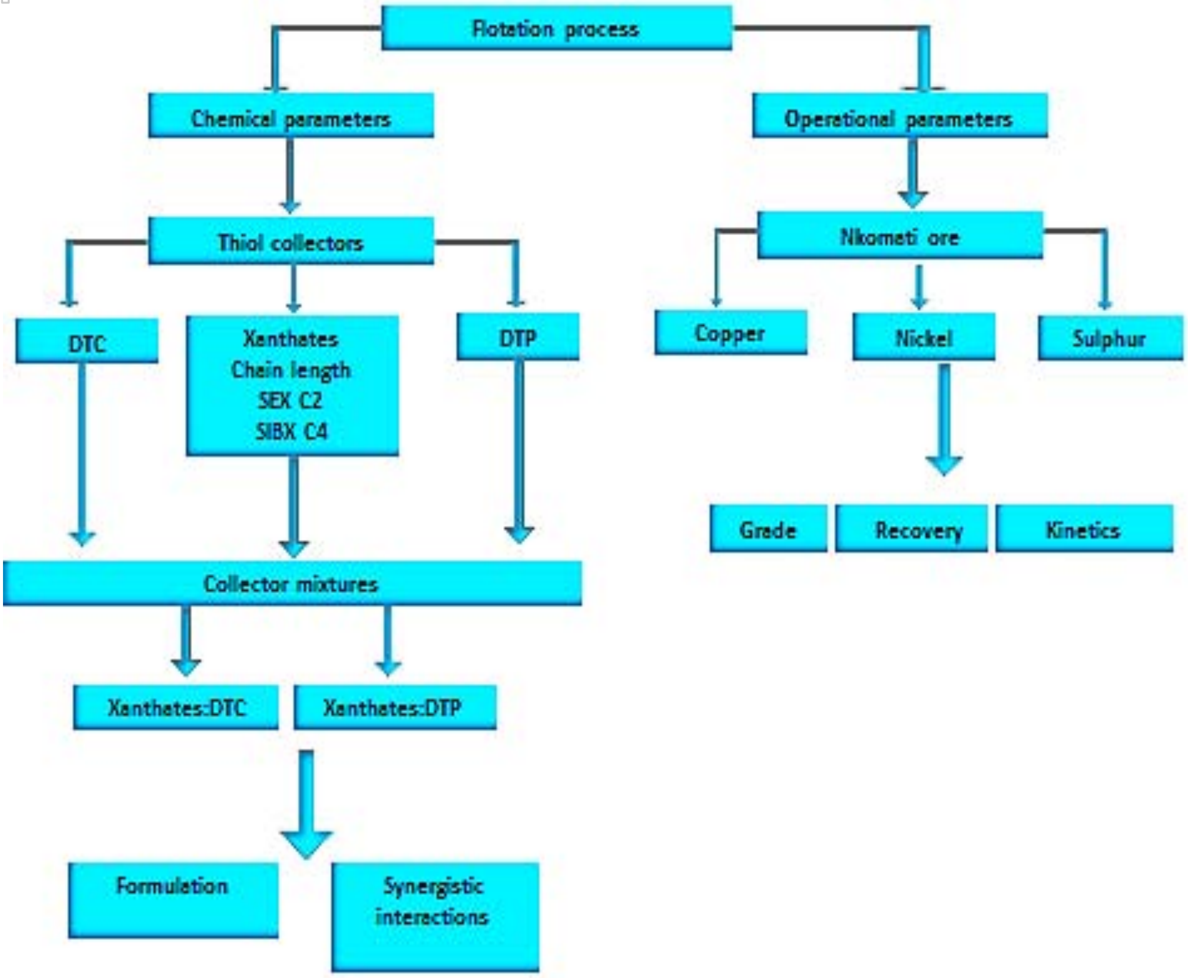

Figure 1.1 The scope of the thesis

1.3 Research objectives

The objectives of this study are to:

- Investigate and compare the metallurgical performance of single collectors, including any frothing effects.

- Determine the optimum ratio of collector mixtures by varying collector ratios of each collector suite (xanthate/DTC, xanthate/DTP).

- To ascertain if the use of a three component collectors system has any synergistic effects, a phenomenon where the combined effect of collectors exceeds the sum of the parts, as indicated by the following;
    i. Increase paymetal recovery i.e. nickel and copper
    ii. Improved concentrate grade
    iii. Increase the rate of flotation
    iv. Reduction in dosage requirement.

- To investigate if the synergistic effect, if observed, occurs as a result of froth phase effects or pulp phase effects.

- To investigate the mechanism of any observed synergistic effects occur by investigating
    i. The electrochemical potential of the pulp in batch flotation tests.
    ii. Sequence of addition of collectors.
    iii. Preferential recovery of different size classes for different collectors.

2 Literature review

2.1 Nkomati ore

Nkomati mine is a small to medium base-metal operation located in the Mpumalanga province of South Africa. The operation exploits complex high grade nickel, copper, cobalt and platinum deposits. The processing plant is highly automated and employs flotation technology to concentrate the minerals. Nkomati mine, located in the Mpumalanga province, is currently South Africa's primary nickel producer. It exploits the Uitkomst complex, a layered, mineralised, mafic to ultramafic intrusion which is believed to be a satellite body of the Bushveld complex because of their similarities in age and composition. (de Waal, 2001). The complex is host to nickel and copper deposits containing a mineral reserve of estimated at 2.9 million metric tonnes with massive ore grades of 2% nickel, 1% copper and 6ppm platinum and palladium. It also has an inferred 98 million metric tonnes of disseminated reserve with 0.6% nickel, 0.2% copper and 1ppm platinum and palladium (Li *et al*, 2002). The location and geology of the Uitkomst complex is shown in Figure 2.1.

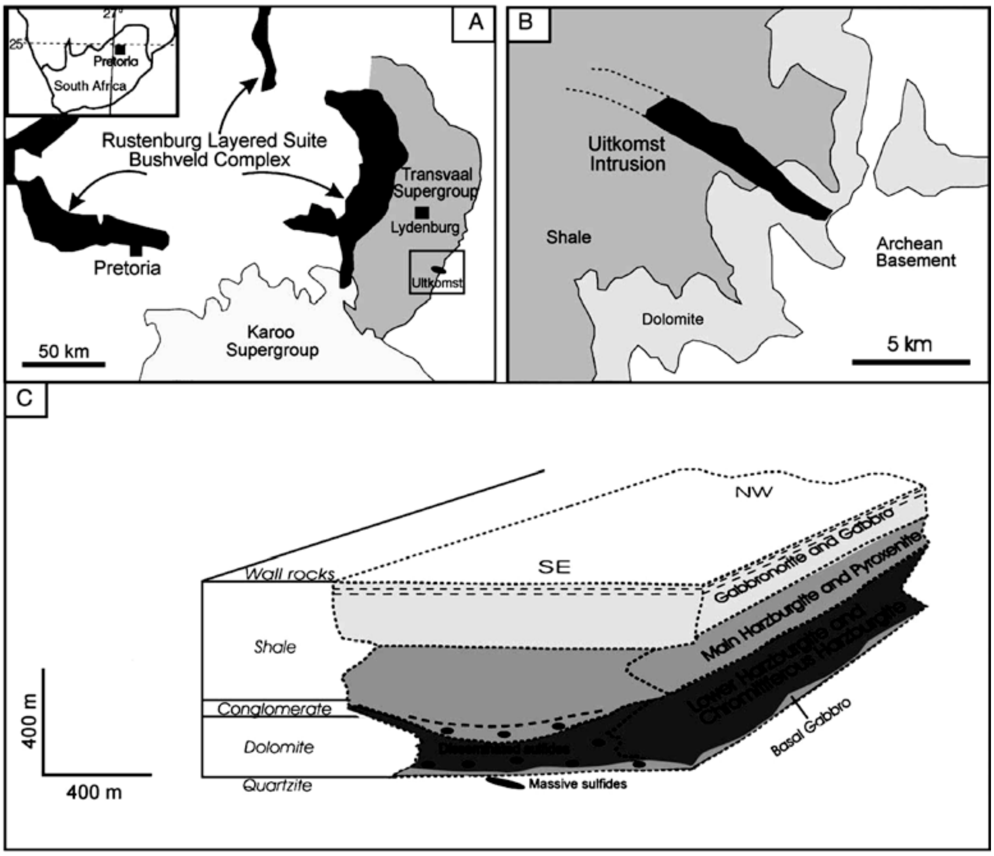

Figure 2.1 Location map of the Uitkomst complex (B) Simplified geological map of the Uitkomst complex (C) Schematic map of the Uitkomst complex (Li et al, 2002)

Ni-Cu-Co-PGM sulfide mineralisation occurs as blebs and stringers in three distinct zones within namely, the Basal Mineralised Zone (BMZ), the Main Mineralised Zone (MMZ) the Massive Sulfide Body (MSB), which was situated mainly in the granite basement of the Uitkomst complex, has been mined out.

The ore used in this study was sourced from the MMZ zone which is hosted by the Lower Pyroxenite Unit (LrPXT) and is composed of pristine to altered, hybrid mafic and ultramafic rocks that vary greatly in size. The MMZ comprises a number of ore types including net textured, blebby and disseminated sulfides as well as minor massive and semi massive bands and lenses (Wolmarans and Morgan 2009. Li et al, 2002). Cobalt, chrome and minor gold are economically important by-products from the mining operation (Guenther et al 2012).

2.2 Introduction to flotation and process description

Flotation is the most widely used and preferred methods of mineral recovery therefore large tonnages of ore are processed by flotation annually. An estimated two billion tonnes of ore are processed annually. The flotation process is advantageous because it is a highly selective as compared to other separation processes (Wills and Napier-Munn, 2006; Pearse 2005).

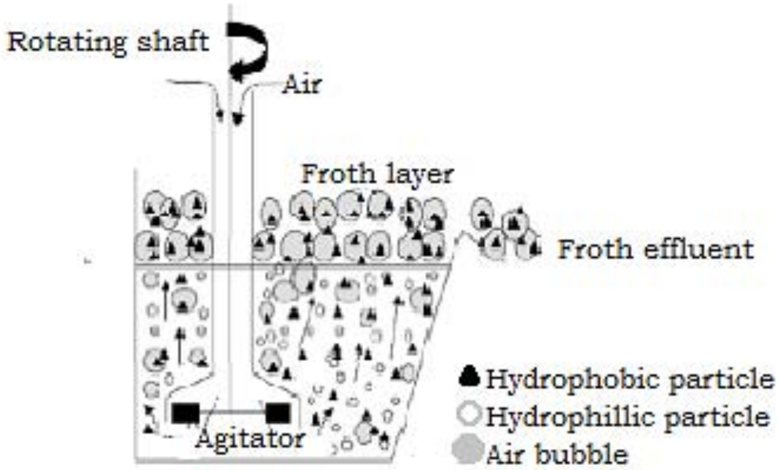

Figure 2.2 Schematic diagram representing the flotation process.

A simplified schematic of the flotation process is shown in Figure 2.2**Error! Reference source not found.**. There are two distinct zones; the pulp zone where mineral recovery takes place and the froth zone where the concentrated mineral is separated from the bulk. Particles report to the froth phase by either entrainment in water or through attachment. The former process is undesirable since it also carries gangue to the froth phase.

During flotation, air bubbles are introduced into the ore slurry, which is referred to as the pulp zone, through an air supply located at the base of the flotation cell. The bubbles rise through the pulp where they come into contact with suspended particles which selectively attach onto the bubble and are carried to the surface as determined by the hydrophobicity of the particles. Each bubble can potentially have many encounters with particles during its ascend therefore it can carry several particles to the surface. Particles can also leave the pulp phase through entrainment at the froth-pulp interface. Agitation of the slurry by an impellor keeps the particles in suspension although heavier particles tend to sink to the bottom of the tank.

A relatively stable layer of is maintained on the surface of the slurry. Bubble bearing particles that have risen through the pulp phase are transferred to the froth phase. The froth which is concentrated with hydrophobic mineral particles is recovered at the lip of the froth weir at the edge of the flotation cell. The recovery of the froth is accomplished through the natural mobility of the froth which causes it to flow over the weir and mechanically through the use of paddles. The hydrophilic particles (the gangue) remain suspended in the aqueous phase where they are flushed away (Whelan and Brown, 1956).

2.2.1 Sub-processes of flotation

As indicated in section 2.2.1 flotation process consists of several sequential steps which contribute to the overall success of the process. These steps can be summarised as;

i. Attachment of collector onto mineral surface which makes it hydrophobic.
ii. Formation of air bubbles by introducing air into the slurry.
iii. Collision of mineral with bubble, attachment and detachment of mineral to the bubble.
iv. Transport of loaded bubble through the pulp phase to the pulp-froth interface.
v. Transfer of loaded bubbles from the pulp phase to the froth phase. At this stage, entrained particles which are transported through entrainment also enter the froth phase.
vi. Transport and collection of the loaded bubble in the froth phase.

2.2.1.1 *Bubble-particle attachment*

An important step in froth flotation is the attachment of the bubble onto the mineral surface. The stability of the attachment is measured by the contact angle shown in Figure 2.3. The strength of attachment is directly proportional to the size of the contact angle, θ. When an air bubble does not displace the aqueous phase, the contact angle is zero and complete displacement is represented by an angle of 180°.

Values of contact angles between these two extremes give a scale by which the hydrophobic character of a surface can be described. A contact angle around 90° is usually sufficient for effective froth flotation but the optimum angle is 70°. (Rao, 2004)

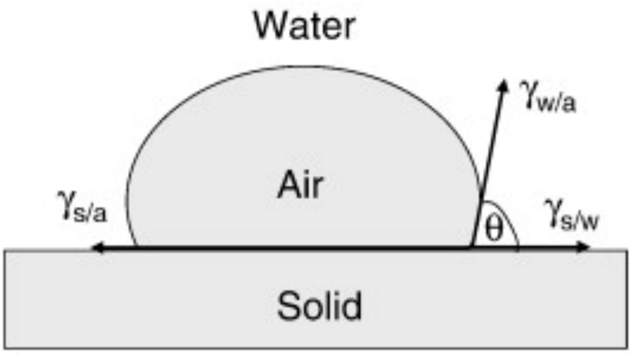

Figure 2.3 Contact angles between air bubble and a solid surface immersed in liquid (from Chau et al, 2009)

The general thermodynamic relationship between the solid, liquid and gas are best described using Young's equation:

$$\gamma_{s/a} = \gamma_{wa} Cos\ \theta + \gamma_{s/w} \ldots \textbf{Equation 1}$$

Where $\gamma_{s/a}, \gamma_{wa}, \gamma_{s/w}$ represent the interfacial energies between solid- air, water- air and solid-water systems and θ iis the contact angle.

For a bubble-mineral interaction to occur the following condition must be satisfied:

$$\gamma_{s/a} - \gamma_{s/w} < \gamma_{wa} \cdots \quad \textbf{Equation 2}$$

and the change in free energy accompanying the replacement of a unit area of solid area of solid-liquid interface by solid-gas interface is given by Dupre's equation:

$$\Delta G = \gamma_{s/a} - (\gamma_{s/w} + \gamma_{s/a}) \ldots \textbf{Equation 3}$$

Dupre and Young's equations can be combined to give an expression for the change in free energy:

$$\Delta G = \gamma_{w/a} (Cos\ \theta - 1) \ldots \textbf{Equation 4}$$

Therefore for any finite value of θ, attachment is preferred. This is because it minimizes the free energy of the bubble thereby representing a thermodynamically favourable situation.

Theoretically, contact angle measurements can be used as an indicator of whether or not flotation will occur. However, most workers agree that contact angle measurements do not fully describe the floatability of a mineral.

This is because in an actual flotation cell other factors such as kinetics, hydrodynamics, and mineral particle size can also play key roles in determining whether the particles will ultimately float (Fuerstenau et al, 2007)

2.2.2 Kinetics of flotation

Researchers generally agree that the recovery of floatable minerals particles during flotation can be described using a first order with respect to particle concentration provided the bubble concentration remains the same (Sutherland, 1955).The usefulness of determining the flotation kinetics is that the flotation response can be expressed in terms rate constants which can then be compared for different minerals. Klimpel (1984) proposed the following the first order rate equation to describe the flotation process:

$$R_{\infty} = R_{max}[1 - (\frac{1}{kt})(1 - exp^{-kt}) \ldots \text{Equation 5}$$

where Rmax = maximum recovery at time t (%)
$R\infty$ = maximum recovery at infinite time
k= first order rate constant (min^{-1})

Evaluation of the effects of altering flotation variables in batch flotation can easily be evaluated by fitting experimental data to the first order rate equation. However, Mathe et al (2000) noted that the rate equation does not distinguish the behaviour of the pulp and froth phases since none of the $R\infty = Rmax[1-(1kt)(1-exp-kt)$ … are explicitly associated with the froth phase. Their findings $R\infty = Rmax[1-(1kt)(1-exp-kt)$ … very well.

2.3 Influential parameters in flotation

Flotation is an intricate process that involves the interplay of physical, chemical and operational parameters as illustrated in Figure 2.4 (Klimpel, 1984). This means that changes in one area will produce a compensating effect in other areas. It is therefore important to take all these factors into account in froth flotation operation.

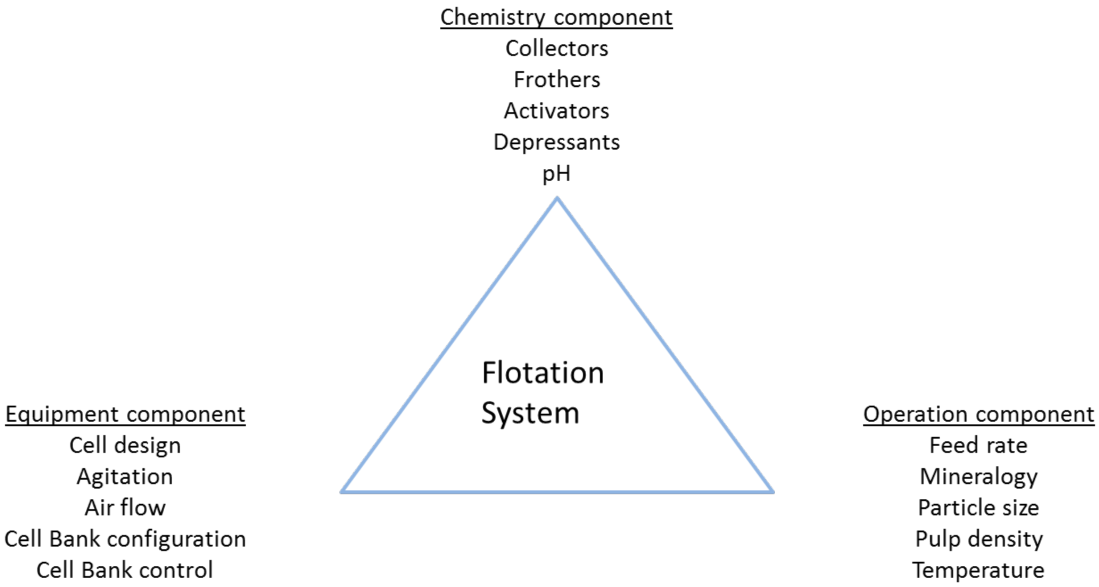

Figure 2.4 An illustration showing the interrelated components of flotation (Klimpel, 1988).

The following section will discuss the components that are relevant to this study i.e. collectors and frothers, which are chemical factors, as well as mineralogy and particle size which Klimpel characterised under operational components.

2.3.1 Operational components

2.3.1.1 Particle size

The effect of particle size recovery has been studied and researchers agree that it is an important parameter in flotation (Trahar et al, 1981; Feng et al 1999). However, as with other parameters in flotation, the interplay between physical and chemical parameters in different flotation systems makes it difficult to predict the effect of particle size. Generally, the 10-100 μm size range has been found to be the optimum for flotation to take place. Within this size range, high flotation response and efficiency has been observed and outside this range recovery drops significantly. This results in an inverted U shape when flotation recovery or flotation rate is plotted against particle size recovery (Pearse et al, 2006).

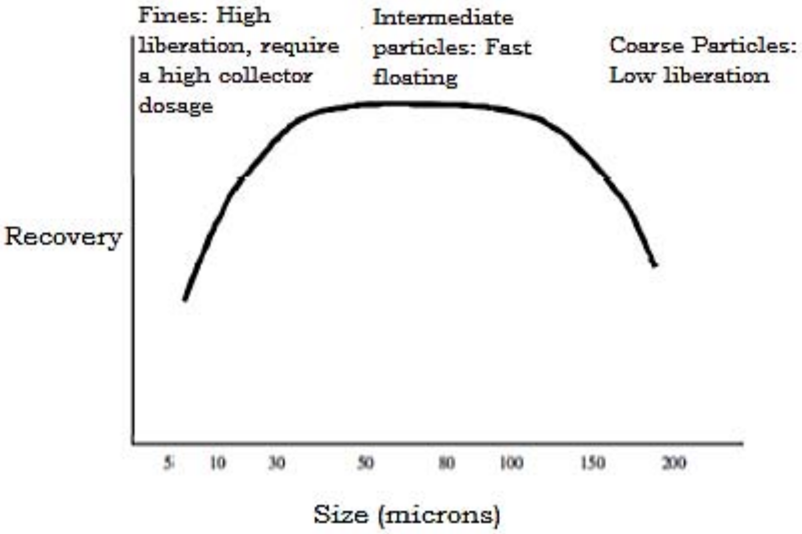

Figure 2.5 A typical U shaped flotation recovery versus particle size curve (adapted from Pearse et al, 2006)

Flotation behaviour of particles in the flotation cell is mainly influenced by hydrodynamic conditions, chemical environment and the behaviour of the froth zone. Fine particles experience a lower number of collisions with bubbles because they have a small inertial force due to their small masses. On the other hand the rate of detachment from the surface of the bubble is higher for coarse particles due to their large mass. Hence turbulent conditions in a flotation cell favour the flotation of fine particles (Schulze, 1984).

The chemical environment, mainly the collector type and concentration, also influences particle size recovery. Gaudin et al (1931), using sphalerite, were the first to note that different particle sizes exhibited different flotation kinetics in the same chemical environment. Klimpel (1997) suggested that fine particles require a small amount of collector to float while larger particles require a higher degree of surface coverage to float; hence they float at higher collector dosages. These findings were supported by work carried out by Crawford and Ralston in 1988 which showed that particles with an average diameter of 71 µm required up to 35% collector coverage while particles with an average diameter of 121 µm required coverage of up to 80% to achieve flotation.

2.3.2 Chemistry

The chemistry of flotation involves numerous interactive factors which make this aspect of mineral processing highly complex. The primary role of chemicals in flotation is to manipulate pulp conditions in order to increase the amount of paymetal recovered as well as the rate of recovery. The main classes of chemicals used in the flotation process are collectors, frothers, depressants and activators. The predominant function of collectors is to induce hydrophobicity onto selected mineral so as to facilitate their attachment onto bubbles. Activators are added to enhance flotation performance by modifying the surface of the particle to make it more amenable to interaction with collector. A classic example of an activator is the role of copper sulphate in the flotation of certain sulfide minerals. Frothers are added to create stable dispersion of appropriately sized bubbles which in turn creates a stable froth by preventing bubble coalescence. The role of depressants is to reduce the collection of unwanted gangue material by increasing the hydrophilic nature of these particles thereby preventing their transfer from the pulp phase to the froth phase. The role of each chemical is not confined to its intended function; they can fulfil other roles within the flotation system. As with other complex systems, there is often interaction of different chemicals generally to enhance the recovery of value minerals. Such synergistic effects have been widely investigated (Bradshaw and O'Connor, 2000; McFadzean et al, 2012).

2.3.2.1 *Collectors*

Particles can be naturally hydrophobic or made hydrophobic chemically through the use of collectors. Collectors are heteropolar organic reagents which consist of a non-polar hydrophobic chain and a polar group which can selectively attach onto the mineral surface. A representation of the structure of a collector molecule is represented in Figure 2.6.

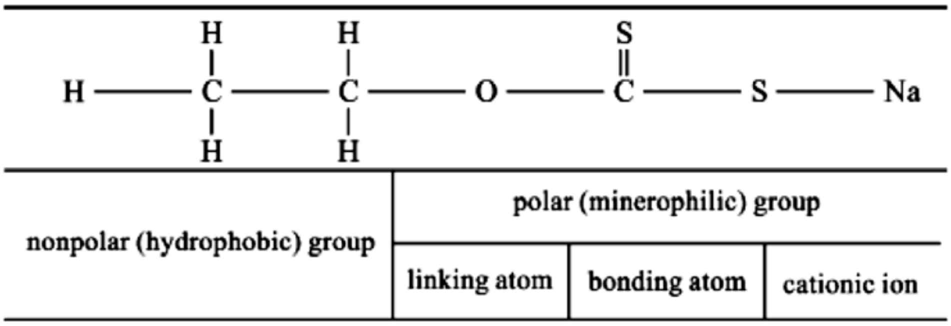

Figure 2.6 A schematic diagram representing the general structure of a collector molecule.

The polar group attaches to the mineral surface and the non-polar group points outwards into the aqueous media as represented in Figure 2.7.

This orientation renders the mineral surface hydrophobic and the hydrophobic particle then moves away from water towards air, resulting in bubble-particle attachment.

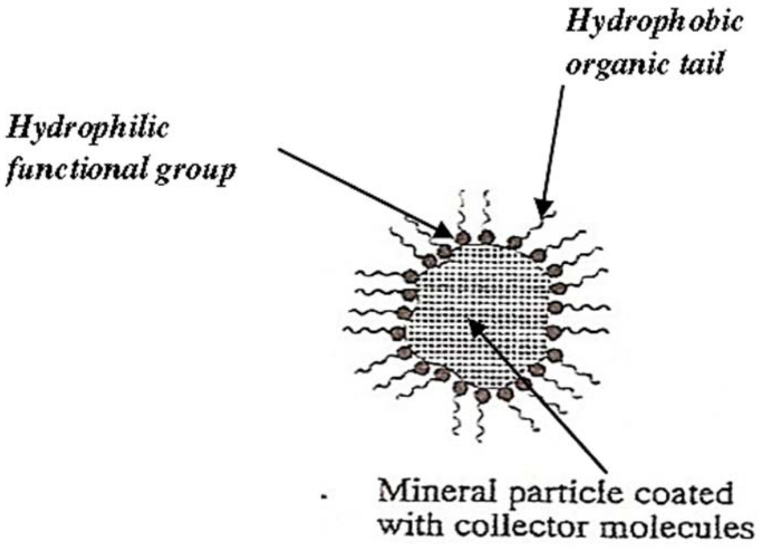

Figure 2.7 A schematic showing collector molecules attached to a mineral surface.

The mechanism of interaction depends on the collector type and the nature of the mineral surface. Physisorption involves amorphous bonds with relatively low Gibbs free energy of adsorption. In the case of chemisorption, the collector interacts with the mineral surface without movement of the metal ions from their lattice sites (Bradshaw, 1997). Collectors usually form monolayers on the mineral surface, which increases the contact angle and in turn improves attachment of the particles to the bubbles (Bulatovic, 2007). Selection of the collector is critical for effective separation through froth flotation. Of interest to this study are xanthates, dithiocarbamates and dithiophosphates. These collectors are anionic and attach to the mineral using a negatively charged sulphur group (Aplan and Chander, 1988).

2.3.2.1.1 Xanthates

Xanthates have been used in flotation from as early as 1923 and remain the most commonly used collectors to date (Rao, 2004). The generic structure of xanthates is shown in **Error! Reference source not found.**Figure 2.8 .

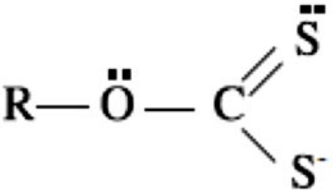

Figure 2.8 The generic molecular structure of xanthates, where R represents a hydrocarbon chain (from Bacgi et al, 2007).

These collectors owe their popularity to their strong collecting power and their relatively low cost. Xanthates are derived from an alcohol (ROH) reacted with sodium/potassium hydroxide and carbon disulfide (CS_2) The functional group is OCS_2. As shown above, there are lone pairs of electrons on the sulphur and the oxygen. R represents the hydrocarbon chain and studies have shown that shorter hydrocarbon chains in xanthates demonstrate higher adsorption densities on sulfide surfaces. (Wakamatsu, 1968) As a result of their chemistry, xanthates are susceptible to decomposition by atmospheric oxygen and water. (Aplan and Chander, 1988)

2.3.2.1.2 Dithiocarbamates

Dithiocarbamates (DTC) have stronger collecting properties in comparison to xanthates (Lotter and Bradshaw, 2010). They are synthesised from an amine ($R-NH_2$) and carbon disulfide (CS_2). There are lone pairs of electrons on the nitrogen and sulphur atoms, as shown in Figure 2.9. The functional group for this collector is NCS_2.

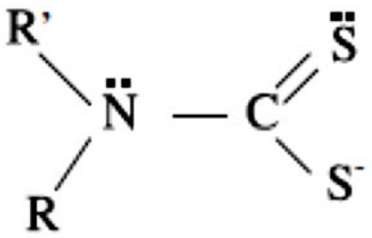

Figure 2.9 The generic structure of dithiocarbamates, where R and R' represent hydrocarbon chains (from Bacgi et al, 2007).

In some instances the second hydrocarbon chain is replaced by single hydrogen. Dithiocarbamates are not widely used in industry because of their expense; however dithiocarbamate salts are used in the manufacture of fungicides, insecticides and clinical medicines (Rao, 2004).

2.3.2.1.3 Dithiophosphates

Dithiophosphates are the weakest and therefore most selective of the collectors under investigation (Bacgi et al, 2007). They are synthesised from an alcohol $(ROH\ )$ reacted with phosphorous pentasulfide P_2S_5 and carbon disulfide (CS_2). The functional generic structure of a dithiophosphate molecule is shown below.

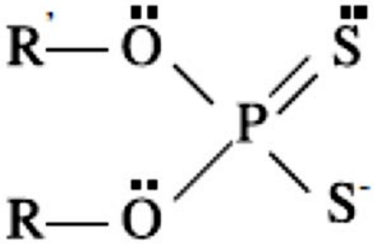

Figure 2.10 The generic structure of dithiophosphates, where R and R' represent hydrocarbon chains (from Bacgi et al, 2007).

The length and structure of the alkyl groups affect collector action. Dithiophosphates with chain lengths greater than C_4 or have been reported to have frothing action in addition to their collecting ability (Adkins and Pearse, 1992).

The structure-function relationship of the collectors and their relative strength and selectivity are discussed in Section 2.3.2.1.4.

2.3.2.1.4 Dithiolates

The mechanism of xanthate interaction with the mineral is strongly dependent on the pulp potential and the mineral surface which behaves as a catalyst. Sulfide minerals are semi-conductors and can aid in electron transfer. Finkelstein and Poling (1977) have presented an extensive review of the role of dithiolates in the flotation of sulfide minerals. They suggested that the action of dithiolates is not crucial to the collecting action of thiolates although it increases floatability. However contact angle studies carried out by Gardener and Woods (1974) have shown that dithiolates have strong collecting properties due to larger contact angles. Allison et al (1972) , using infrared spectroscopy (IR), found that the formation of dithiolates in solution can be predicted by comparison of the dithiolate/thiolate couple with rest potential of the metal sulfide.

2.3.2.2 *Collector strength and selectivity*

Collector strength and selectivity is influenced mainly by the functional group and to some extent the chain length. Dithiocarbamates are the strongest and least selective, followed by xanthates and dithiophosphates are the weakest and most selective (Nagaraj, 1988). The two RO groups on DTP have an electron withdrawing inductive effect because oxygen is more electronegative than nitrogen and phosphate. The electrons around the functional group (PS_2) are delocalised, this makes the anion more stable and less likely to donate electrons, and as a result DTP is the weakest collector. The R_2N group in DTC has a mesomeric electron donating effect which enhances the electron donating ability of the donor S atoms (Bhaskar *et al*, 1984).

Xanthate collectors of different alkyl chain lengths may display similar characteristics but their reactivity, solubility and selectivity may also be affected by the difference in chain length. Harris (1984) showed that the stability of xanthates in solution was influenced by the chain length in the following sequence: methyl < ethyl < n-propyl < n-butyl < isopropyl. Increase in alkyl chain length decreases the concentration of collector required for effective flotation and decreases the solubility of products formed but shorter chain lengths demonstrate higher adsorption densities In addition, Nagaraj (1988) proposed that longer chain xanthates are stronger collectors, but have slower reaction time and short chain collectors are weaker collectors but have a faster reaction time.

2.3.2.3 Electrochemical potential (Eh)

Eh is a useful diagnostic parameter which plays a key role in dictating the properties of the mineral-solution interface. Under dynamic conditions, such as those encountered in flotation, the electrochemical potential is a mixed potential and involves several charge transfer reactions. Allison *et al* (1972) carried out an investigation aimed at correlating Eh and the reaction products formed when sulfide minerals reacted with collectors.

Gardner and Woods (1974), using cyclic voltammetry, also found a correlation between floatability and Eh. Both researchers established that flotation of galena is not induced until the potential of the solid/liquid interface is more anodic than that observed for the formation of lead xanthate or more anodic than the reversible potential for the oxidation of xanthate to dixanthogen.

2.4 Interaction of thiol with sulfide minerals

2.4.1 Proposed mechanisms of collector-mineral interaction

The nature of products formed at the surface when sulfide minerals react with aqueous solutions of thiol collectors is still subject to investigation. Knowledge of these products of reaction is essential in understanding what confers hydrophobicity to a sulfide mineral. A number of studies have been carried out to ascertain the interaction between thiol collectors and mineral surfaces. Three major theories have been put forward; the chemical theory by Taggart (1934), the ion exchange mechanism by Cox and Wark (1934) and the mixed potential theory proposed of Nixon (1957). These mechanisms are described briefly below.

2.4.1.1 Chemical theory

The chemical theory is a simple theory which describes the formation of an insoluble metal/collector compound. The formation of this compound is described by the Equation 6.

$M^{z+}S^{z-} + zX^{-} \rightarrow MX_2$ **...Equation 6**

Where z is the valence of the metal cation

X^{-} is the thiol ion

MX_2 is the metal thiol salt

S^{z-} is the anion.

The solubility of the metal-collector salts is given as:

$K_{sp} = [M^{z+}][X^{-}]^{Z}$ **...Equation 7**

The magnitude of the solubility product can be used to predict the extent to which the reaction can proceed. Sutherland and Wark (1955) drew attention to the fact that this model was inconsistent with established values for the solubility products of the species involved.

2.4.2 Ion exchange mechanism

Cox and Wark (1934), proposed the direct adsorption of the thiol collector whereby the collector displaced OH^- ions on the surface of the mineral as shown in Equation 8.

$$MS|OH^- + X^-(aq) \rightarrow MS|X^- + OH^- \text{...Equation 8}$$

This theory was discounted on the basis that the resultant mineral surface would be too charged to be hydrophobic (Woods, 1994).

2.4.3 Mixed potential model

The mixed potential theory was first mentioned in literature by Salamy and Nixon in 1952. In this model, the process leading to hydrophobicity is the anodic oxidation of the collector at the mineral surface which results in electron transfer from the collector to the mineral, driven by cathodic reduction of oxygen. Anodic reactions and the cathodic reactions can occur simultaneously to give a single electrode potential, with a net electrode current of zero. Such a potential is termed a mixed potential. The mixed potential theory reconciled previous concepts and overcame their shortcomings.

Oxidation of the mineral to form a metal deficient sulfide is known as the electrochemical step (Equation 9).

$$MS \leftrightharpoons M^{2+} + S^0 + 2e^- \text{...Equation 9}$$

Oxidation of thiol into its dimer (Equation 10) is catalysed by the electron deficient mineral which acts as a catalyst for electron transfer. This formation of the dithiolate can occur on an unaltered surface or a surface which has chemisorbed the collector.

$$2X^- \rightarrow X_2 + 2e \text{...Equation 10}$$

The chemical reaction of thiol with the sulfide mineral to form a metal thiol compound is shown in Equation 11.

$$2X^- + MS \rightarrow MX_2 + S + 2e \text{...Equation 11}$$

The role of oxygen as an electron acceptor in the anodic reaction is shown in Equation 12. This is a cathodic reaction and is also controlled by Eh. (Woods, 1984)

$$O_2 + 2\,H_2O + 4e \rightarrow 4\,OH^- \text{...Equation 12}$$

It is of interest to note that studies carried out by Ahlberg and Broo (1996), have shown galena to be poor catalyst for the reduction of oxygen and pyrite a good catalyst.

2.4.4 Collector interaction with minerals

Sulfide ores are the largest group of ores treated by the flotation process, as a result, thiol collectors account for over 65% of collectors employed industrially (Aplan and Chander, 1988). Generally, thiol collectors make good collectors for sulfide minerals because sulphur atoms on the collectors have easily accessible, vacant d-orbitals which are capable of accepting electrons into π back-bonds from the metal ions. This results in the formation of a π bond in addition to the σ bond. (Bhaskar et al, 1984) In addition, sulphur has a unique ability for catenation (forming bonds with itself) and therefore it is possible that adsorption of thiol collectors on sulfide minerals involves some catenation with sulphur atoms on the mineral surface.

2.5 Mixed collectors and synergism

Xanthate collectors are widely used in sulfide and platinum group mineral (PGM) flotation. However single xanthate systems cannot span the full needs of an ore containing different minerals. Collectors such as dithiocarbamates and dithiophosphates are frequently used as co collectors in two component collector suites to improve metallurgical performance of xanthates. When a mixture of collectors results in enhanced recovery, over and above the performance of each individual collector, the two reagents are said to be interacting synergistically and the effect is known as synergism (Rao, 2004). The benefits of using mixed collectors have long been recognised in plant practice and have been reported for a wide variety of collectors. In most cases a specified ratio of constituent collectors gives the desired effect. (Bacgi *et al*, 2007).

Table 2.1 summarises the recent literature on the performance of mixed collectors when used in flotation experiments.

Table 2.1 The effects of using mixed collectors in flotation experiments (Adapted from Castelyn, 2011).

Reagents (ratio tested)	***Mineral system***	***Observation***	***Reference***
Butyl X: Butyl DTP (50:50)	Galena	Preferential DTP adsorption from	Wakamatsu and Numata (1979)

		mixture with no increased mass picked up by bubble	
Isopropyl DTC: Isopropyl xanthate (1:2 mass)	Chalcopyrite ore	Better results with DTC:X mixture than with pure DTC	Falvey (1990)
Di-isobutyl DTP: iso butyl (30:70, 50:50, 70:30 mass)	Platinum group metal (PGM) ore	Recovery improved by 11% when pure X was replaced with a 70:30 mixture	Mingione (1984)
n-butyl X: cyclohexal DTC (90:10)	Pyrite	Increased bubble loading	Bradshaw (1997)
Isopropyl X: dicresyl DTP (95:5)	Mixed copper sulfide ore	Enhanced copper recovery with mixture, from 80% to 83% and improved rate of recovery	Adkins and Pearse (1992)
SEX:SEDTP (90:10; 75:25) SEX:SEDTC (90:10; 75:25)	Galena and pyrite		McFadzean and Mhlanga (2012)
SEX:SEDTP (10:90; 50:50; 90:10;) SEX:SEDTC (10:90; 50:50; 90:10;)	Galena and pyrite	Recovery improved for the following mixtures; 10:90 SEX:SEDTP (17%) 90:10 SEX:SEDTC (29.5%)	McFadzean, Castelyn and O'Connor (2012)

The benefits of using mixed collectors can be summarised as follows;

- Reduction in dosage requirement.

- An increase in paymetal recovery.
- Improved concentrate grade
- Improvement in the rate of flotation.
- Preferential recovery of different size classes for each collector suite.
- Proposed mechanisms of synergism

Although research into mixed collectors started from as early as 1958 (Glemboskii, 1958), the exact mechanism by which synergism may occur still remains unclear although a number of mechanisms s have been proposed to explain synergism. These will be discussed in the following sections.

2.5.1 Strong and weak adsorption sites

Plaskin and Zaitseva (1960) were the first to put forward the idea that when mixed collectors are used there is more even dispersion of collectors on the mineral surface. They used microradiographic studies to study the distribution of a mixture of xanthates on the surface of galena. This idea was developed further developed by Bradshaw and O'Connor (1993), who put forward the strong and weak site theory. They postulated that the surface of sulfide minerals is not uniform and consists of sites with different activities. These sites consist of more oxidised spots which are referred as weak sites and less oxidised spots which are referred to as strong sites.

It is assumed that after adsorption of the weaker, more selective collector on the stronger active sites, there will residual weak sites onto which the stronger, less selective collectors can adsorb. This is illustrated in Figure 2.11 where di-isobutyl dithiophosphinate (DTPI) is the weaker, more selective, collector and isopropyl xanthate (SIPX) is the stronger, less selective collector (Bacgi et al, 2007).

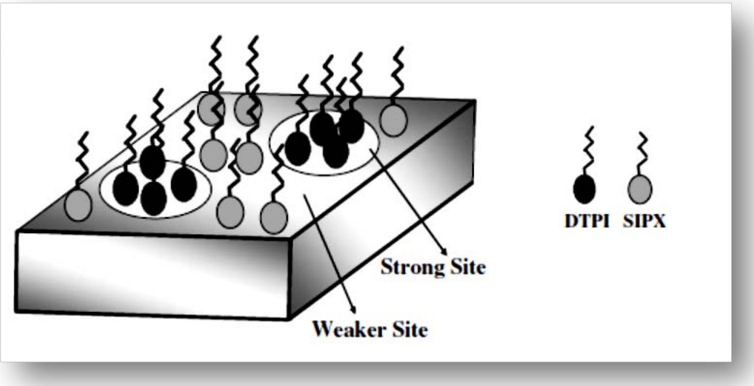

Figure 2.11 Schematic illustration of adsorption collectors on chalcopyrite (from Bacgi et al, 2007)

Sequential addition of collectors in specified ratios was carried out and it is believed that each collector adsorbs to the site most suitable for its polar group. As a result, there is improved surface coverage. Sulphur/ metal ratios are also thought to influence the distribution of collector (Bradshaw et al, 1995 and Bacgi et al, 2007).

2.5.2 Catalysed formation of xanthate dimers

Bradshaw et al (1995) studied the behaviour of sodium cyclohexyl dithiocarbamate and potassium n-butyl xanthate on pyrite using various techniques. Based on this work they proposed that the DTC catalyses the formation of neutral and strongly hydrophobic xanthate dimers. These dimers are believed to attach onto the hydrocarbon chains of dithiocarbamates attached to the mineral surface through van der Waals interactions and form a more hydrophobic multilayer.

Illustrated in Figure 2.12, is a similar study carried out by Bacgi et al (2007) using cyclic voltammetry, where SIPX is proposed to form dimers which attach to the hydrophobic chains of DTPI.

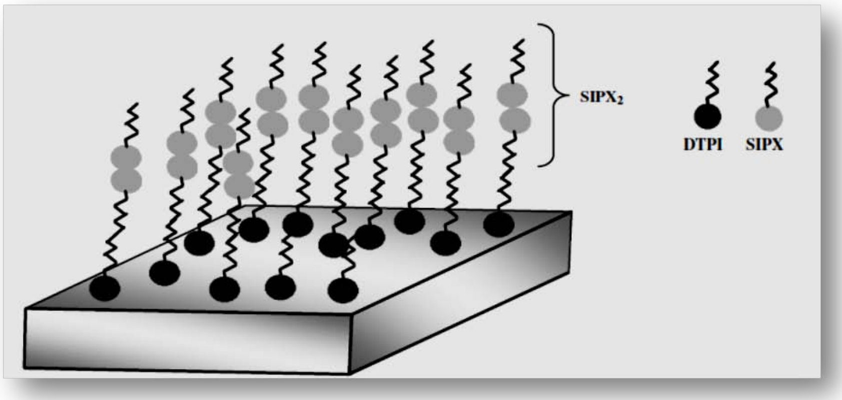

Figure 2.12 A schematic illustration of $(SIPX)_2$ attached to the hydrocarbon tail of DTPI (from Bacgi *et al,* 2007) .

Formation of the multilayer increases the overall hydrophobic properties of the mineral. This hypothesis was supported by microcalorimetric studies which show that the enthalpy of reaction of the mineral and mixed collectors is greater than the enthalpy of reaction using individual collectors.

Studies carried out by Bradshaw *et al* (1995), using potassium n-butyl xanthate, cyclohexyl dithiocarbamate and pyrite, showed the exothermic heat of adsorption evolved changed from -67 kJ/mol to -90 kJ/mol when single collectors where replaced with mixed collectors. They postulated that the increase was due to catalysed oxidation of xanthate to dixanthogen and stronger bonds forming between mixed collectors and the mineral surface as a result of the interactions of pure collectors. Studies were also carried out on pure collectors which showed that the adsorption of dithiocarbamates reached an equilibrium value while that of xanthates continued until the collector was depleted. This shows that the collectors undergo different surface reactions. This finding can be used to support the theories that have been put forward to explain synergism.

Work carried out by Corin et al (2012) on a PGM ore indicated that DTP does not act at the mineral surface but behaves as a froth modifier. Their work showed that DTP, when used with a xanthate, increased the recovery of fine particles (<25 µm) and they attributed this to the increased stability of the froth phase rather than any synergistic enhancement.

2.5.3 Three component collector suite

The use of three component collector suites was suggested by Lotter and Bradshaw (2010). They proposed the use of two xanthates, one long chain and one short chain, with either dithiophosphate or dithiocarbamate. The idea behind this formulation is to take advantage of the different properties that collectors have due to different chain lengths and functional groups in order to create a broad spectrum collector that is strong enough to enhance recovery but weak enough to enhance selectivity. According to literature, longer chained xanthates are strong collectors but have slow reaction time whereas short chained xanthates are relatively weaker collectors but have a faster reaction time. For example, DTP is a weak collector but is highly selective; hence combining it with a mixture of xanthates is expected to yield a relatively strong collector with fast kinetics and high selectivity.

2.6 Objectives of this research

The objectives of this investigation are as follows;

1. To determine an appropriate collector concentration for use in batch tests in order to observe the effects of different collector systems.
2. To determine the effect of single collectors on the froth phase.
3. Determination of optimum ratio of collector mixtures by varying collector ratios of each collector suite (xanthate/DTC, xanthate/DTP). The optimum concentration of collector obtained in part 1 above will be used to constitute the collector suites.
4. To try and ascertain the method by which collector mixtures enhance the metallurgical performance.

2.7 Hypothesis

The proposed hypothesis is as follows:

- The use of mixed thiol collector suites, (X:DTP and X:DTC), will increase the recovery of sulfide minerals, namely copper and nickel, due to more even coverage of the mineral surface, which in turn results in increased hydrophobicity.

3 Experimental procedure

3.1 Introduction

Laboratory batch flotation tests play a vital role in the optimization of the flotation process since they simulate commercial plants. They are used investigate the effect of flotation reagents on the efficiency of the flotation process before they can be tested on an industrial scale .The efficiency of the flotation system is determined mainly by the amount and grade of the mineral that is recovered by true flotation, that is the particles that attached to the bubbles (Willis, 2006).

Batch flotation experiments were carried out in order to investigate the effect of pure constituent dithiocarbamate, dithiophosphate and xanthate collectors as well as mixtures of different ratios of xanthates/DTP, xanthates/DTC as collector suites on the recovery of copper and nickel from Nkomati ore. Scoping tests were carried out at different concentrations of the SIBX/SEX mixture to determine an appropriate collector dosage to be used for all tests. These tests were also used to compare dosage requirement between the xanthate collector system and mixed collectors. Determination of optimum ratio of collector mixtures was obtained by varying collector ratios of each collector suite (xanthate/DTC, xanthate/DTP). The appropriate concentration of collector obtained in the scoping tests was used to constitute the collector suites.

Two phase tests were carried out to determine the frothing properties of the collectors and collector mixtures. All batch flotation tests were carried out in duplicate. Flotation performance was evaluated from solids recovery, water recovery, and rate of flotation as well as the grades, recoveries of copper, nickel and sulphur.

3.2 Ore preparation

A bulk Cu-Ni sulfide Nkomati ore sample from the Main Mineralised Zone (MMZ), approximately 200 kg in mass, was delivered to the Centre for Minerals Research (CMR) for test work. As a precautionary measure, the ore was checked for the presence of asbestos containing minerals using Scanning Electron Microscopy (SEM) and the images shown in Figure 3.1 were obtained.

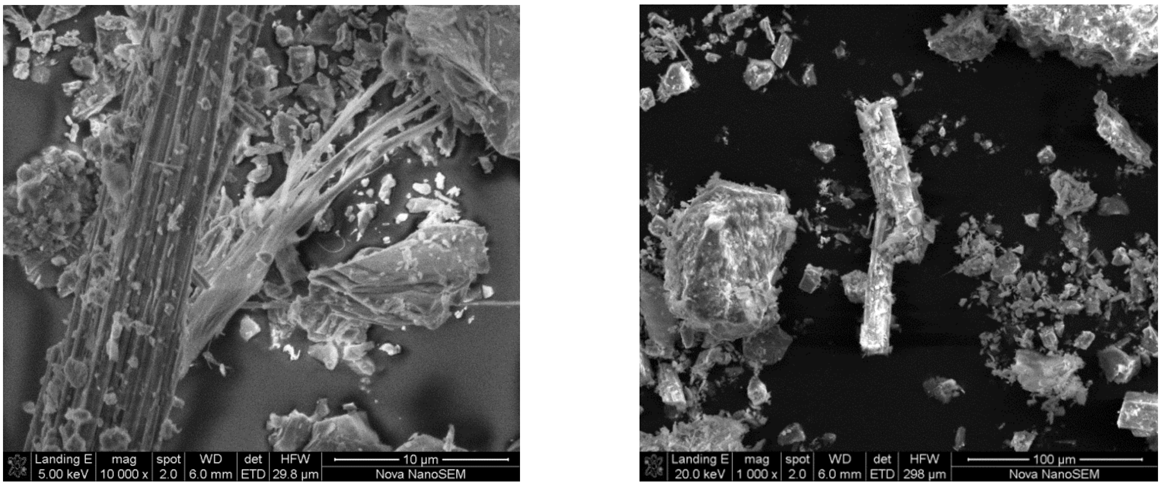

Figure 3.1 Micrographs of Nkomati ore

The SEM photos show some long, thin needles of serpentine. It was determined that the needles did not qualify as asbestos and therefore were not considered harmful. Nevertheless caution was taken in handling the samples; handling of dry ore was minimised, dust masks were worn and a fume hood was used wherever possible.

3.2.1 Sizing and comminution

The entire sample was screened using a 3 mm aperture size. The plus 3 mm size fraction was cone crushed to obtain a size fraction of 100% passing 3 mm. The sample was then blended, riffled and split into representative 1 kg portions using a rotary splitter manufactured by Dickie and Stockler. This approach reduces the variation in composition of each sample. The mineral composition of the ore was determined using Bruker S4 Explorer XRF Spectrophotometer as shown in Table 3.1.

Table 3.1 Modal mineralogical composition of Nkomati MMZ feed.

Major minerals	Composition (%)	Minor minerals	Composition (%)	Trace minerals	Composition (%)
Actinolite	24.62	Lizardite	8.97	Pyrrhotite	3.42
Diopside	20.46	Chromite	8.14	Quartz	3.05
Talc	17.71	Biotite	7.82	Enstatite	2.76
				Chalcopyrite	1.29
				Forsterite iron	0.68
				Pyrite	0.57
				Pentlandite	0.53

Milling was conducted using an Eriez laboratory scale stainless steel rod mill. The mill was charged with 20 stainless steel rods which were in three sets according to their diameters. The sets were made up as follows: 6 x 12 mm, 8 x 16mm and 6 x 21mm. Three 1 kg ore samples were milled at 67 % solids in synthetic plant water for different lengths of time in order to establish the milling curve shown in **Error! Reference source not found.**Figure 3. 2. The milling time required to achieve the target grind of 60 % passing 75 µm was 8 minutes 30 seconds. No reagents were added the mill.

The sample was screened and the particle size distribution as well as the mineral composition of the feed sample was determined as shown in Table 3.2.

Table 3.2 Modal feed values for obtained from XRF and LECO.

Size Fraction	**Cu, wt%**	**Ni, wt%**	**S, wt%**
+75 µm	0.0575	0.193	2.05
-75 µm to +45 µm	0.0109	0.358	2.99
-45 µm	0.243	0.685	2.78

3.2.2 Preparation of plant water

All batch flotation tests were conducted using synthetic plant water consisting of distilled water with the salts composition shown in Table 3.3 (Weise et al, 2011).

Table 3.3 The concentrations of ions present 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

3.3 Flotation reagents

3.3.1 Collectors

The collectors used in this study were sodium ethyl xanthate (SEX), sodium iso-butyl xanthate (SIBX), sodium diethyl dithiophosphate (SEDTP) and sodium diethyl dithiocarbamate (SEDTC). All collectors were supplied by Senmin (Pty) Ltd South Africa. Xanthates were received in powder form while the dithiophosphate and dithiocarbamate were received as solutions. The collector samples were stored in a refrigerator at approximately 5 ˚C. Collector solutions were prepared fresh daily and made up to 1 % (w/v) active content by adding 1 g or 1 ml of collector to a 100 ml volumetric flask and topping up to the mark with deionised water. No depressant was used throughout this work. A polyglycol ether frother Dowfroth 200 was used at a constant concentration of 15 ppm. Table 3.4**Error! Reference source not found.** lists the abbreviations and the physical properties of the collectors used in this study. For simplification in the results and discussion sections, the collectors are referred to using the abbreviated names.

Table 3.4 Properties of the collectors considered in this study.

Collector name	**Abbreviation**	**Molecular Structure**	**Molecular weight (g/mol)**	**Purity (weight %)**
Sodium ethyl xanthate	SEX	$C_2H_5OCS_2Na$	144.14	98.9
Sodium iso-butyl xanthate	SIBX	$C_4H_9OCS_2Na$	171.06	97
Sodium O,O-di ethyl dithiophosphate	SEDTP	$C4H_{10}O_2PS_2Na$	208.21	46.2
Sodium ethyl dithiocarbamate.	SEDTC	C_2H_6 NCS_2Na	147.25	44.1

3.3.2 Determination of appropriate collector dosage

It was important to determine the appropriate collector dosage because if the dosage is too high there may be no observable effects between when different collectors were tested. If the dosage is too low there may be no observable effects when compared to flotation without collector. Preliminary tests were carried out to determine the optimum collector dosage. This was done using SIBX: SEX 50:50 (mole ratio) mixtures. A mixture of SIBX and SEX was chosen as the primary collector in order to take advantage of the quick reaction time of short chained collectors and the collector strength of long chained collector, as well as to increase collector coverage as explained in Section 2.5. Experiments were carried out using the following collector concentrations; 0 g/tonne, 30 g/tonne, 50 g/tonne, 70 g/tonne and 100 g/tonne as shown in

.

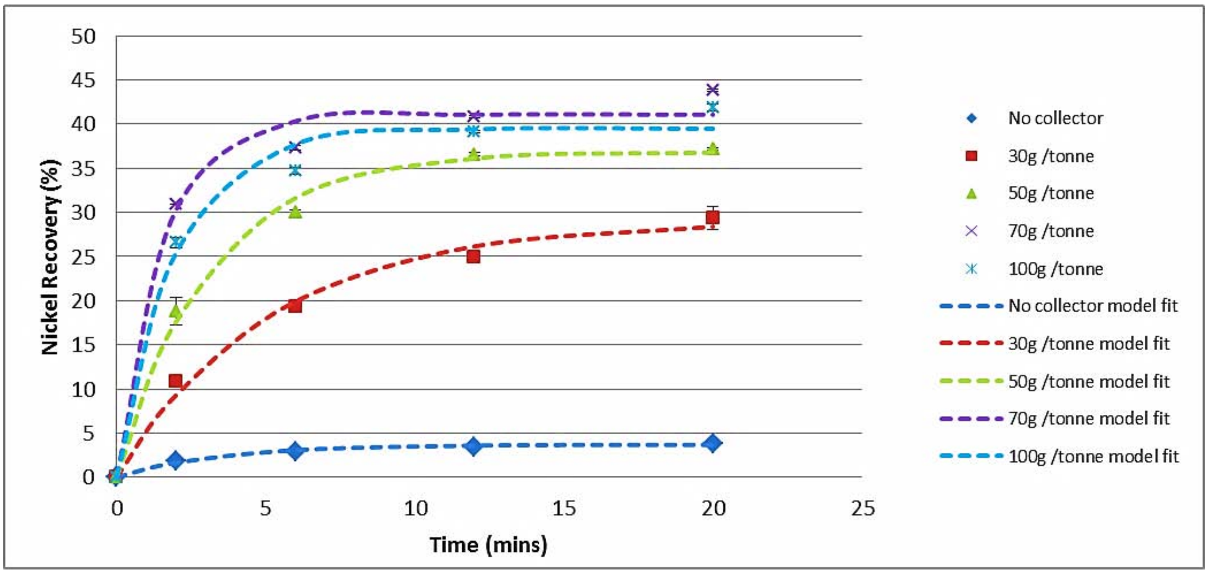

Figure 3.2 Cumulative nickel recovery for SIBX/SEX collector at different dosages. Error bars represent standard error between duplicate tests.

Figure 3.2 shows the recovery of nickel at selected SIBX/SEX collector dosages. The collector's effectiveness in the flotation cell was a function of its concentration up to 50 g/tonne. At 70 g/ tonne the maximum recovery was 41%, however at 100 g/ tonne the recovery decreases slightly to 39%. The 30 g /tonne dosage was chosen as the most appropriate dosage since it shows improvement in flotation above that of collector- less flotation without over-dosing.

The 30 g/tonne dosage was equivalent to a molar dosage of 190 mmol/tonne. This molar dosage was maintained for all subsequent tests. The mole ratios for the collector suites were varied as shown in Table 3.5. For simplicity, the SIBX/SEX is treated as single collector when used in combination with DTP and DTC.

Table 3.5 Mole ratio used to formulate collector suites.

	Collector SIBX	Collector SEX	Co-Collector DTP or DTC
Mole ratios	50	50	0
	35	35	30
	25	25	50
	15	15	70
	5	5	90
	0	0	100

3.4 Batch flotation tests

3.4.1 General batch flotation procedure

The milled slurry was transferred to a 3 L modified Leeds cell shown in Figure 3.3. The percentage solids were adjusted to 30 % by adding sufficient synthetic water and the pulp level was controlled manually by adding synthetic plant water to maintain a froth height of 2 cm. The flotation cell was made of Perspex, which facilitated pulp level control. The air flow rate was maintained at 7 L/min and the impellor speed was kept at 1200 rpm. For experiments that involved collector mixtures, collector was premixed before being added to the flotation cell. Sequential addition tests were carried out on the DTP: SIBX/SEX 30:70 mixture, where the xanthate mixture was added first, followed by the DTP, this was repeated in the reverse order. .

A 50 mL feed sample was taken from the stirred slurry using a syringe. Two 50 mL tailings samples were taken at the end of each flotation test after the air was turned off. Water recoveries were measured for each test. Feeds, concentrates and tails were filtered, dried and weighed before being assayed.

Figure 3.3 Photograph of the modified Leeds cell used in batch flotation tests.

Chronological order of reagent conditioning and concentrate collection in a batch flotation experiment is shown in Table 3.6. The froth was scraped into a collecting pan every 15 seconds. All tests were conducted in duplicate.

Table 3.6 Summary of batch flotation procedure

Action	Time (mins)
Collection of feed sample	0
Collector (30g/tonne)	2
Frother (15ppm)	4
Air turned on	5
C1	7
C2	11
C3	18
C4	30
Collection of tailings samples	

3.4.2 Pulp potential measurement

An ORP electrode (YSI Multiprobe) was inserted into the pulp and the change in pulp potential was measured as the different flotation chemicals were added to the flotation cell. This was performed for the single collectors.

3.4.3 Two phase tests

Two phase tests in which no ore was present were carried out to investigate the frothing properties of collectors and the effect of different collector mole ratios on the water recovery. These tests were carried out at a frother concentration of 15 ppm. The mole ratios of each collector suite (xanthate/SEDTP, xanthate/SEDTC) were varied as shown in Table 3.7. Water recovery was used as an indicator of froth stability.

Table 3.7 The mole ratios of collectors used in the two phase test.

SIBX/SEX (50:50 mole ratio)	SEDTP	SEDTC
0	0	0
0	100	0
0	0	100
10	90	0
10	0	90
50	50	0
50	0	50
90	10	0
90	0	10
100	0	0

3.5 Analysis of flotation performance

3.5.1 Concentrate mass and water recovery.

Dried feeds, concentrates and tailings were analyzed for copper and nickel using a Bruker S4 Explorer XRF Spectrophotometer. Sulphur analysis was carried out using a LECO DR 432 sulphur analyzer. The results obtained from these chemical assays are used to calculate grade and recovery, an Example of these calculations is shown in Appendix B. Mineral recoveries are reported as copper and nickel, not as their respective mineral phases; chalcopyrite and pentlandite.

4 Results

This chapter outlines the results obtained from batch flotation tests when using:

- The SIBX/ SEX collector suite at different dosages. These experiments were done in order to determine the optimum collector dosage for all the batch flotation tests.
- Single collectors. These experiments served as a baseline for assessing improvement in flotation when single collectors were compared with single collectors.
- Collector suites with SEDTP and SEDTC as co- collectors respectively.

As batch flotation tests do not give a fundamental understanding of the cause of enhanced flotation performance, the following further tests were carried out to characterise the differences in flotation performance for different collector systems:

- Kinetic modelling of batch flotation tests using the Klimpel model.
- Sequential addition of collectors to infer a mechanism for the reaction.
- Flotation behaviour of individual size classes assessed through Malvern analysis of flotation concentrates.

For convenience, some of the results shown in graphs are also given in tables. Tables that are not shown in the results section can be found in the appendix.

4.1 Reproducibility

4.1.1 Feed particle size distribution.

For the comparison between different collectors to be meaningful, the feed samples used in each experiment have to be comparable. Three random samples of feed material used for flotation tests were analysed for particle size distribution (PSD) using Malvern. The results in Figure 4.1**Error! Reference source not found.** show that the samples had very reproducible particle size distributions of P_{60}75 µm ± 5 µm.

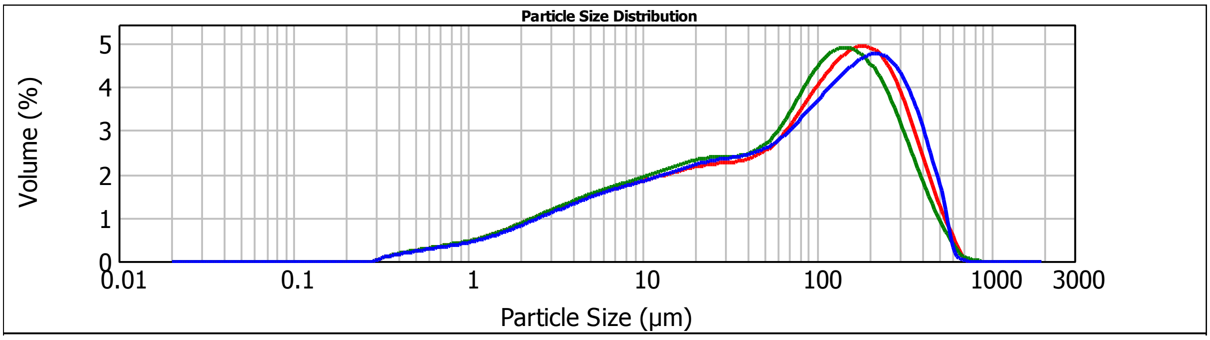

Figure 4.1 Particle size distribution of three randomly chosen batch flotation feed samples to illustrate reproducibility.

4.1.2 Reproducibility of batch flotation results

Batch flotation tests were carried out in duplicate in order to determine the standard error associated with a particular result. Standard error was calculated by dividing the sample standard deviation by the square root of the sample size. Tests were considered reproducible if the standard error for solids and water recoveries did not exceed 10 %. For copper and nickel recovery and assays, the tests were considered reproducible when the standard error did not exceed 5 %. The standard error is shown as error bars in all subsequent graphs in this thesis.

4.2 Single collectors

4.2.1 Assessing the frothing properties of the single collectors

The results for the two phase tests which were carried out to investigate the possible frothing properties of the collectors are shown in Figure 4.2 and Table 4.1. These tests were carried out with collector (190 mmol/tonne) and DOW 200 frother (15ppm) only. There was a general increase in water recovery when collector was added to frother.

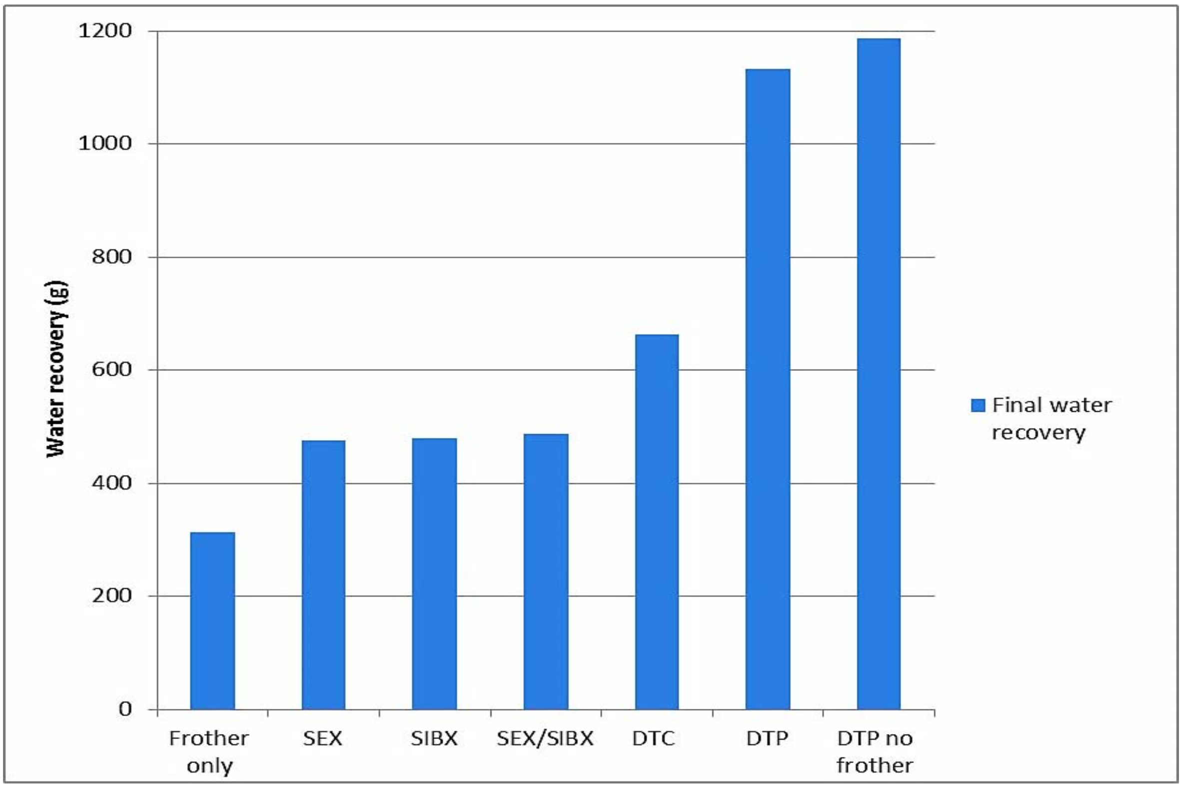

Figure 4.2 Final water recoveries for two phase tests carried out with single collectors.

Table 4.1 Final water recoveries for two phase tests carried out with single collectors

Collector	Final water recovery (g)	Increase in water recovery when collector is added compared to frother only (%)
Frother only, no collector	314.0	-
SEX	475.5	51
SIBX	478.7	52
SEX/SIBX	487.4	55
DTC	663.3	111
DTP	1131.8	260
DTP only, no frother	1186.8	277

Water recovery for xanthate collectors was similar and falls within a narrow range between 475 g and 487 g which were over 50% higher than when frother only is used. DTC recovers 663 g of water, which is more than double the water recovery for collector-less flotation. These are unexpected results since the xanthates and DTC were not expected to have any frothing properties. Of interest are the results obtained for DTP, in the absence and presence of a frother. Addition of DTP to the frother gives a four-fold increase in water recovery and similar results are obtained in the absence of frother. DTP has a strong frothing effect which can mask any frothing due to the frother.

Further investigations were carried out on a three-phase system using a standard batch flotation test. The final cumulative solids and water recoveries the results are shown in Figure 4.3. The collector dosage and frother dosage from the two phase tests were maintained.

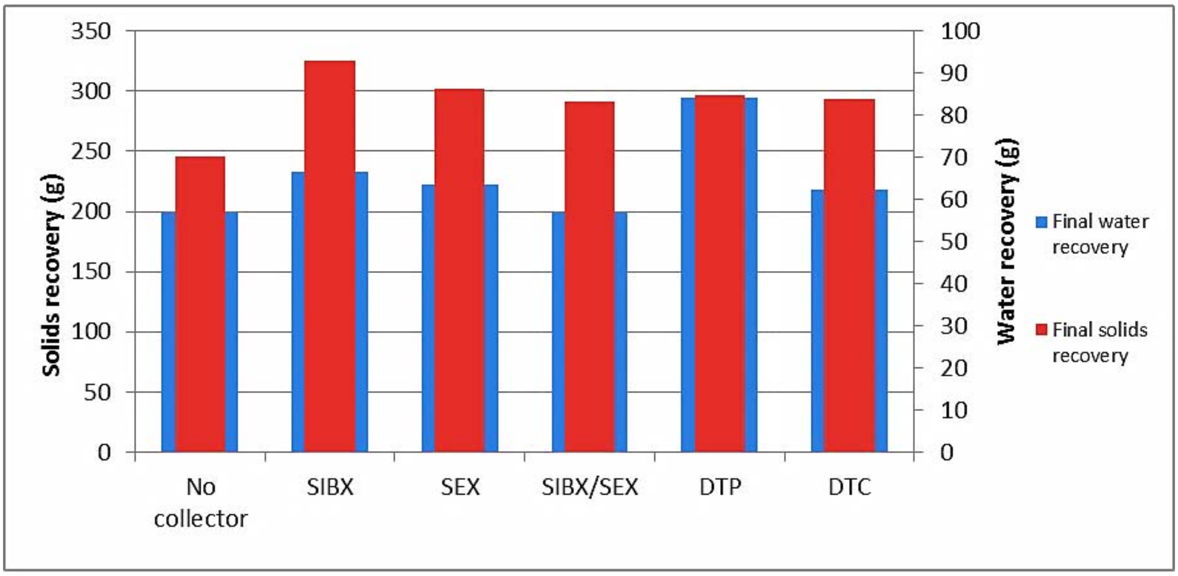

Figure 4.3 The final solids and water recoveries for single collectors in a three phase system.

Table 4.2 Final water and solids recoveries for batch flotation tests carried out with pure collectors

	Final water recovery (g)	Final solids recovery (g)	Solids: water recovery Ratio
Frother only, no collector	199.1	70.3	0.35
SIBX	233.2	92.9	0.40
SEX	222.6	86.3	0.39
SIBX/SEX	199.5	83.2	0.42
DTP	294.2	84.7	0.29
DTC	218.4	83.9	0.38

Water recoveries for all collectors, except DTP, fall within the range 200 g and 233 g. This is only marginally higher than the 199 g recovered for collector-less flotation. The water recovery observed for DTP was almost 34% higher than the other collectors. This suggests that the frothing properties observed for DTC and the xanthates in the two phase tests were not carried over to the three phase tests. However, DTP appears to have some frothing properties even in the presence of solids. SIBX had the highest mass pull of 93 g; the cumulative solids recoveries for DTP, DTC, SEX and SIBX/SEX were largely invariant, they all fell within a narrow range between 83 g and 86 g. It is interesting to note that the solids: water recovery ratio was lowest for DTP and highest or the SIBX/SEX mixture.

4.2.2 Cumulative nickel recoveries and grades for single collectors

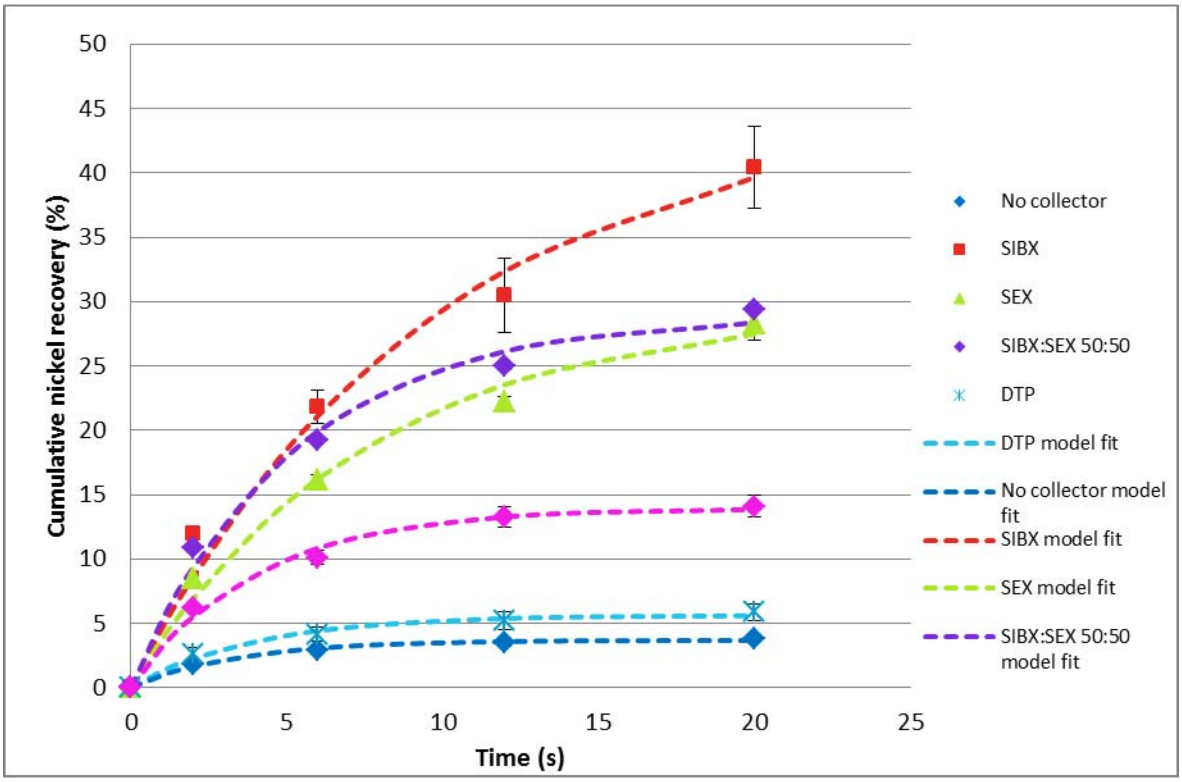

Figure 4.4 Cumulative nickel recovery vs time for pure collectors. Error bars represent standard error between duplicate tests.

The highest recoveries for nickel were obtained from using the xanthates with SIBX affording the highest recoveries and SEX gives the lowest. The nickel final recovery for the SIBX/SEX was only marginally better than SEX; however the rate of flotation (*k*) for SIBX/SEX is higher than that for SEX and SIBX alone and this is shown in Table 4.3. Notably, the mass pull for DTP was similar to that of other collectors as previously shown in Figure 4.3, but nickel recoveries are up to 35% lower than the xanthates. DTC gives similar solids and water recoveries as compared to the xanthates; however the nickel recovery is almost 10% lower than that for the xanthates.

Table 4.3 The rate of flotation (*k*) and the maximum recovery for nickel recovery (Rmax) using pure collectors.

Collector	**Rate constants**	
	k (min^{-1})	**R_{max} (%)**
No collector	0.08	3.7
SIBX	0.44	43.2
SEX	0.34	29.6
SIBX:SEX 50:50	0.47	29.0
DTP	0.11	5.6
DTC	0.27	14.0

SIBX yielded, by far, the highest recoveries of nickel and faster rates of flotation as shown in Table 4.3. SIBX has the longest hydrocarbon chain hence it is expected to form more insoluble and strongly hydrophobic species on the mineral surface which result in superior recoveries and faster rates of flotation. SIBX/SEX collector did not show any difference in recovery when compared to SEX and gave lower recoveries when compared to SIBX. This was unexpected since the mixture of long and short chains was expected to have a better arrangement on the mineral surface. DTC is theoretically the strongest collector, however it recovered less nickel than the xanthates and DTP is classified as a weak collector hence it was expected to give poor recoveries. However the actual recoveries obtained were much lower than expected, almost the same as collector-less flotation.

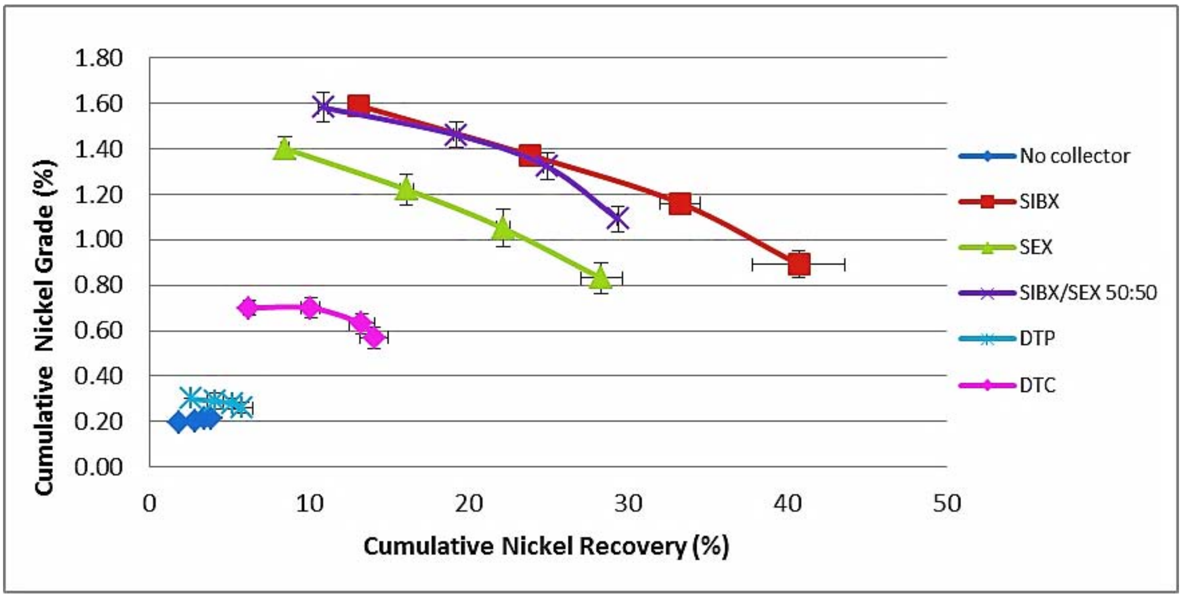

Figure 4.5 Nickel grade vs nickel recovery curve for pure collectors. Error bars represent standard error between duplicate tests.

Figure 4.5 shows the grade vs recovery curves for the flotation of copper using single collectors. Grade recovery curves indicate the metallurgical performance of flotation, with increasing metallurgical performance of flotation represented by the point furthest from the origin. It can be seen that DTP only shows a slight enrichment over collector-less flotation. DTC gives a 0.37% increase in cumulative grade and about 10% increase in cumulative recovery above that of the collector-less flotation. Nickel grades and recoveries increased with the addition of xanthates as shown in the three upper most curves. For the xanthates, lowest grades and recoveries were observed for the SEX. The highest recoveries were observed with SIBX with similar grades as for SIBX/SEX. Going from SIBX to the SIBX/SEX mixture there is a 10% drop in recovery and a 0.2% increase in grade.

4.2.3 Cumulative copper recoveries for single collectors

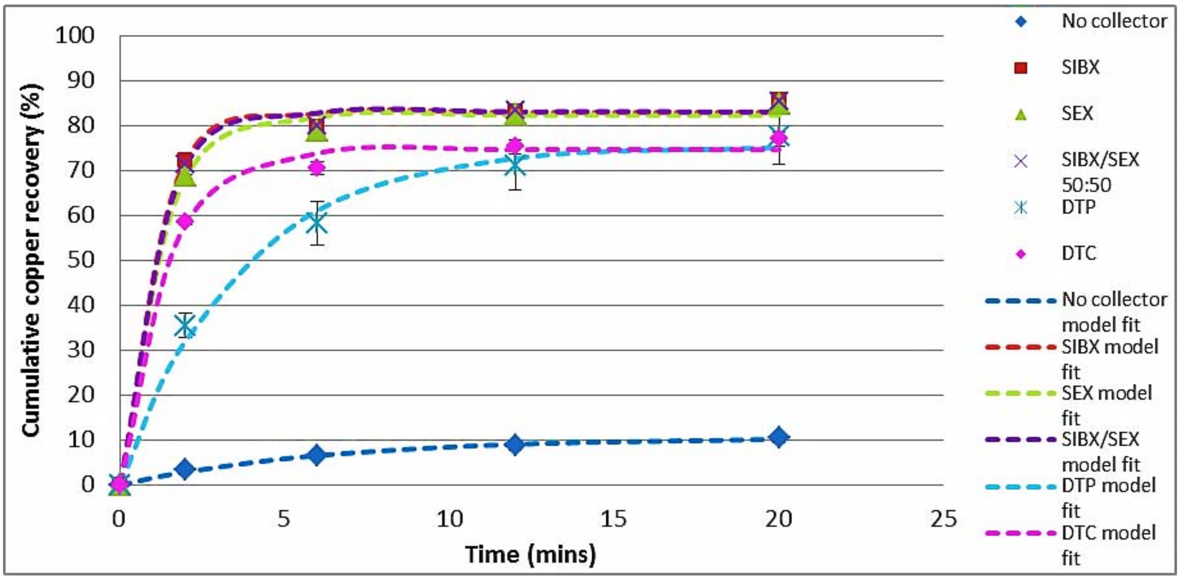

Figure 4.6 Cumulative copper recovery for pure collectors. Error bars represent standard error between duplicate tests.

Table 4.4 The rate of flotation (K) and maximum recovery (Rmax) for copper recovery using pure collectors.

Collector	**Rate constants**	
	***k* (min^{-1})**	**R_{max} (%)**
No collector	0.15	10.7
SIBX	3.61	82.9
SEX	3.42	82.3
SIBX:SEX 50:50	3.56	83.1
DTP	1.61	75.4
DTC	2.91	74.7

The same trends as were seen for nickel are reflected for copper as shown in Figure 4.6 and Table 4.4 However, all collectors have rapid copper flotation rates and final recovery was attained after about 3 minutes of flotation for the xanthates and 5 minutes for DTC and DTP. Even DTP which showed almost no activity as a collector for nickel gave a yield of over 70% although it remained the worst performing collector. This was expected since chalcopyrite is known to be readily floatable. However the copper recovery for the collector-less experiment is lower than expected.

4.2.4 Change in mixed potential of the pulp (ΔEh), after addition of pure collectors during flotation.

Eh measurements record the mixed potential which is the net result of anodic reactions (electron transfer from collector anion) to the mineral surface and cathodic processes (reduction of oxygen). These measurements are a useful diagnostic parameter for electron transfer reactions occurring in the pulp. From Figure 4.7 there is evidence of electron transfer reactions occurring upon addition of SIBX, SEX, SIBX/SEX and DTC. DTC shows the largest change in Eh (182 mV) after addition of collector. The difference in Eh before and after collector addition is similar for all xanthate collectors as shown in Table 4.5.

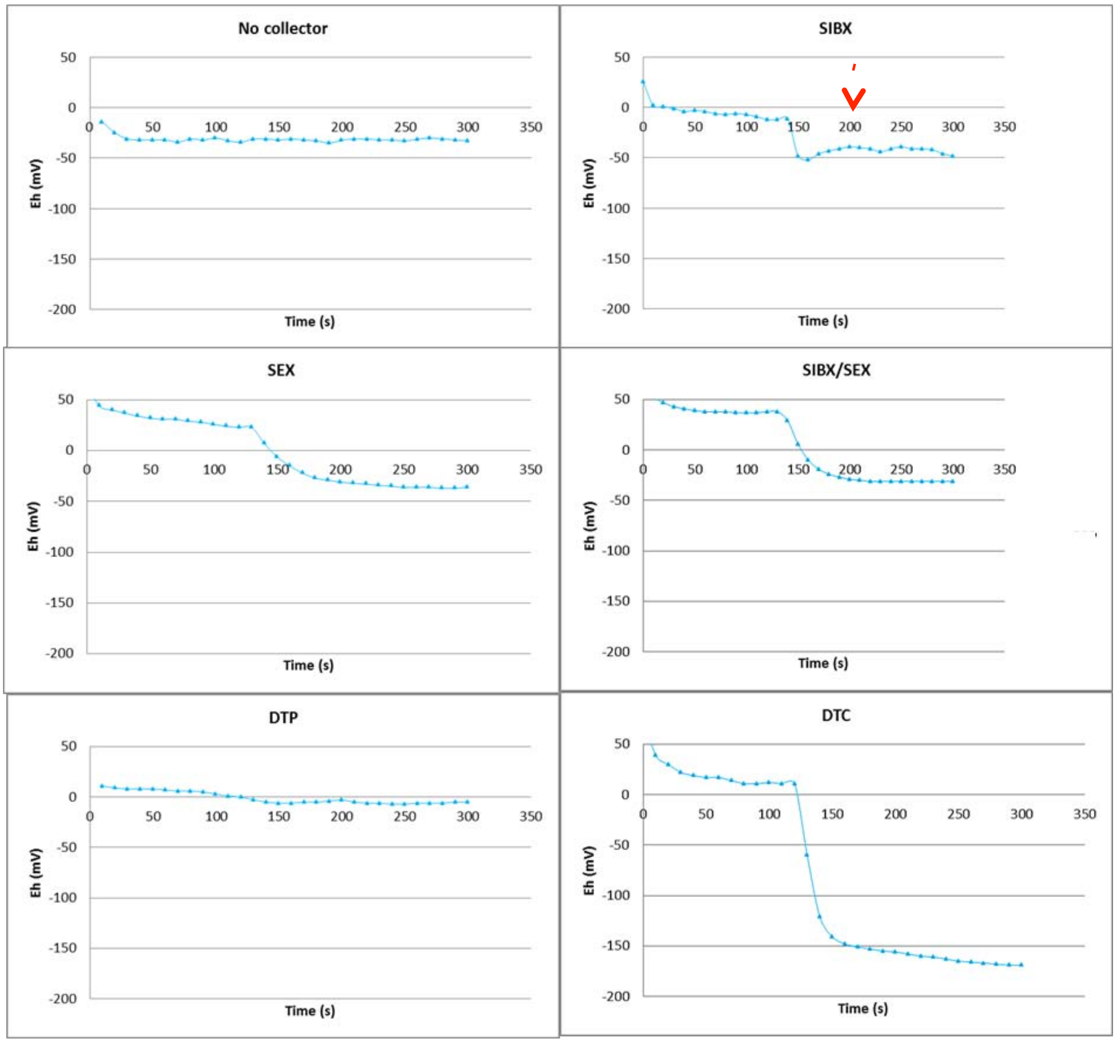

Figure 4.7 Graphs showing the change in Eh before and after the addition of collector. Collector was added at 120 seconds.

Table 4.5 The change in pulp potential(ΔEh) after addition of collector.

Collector	**Δ Eh (mV)**
No collector	1
DTP	12
SIBX	48
SEX	65
SIBX/SEX 50:50	69
DTC	182

DTC gives by far the largest ΔEh when added to the pulp. The ΔEh for the xanthates is largely invariant and the lowest activity by far, was observed for DTP. Although minimal, some electron transfer reactions occurring upon addition of DTP to the pulp.

4.3 Collector mixtures

This section describes the results of the batch flotation tests conducted to investigate the effect of varying the proportion of DTP or DTC in collector suites on the pulp phase when using mixtures of either SIBX/SEX and DTP or SIBX/SEX and DTC. As mentioned previously, in Section 3.3.1, the SIBX/SEX collector mixture will be used as a single collector. These collector suites were compared to the results obtained for the pure collectors used to make up the collector suites. Flotation conditions were identical to those used for pure collectors and total dosage of all the mixtures was also kept constant at 190 mmol/tonne. The collector proportions were varied according to the following mole ratios: 90:10, 70:30, 50:50, 30:70 and 10:90. The naming convention for the mixtures is such that the co-collector (DTP or DTC) contribution is always shown first. For example DTP: SIBX/SEX 90:10 represents a mixture 90% DTP and 10% SIBX/SEX. As stated in the experimental chapter, the collector was premixed before being added to the flotation cell. As with the xanthates, flotation performance was evaluated from copper and nickel recovery, copper and nickel concentrate grades, water recovery and solids recovery.

4.3.1 DTP collector suites

4.3.1.1 Solids and water recoveries for DTP mixtures

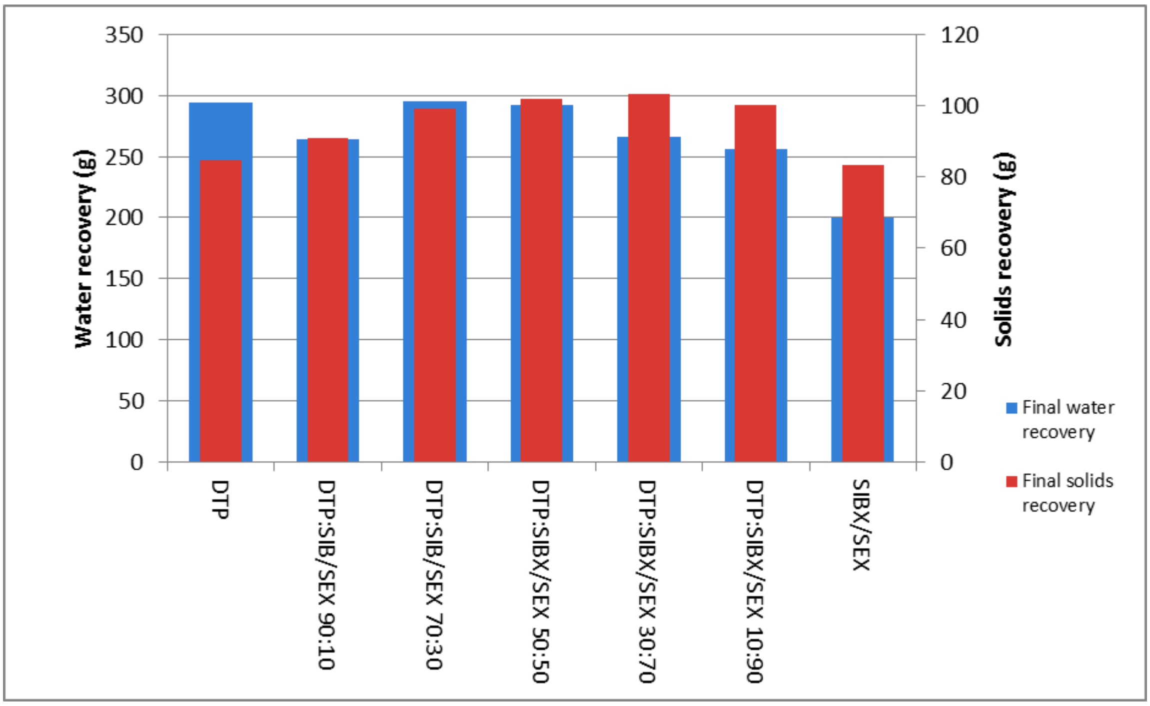

Figure 4.8 Final solids and final water recoveries for DTP: SIBX/SEX collector suites.

Table 4.6 Final water recoveries for batch flotation tests carried out with DTP: SIBX/SEX collector suites.

	Final water recovery (g)	**Final solids recovery (g)**
DTP	294.2	84.7
DTP:SIBX/SEX 90:10	264.4	90.9
DTP:SIBX/SEX 70:30	294.8	99.2
DTP:SIBX/SEX 50:50	291.9	102.0
DTP:SIBX/SEX 30:70	266.1	103.1
DTP:SIBX/SEX 10:90	256.5	100.2
SIBX/SEX	199.5	83.2

Figure 4.8 shows the final solids for varying proportions of DTP. In general the collector mixtures gave slightly higher solids recovery than their constituents' i.e. DTP and SIBX/SEX.

Figure 4.9 shows the solids recovered per unit of water recovered by DTP collector suites in relation to the amount of DTP in the collector suite. A large ratio is indicative of large mass of solids being recovered for a relatively small amount of water. The relationship between the proportion of DTP in the mixture and water recovery is approximately linear, as the proportion of DTP increases in the collector suites the mass to water ratio increases.

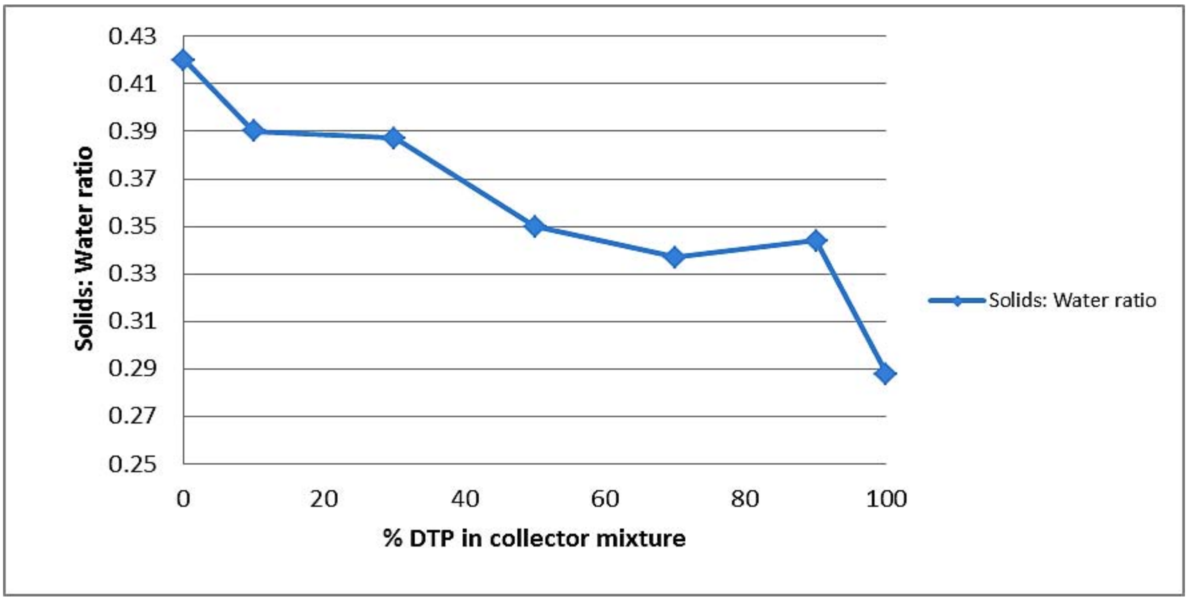

Figure 4.9 Solids recovered per unit of water for DTP collectors recovery as a function of the proportion of DTP in collector suite.

4.3.1.2 Nickel recoveries and grades for DTP collector mixtures

Figure 4.10 compares the recovery of nickel obtained with five different collector suites with that of single collectors used to make up the collector suites i.e. DTP and SIBX/SEX collectors.

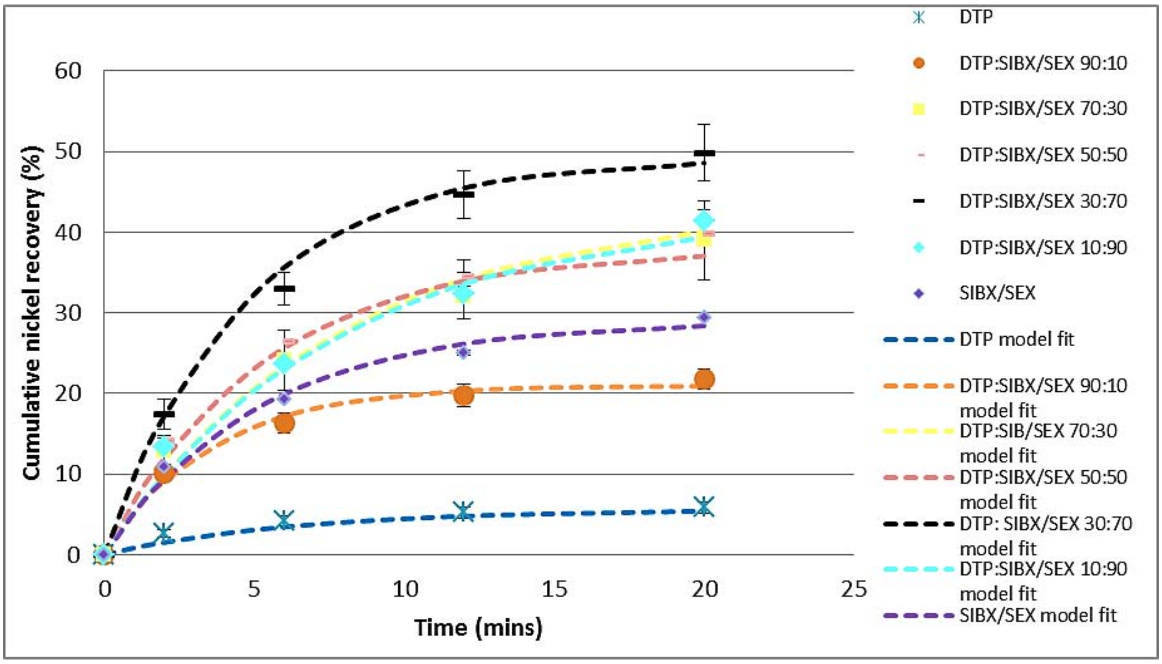

Figure 4.10 Cumulative nickel recovery vs time for DTP collector suites. Error bars represent standard error between duplicate tests.

It can be seen that all substitutions of DTP for SIBX/SEX, except the DTP: SIBX/SEX 90:10 ratio, improved the recovery of nickel as compared to the single collectors. Generally, addition of all proportions of DTP gave between 9 and 20% improvement in recovery. The overall best recovery was obtained for the DTP 30:70 collector suite, which increased nickel recovery by almost 20% more than the SIBX/SEX collector mixture and a 10-fold improvement from using DTP only. The DTP 30:70 collector mixture gave almost double the rate of nickel recovery as compared to the other collector suites.

Table 4.7 The rate of flotation (*k*) and maximum recovery (Rmax) for nickel recovery using DTP collector suites.

Collector	**Rate constants**	
	***k* (min^{-1})**	**R_{max} (%)**
DTP	0.11	5.6
DTP: SIBX/SEX 90:10	0.45	21.0
DTP: SIBX/SEX 70:30	0.49	43.5
DTP: SIBX/SEX 50:50	0.59	37.9
DTP: SIBX/SEX 30:70	0.85	49.3
DTP: SIBX/SEX 10:90	0.49	42.6
SIBX:SEX 50:50	0.47	29.0

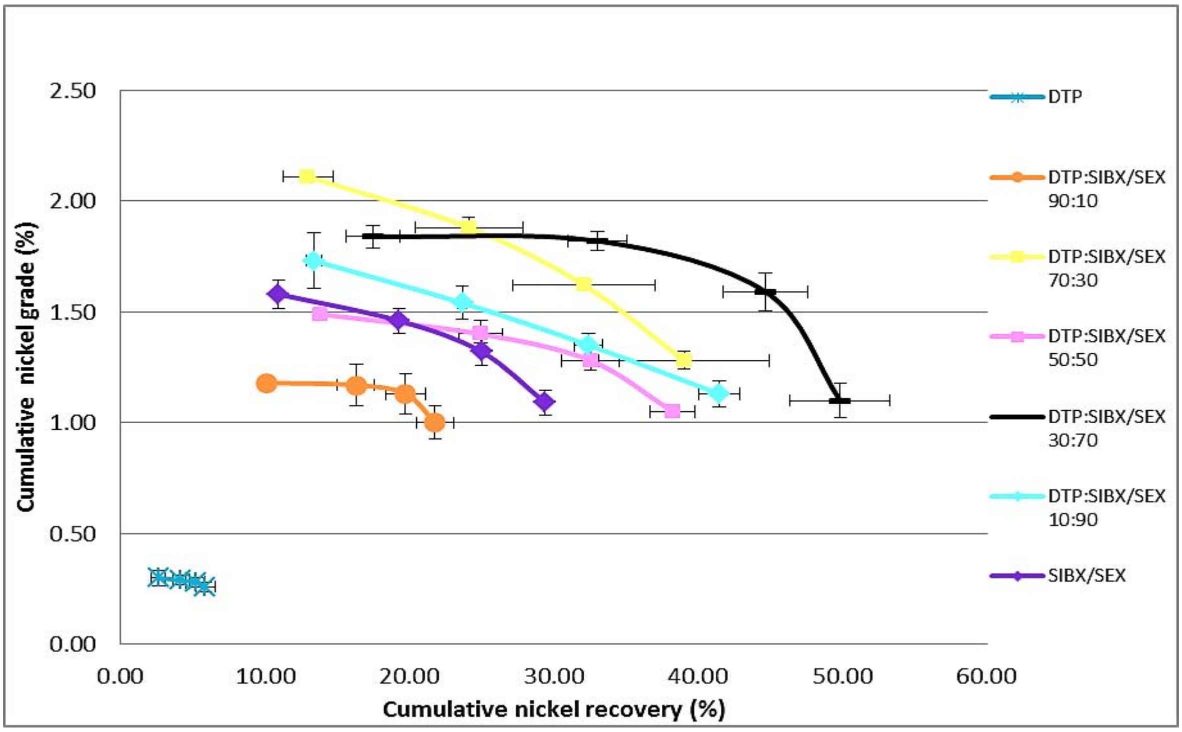

Figure 4.11 Cumulative nickel grade vs recovery for DTP collector suites. Error bars represent standard error between duplicate tests.

Figure 4.11 shows the grade vs recovery curves for DTP collector suites. The best performances as shown by the highest grade vs recovery curves was obtained for the 70:30 and 30:70 mole ratios of DTP to SIBX/SEX. The 70:30 ratio gave a 0.2% higher final grade as compared to the 30:70 mixture, however the 30:70 mixture gives almost 10% higher recovery. The DTP: SIBX/SEX 90:10, gave the lowest grade recovery curve with respect to other collector suites. The DTP: SIBX/SEX 50:50 and 10:90 mixtures gave very marginal improvements with respect to grade when compared to SIBX/SEX; however, they showed a 9% and 12% improvement in cumulative recovery, respectively, when compared to SIBX/SEX.

In order to ascertain whether the improved flotation performance was not merely due to linearly additive contribution of the individual collectors in the mixture, the final grade and recoveries were plotted as a function of the proportion of DTP in the collector mixture, as shown in **Error! Reference source not found.**Figure 4.12 below. On the x-axis, 0% DTP refers to the SIBX/SEX collector.

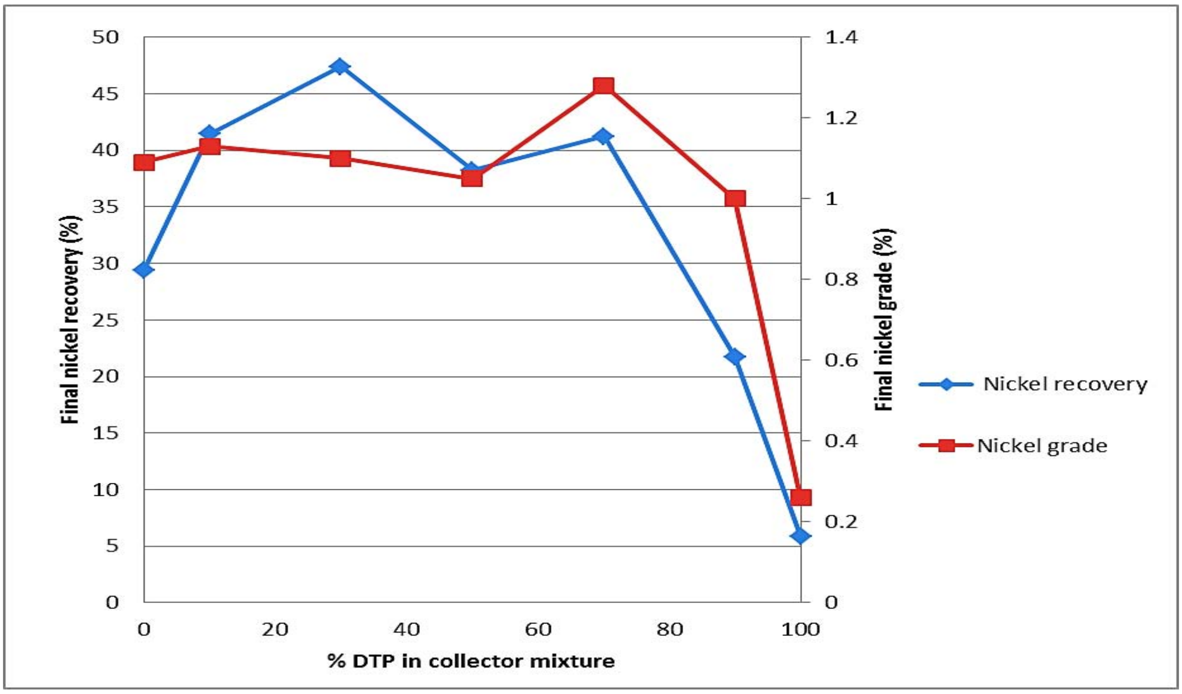

Figure 4.12 Comparison of final nickel grades and final nickel recoveries for DTP collector suites.

It can be seen that the recovery was highest for the DTP: SIBX/SEX 30: 70 collector suite and grade was highest for the DTP: SIBX/SEX 70:30 collector suite. There appears to be trade-off between grade and recovery as you vary the proportions of collector. As mentioned before, comparing the DTP: SIBX/SEX 30: 70 to the DTP: SIBX/SEX 70:30 collector suite there is a 0.2% increase in grade and a 10% drop in recovery where DTP is in higher proportions. The small increase in grade for a large decrease in recovery shows that overall that the DTP: SIBX/SEX 30: 70 is a better collector. The trends in Figure 4.12 show, the effect is not linearly additive which suggests a synergistic effect.

4.3.1.3 Copper recoveries and grades for DTP collector suites

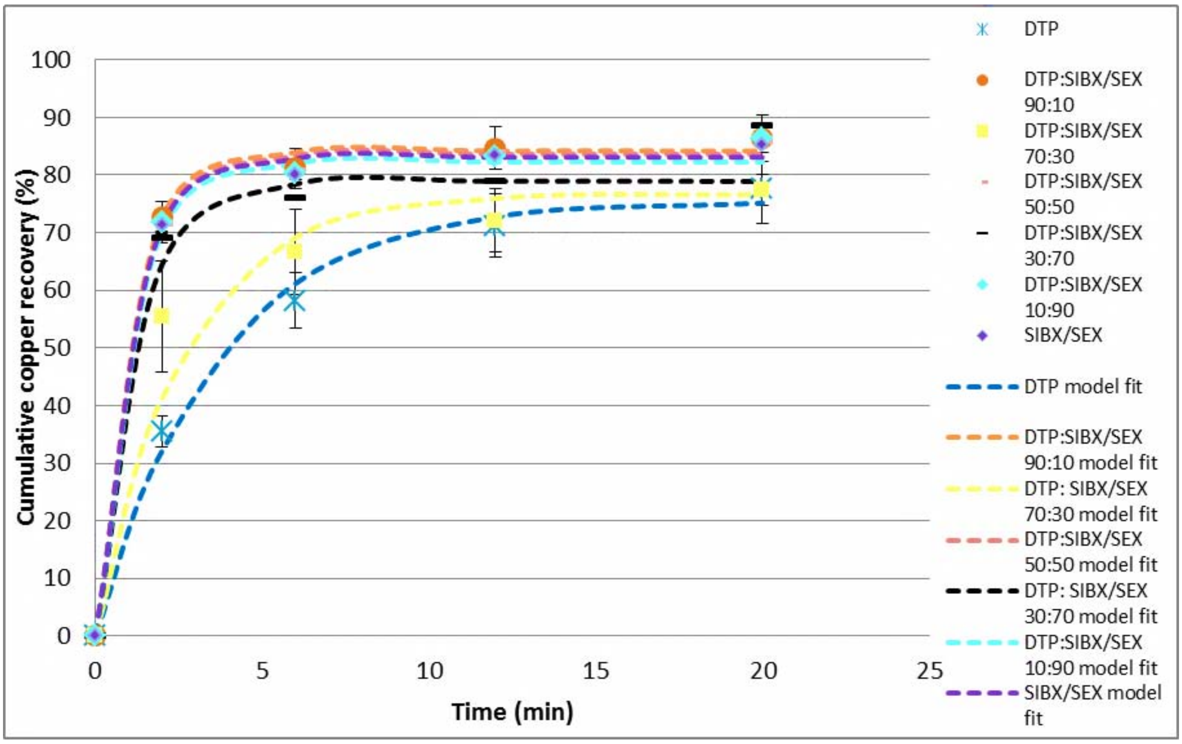

Figure 4.13 Comparison copper recoveries vs time for DTP collector suites. Error bars represent standard error between duplicate tests.

Table 4.8 The rate of flotation (k) and maximum recovery (Rmax) for copper recovery using DTP collector suites.

Collector	**Rate constants**	
	k (min^{-1})	**R$_{max}$ (%)**
DTP	1.61	76.7
DTP: SIBX/SEX 90:10	3.62	84.2
DTP: SIBX/SEX 70:30	2.73	77.7
DTP: SIBX/SEX 50:50	3.58	83.6
DTP: SIBX/SEX 30:70	3.10	78.9
DTP: SIBX/SEX 10:90	3.51	82.3

There are small, but definite difference in the final recoveries and the recovery rate of copper for the DTP collector mixtures as shown in Figure 4.13 and Table 4.8. Comparing the performance of the best collector (DTP: SIBX/SEX 90:10) and the weakest collector mixture (DTP: SIBX/SEX 70:30) shows that the there is a 7.5% difference in recovery. Ultimately the differences in recovery and rate of recovery are not nearly as marked as those for nickel recovery.

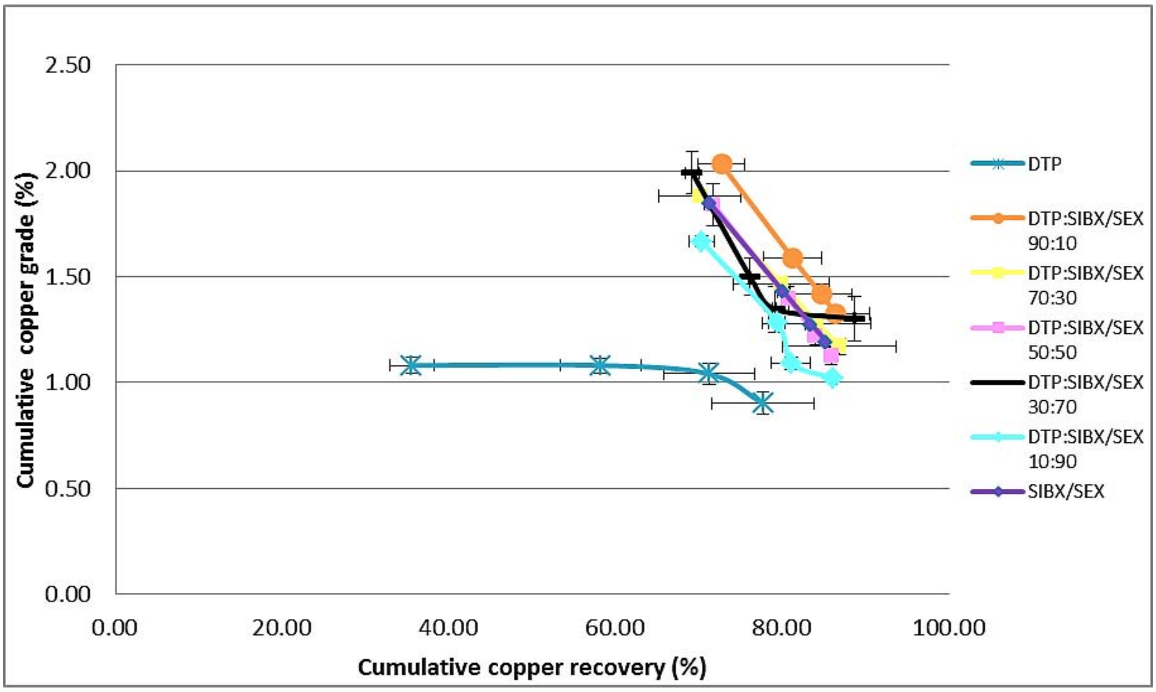

Figure 4.14 Copper grade vs recovery for DTP collector suites. Error bars represent standard deviation between duplicate error bars.

The cumulative copper grade when using DTP collector suites did not vary very much as shown by the clustered curves in Figure 4.14. The best grades were obtained for the DTP: SIBX/SEX 90:10 collector suite. This is different for the nickel recovery where the DTP: SIBX/SEX 70:30 gave the best grades.

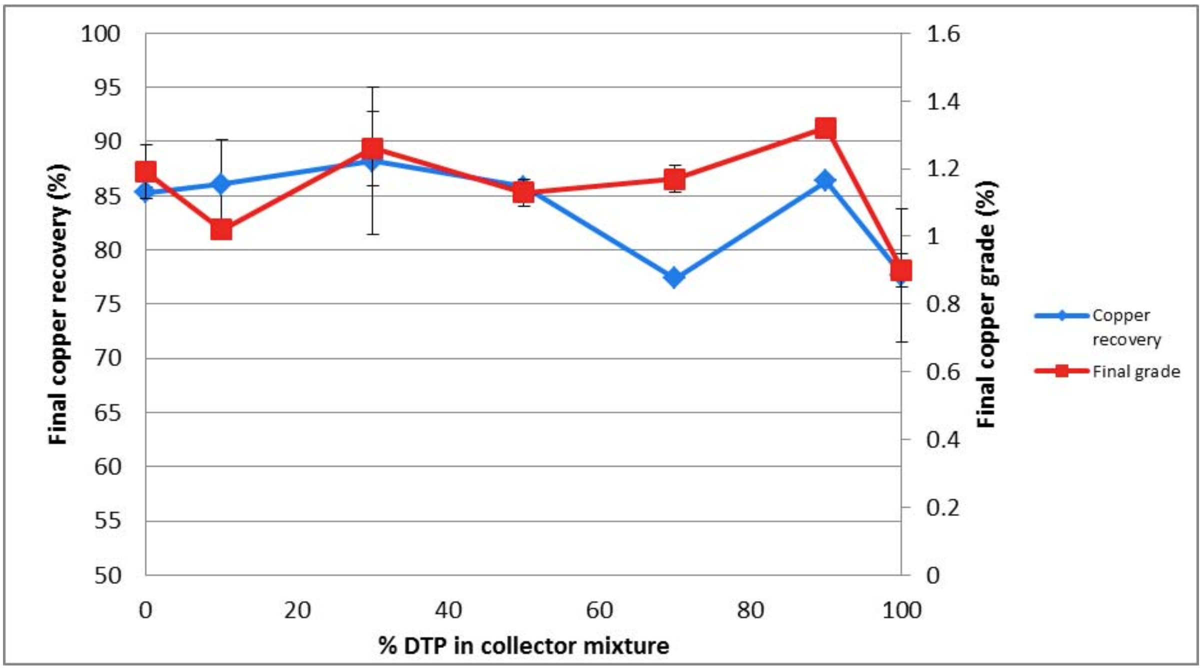

Figure 4.15 Comparison of final grades and recoveries of copper for DTP collector suites

4.3.2 DTC: SIBX/SEX collector suites.

4.3.2.1 Solids and water recoveries for DTC suites

Shown in Figure 4.16 are the solids and water recoveries for DTC: SIBX/SEX collector suites. In general the solids and water recoveries for the collector suites are slightly higher than their constituents. The highest water and mass recovery was obtained for the DTC: SIBX/SEX 70:30 collector suites, however these were only marginally higher than the other DTC collector suites.

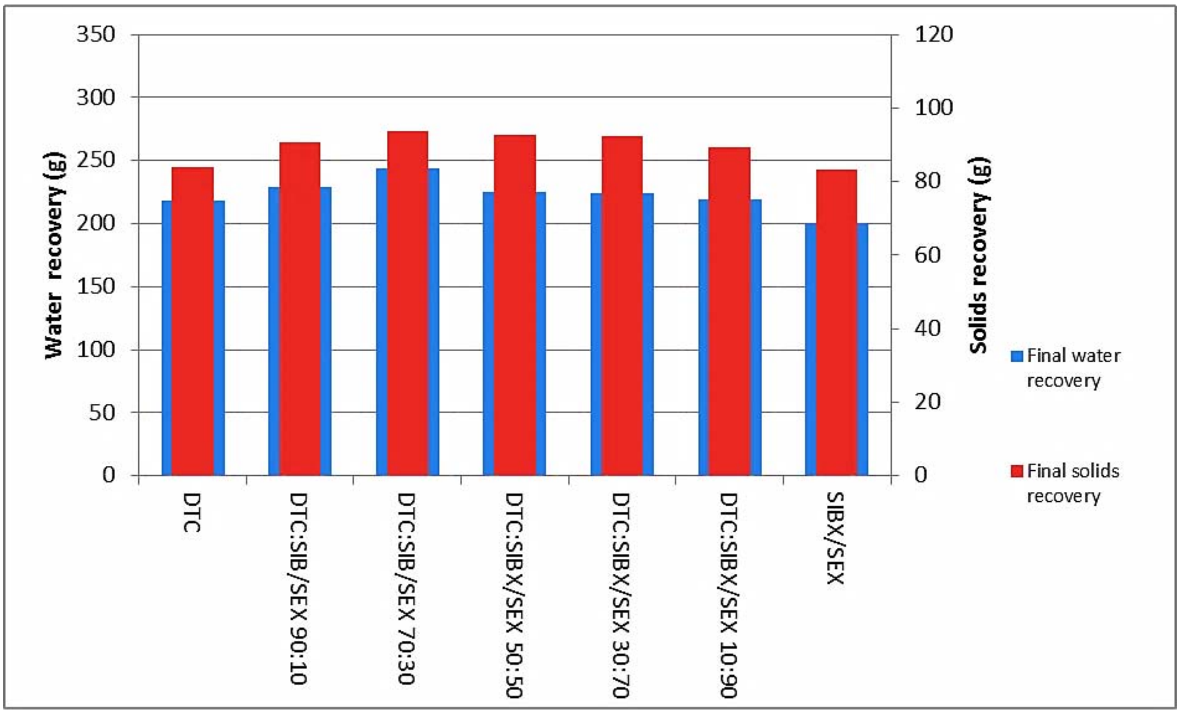

Figure 4.16 Final solids and final water recovery for DTP collector suites.

Table 4.9 Final water and solids recoveries for three phase tests carried out with DTC: SIBX/SEX collector suites.

	Final water recovery (g)	**Final solids recovery (g)**
DTC	218.4	83.9
DTC:SIB/SEX 90:10	229.4	90.6
DTC:SIB/SEX 70:30	243.9	93.6
DTC:SIBX/SEX 50:50	225.4	92.8
DTC:SIBX/SEX 30:70	224.4	92.4
DTC:SIBX/SEX 10:90	218.9	89.3
SIBX/SEX	199.5	83.2

Generally the water recovered for the DTP collector suites was higher than those for the DTC collector suites (c.f. Table 4.6 and

Table 4.9). It is interesting to note that although pure DTP recovered roughly 25 % more water than pure DTC, the mass of solids recovered was almost identical, (83.93g) and (84.67g) respectively.

4.3.2.2 Nickel grades and recoveries for DTC collector suites

Figure 4.17 shows the flotation behaviour of DTC and its collector suites. It can be seen that all substitutions of DTC for SIBX/SEX, except the DTC: SIBX/SEX 90:10 ratio, improved the recovery of nickel as compared to the single collectors. Generally addition of all proportions of DTC gave roughly 5% improvement in recovery. The best recoveries were obtained from the DTC 70:30 collector suites which collected almost 8% more nickel than the SIBX/SEX collector mixture and gave a 23% improvement from using DTC only. As shown in

Table 4.10 the 10:90 suite gave highest rates of nickel recovery. Overall, the nickel recovery results for the DTC collector suites did not vary significantly and gave final recoveries lower than that for DTP collector suites.

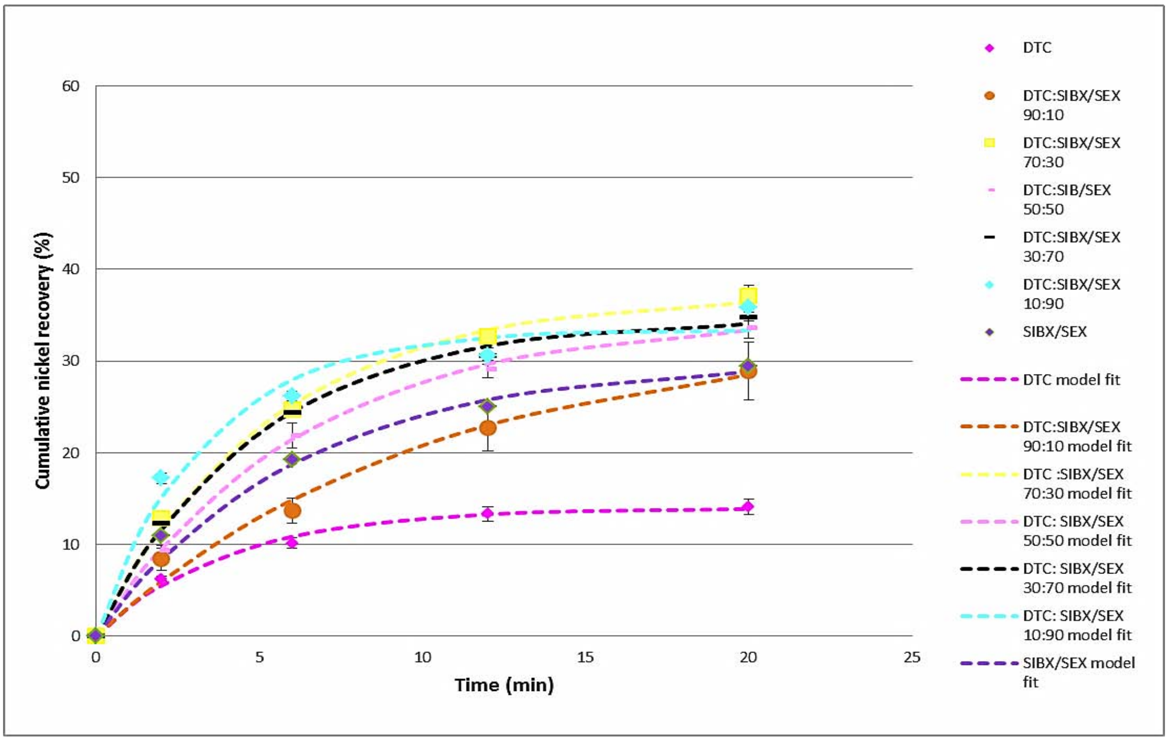

Figure 4.17 Comparison nickel recoveries vs time for DTC collector suites. Error bars represent standard error between duplicate tests

Table 4.10 The rate of flotation (K) and maximum recovery (Rmax) for nickel recovery using DTC collector suites.

Collector	Rate constants	
	k (min^{-1})	**R_{max} (%)**
DTC	0.27	14.0
DTC: SIBX/SEX 90:10	0.30	33.1
DTC: SIBX/SEX 70:30	0.58	37.3
DTC: SIBX/SEX 50:50	0.48	34.8
DTC: SIBX/SEX 30:70	0.58	34.7
DTC: SIBX/SEX 10:90	0.70	33.4
SIBX:SEX 50:50	0.47	29.0

Figure 4.18 shows the grade-recovery curve for all the DTC collector suites. The highest concentrate grades were obtained for the collector suite where DTC and SIBX/SEX were in equal molar proportions; however the final grade and final recoveries were comparable to those of other collectors.

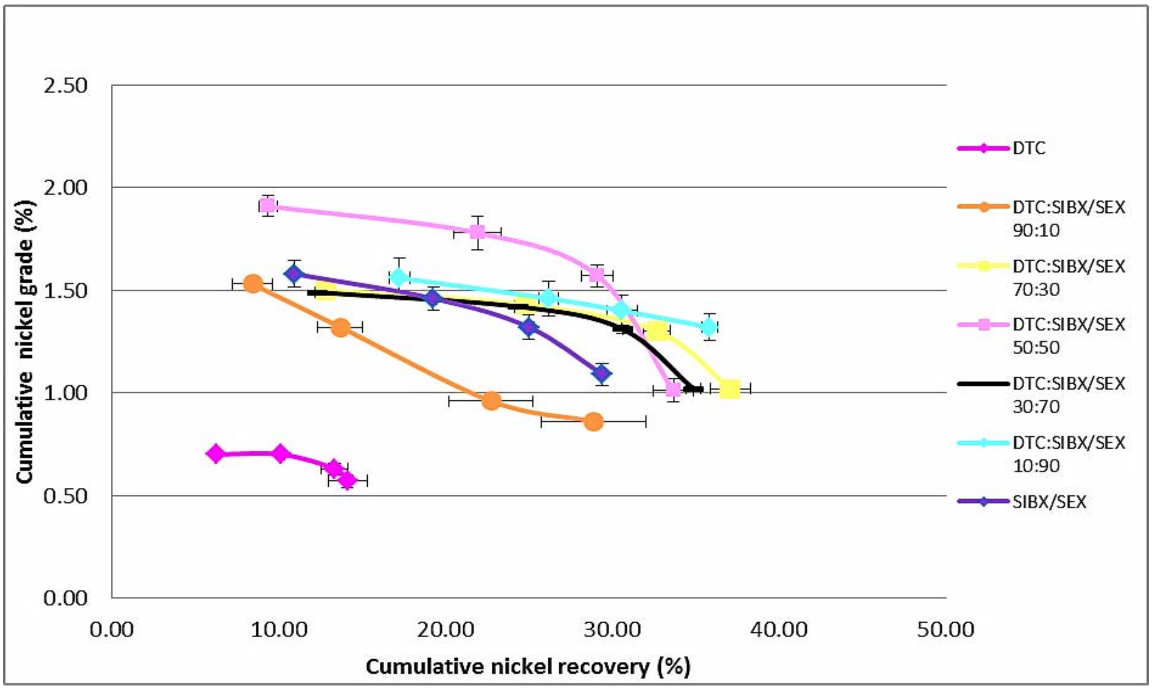

Figure 4.18 Nickel grade vs nickel recovery for DTC collector suites. Error bars represent standard q between duplicate tests.

All collectors gave roughly 0.5% enrichment compared to the use of DTC alone and gave roughly the same final grade as the SIBX/SEX collector. This is illustrated in **Error! Reference source not found.**Figure 4. 19;which shows the final grades and final recoveries as a function of the proportion of DTC in the mixture. The DTC: SIBX/SEX 10:90 mixture was chosen as the best performing DTC collector suite owing to its improvement in grade of recovered nickel. Although the improvements in grade and recovery were not as marked for DTC as they were for DTP, there was still some synergistic effect observed upon the addition of DTC to the xanthate mixture. A simple dilution effect would have resulted in a linear relationship in **Error! Reference source not found.**Figure 4. 19.

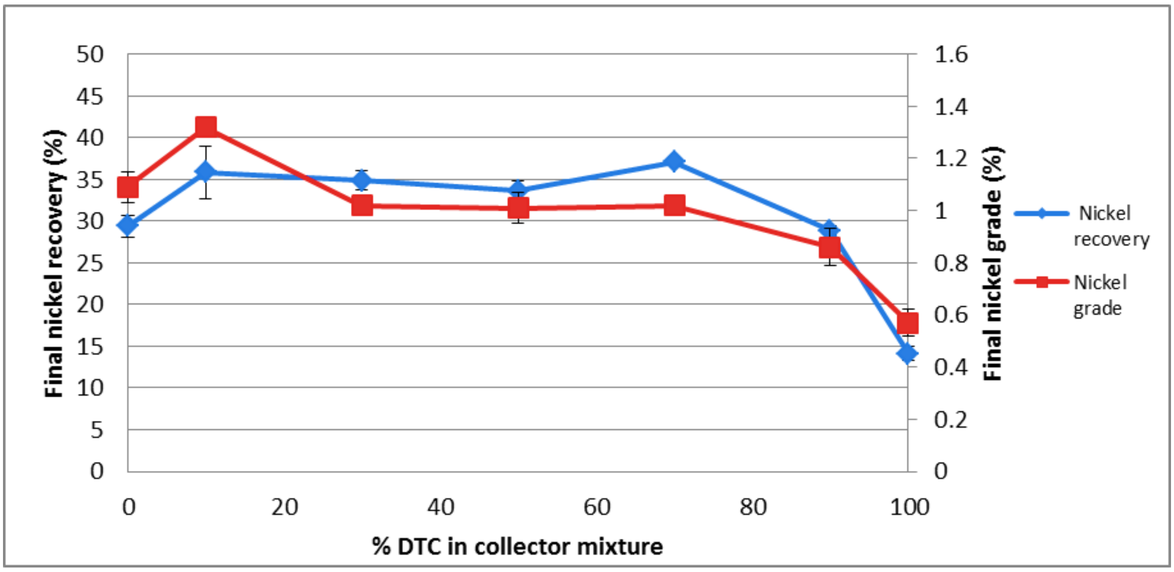

Figure 4.19 Final nickel grades and final copper recovery curves for DTC collector suites.

4.3.2.3 Copper grades and recoveries for DTC collector

The results for copper recovery for DTC collector suites are shown in Figure 4.20. There is an almost 10% difference between the best performing collector which is DTC: SIBX/SEX 30:70 and the worst performing collector which is DTC: SIBX/SEX 10:90. However the only mixture that performed comparably with SIBX/SEX was the DTC: SIBX/SEX 10:90 mixture. The differences between the performances of the different collector systems were smaller for chalcopyrite than pentladite because of the fast floating nature of chalcopyrite.

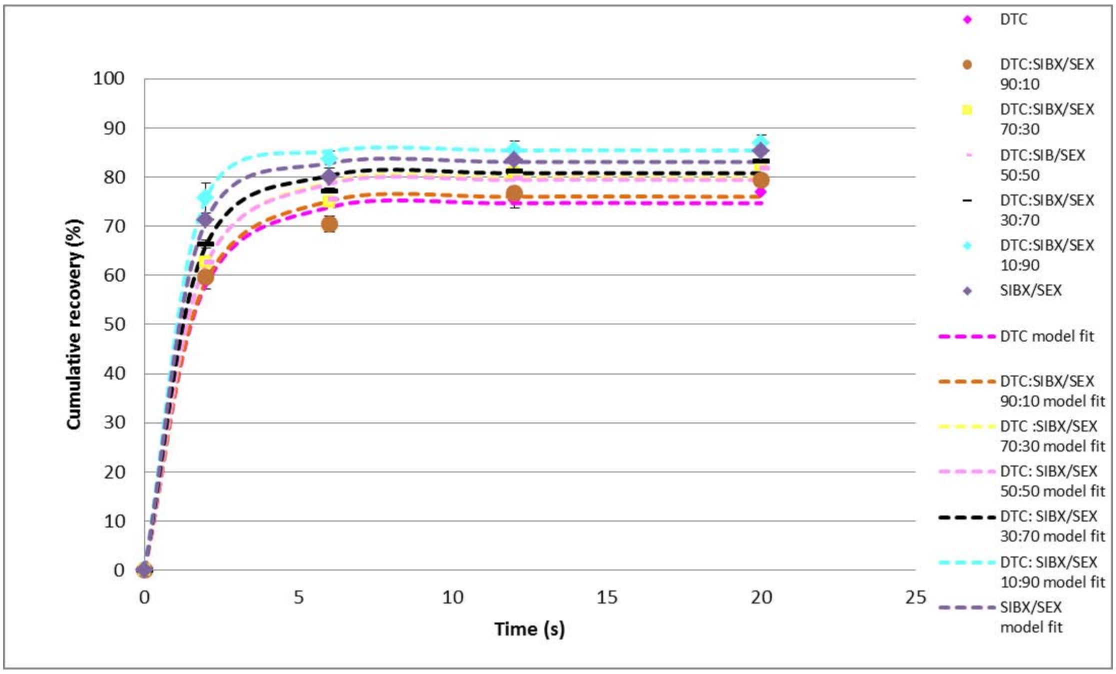

Figure 4.20 Copper recoveries vs time for DTC collector suites. Error bars represent standard deviation between duplicate tests.

Table 4.11 The rate of flotation (k) and maximum recovery (Rmax) for copper recovery using DTC collector suites.

Collector	**Rate constants**	
	***k* (min^{-1})**	**R$_{max}$ (%)**
DTC	2.91	74.7
DTC: SIBX/SEX 90:10	2.94	76.0
DTC: SIBX/SEX 70:30	3.11	79.9
DTC: SIBX/SEX 50:50	3.11	79.4
DTC: SIBX/SEX 30:70	3.31	80.8
DTC: SIBX/SEX 10:90	3.78	85.4
SIBX/SEX 50:50	3.56	83.1

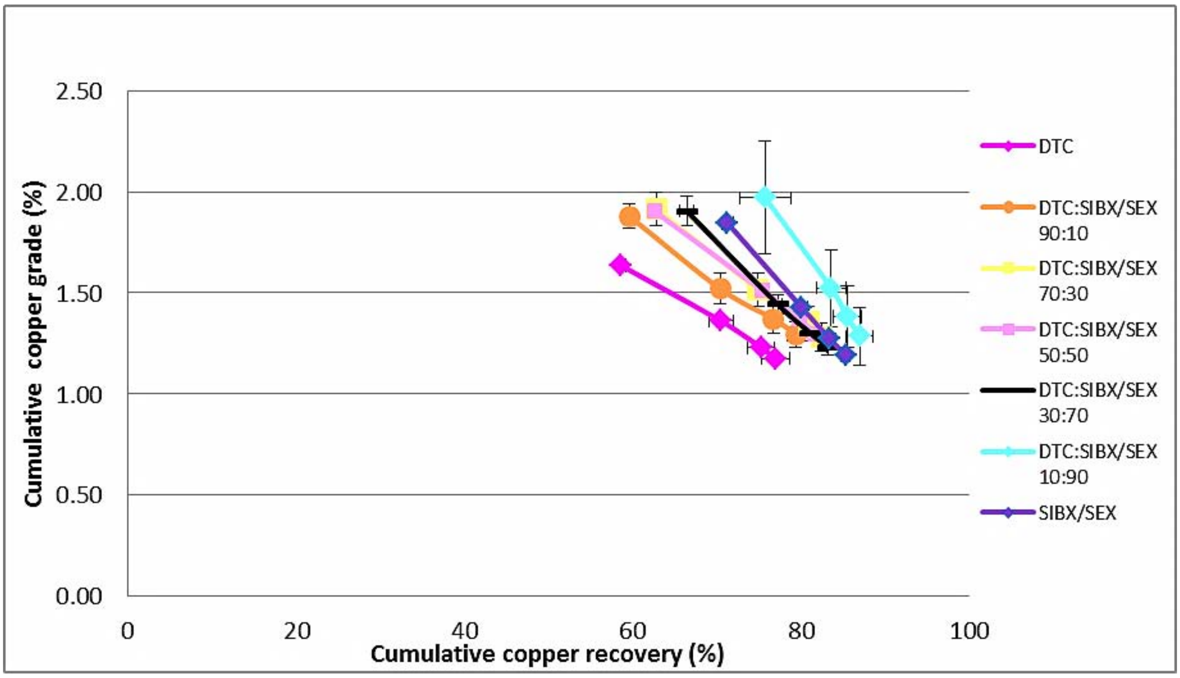

Figure 4.21 Copper grade vs copper recoveries for DTC collector suites. Error bars represent standard deviation between duplicate tests.

There is little difference in cumulative grade for many of the collector suites as shown in Figure 4.21. The 10:90 mixture shows the slightly higher cumulative grade and recovery as compared to the other collectors.

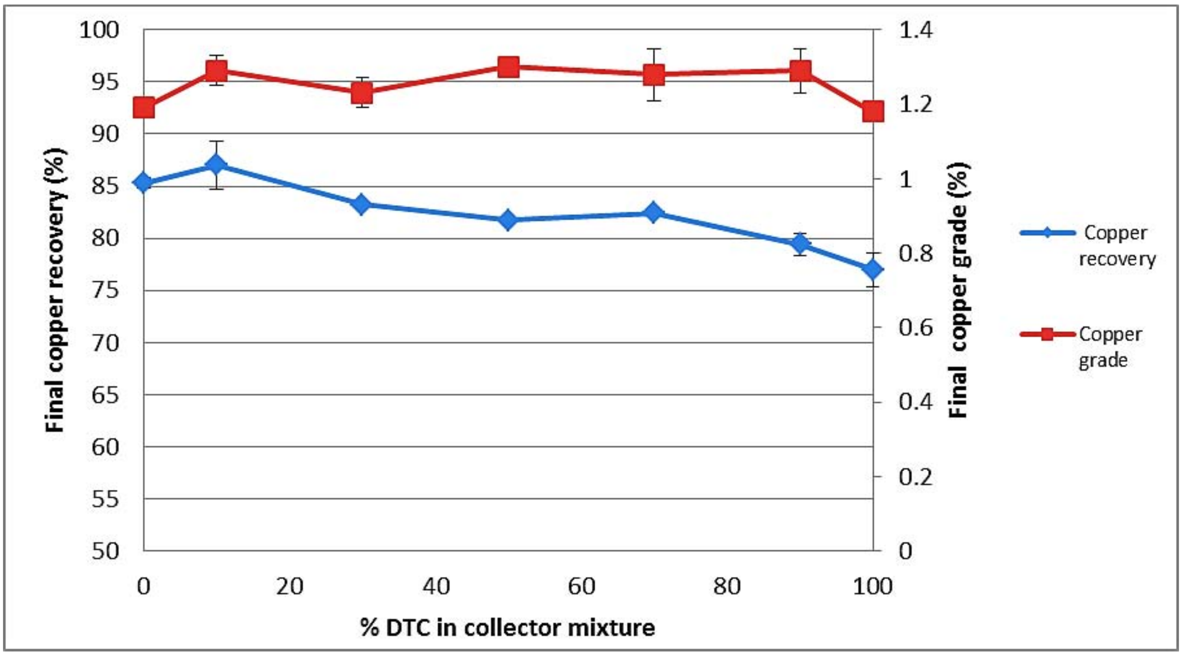

Figure 4.22 Final copper grades and recovery curves for DTC collector suites

4.4 Comparison of single collectors vs the best performing DTP and DTC collector suites

This section will compare the performance of the single collectors with the best performing collector suites i.e. DTP: SIBX/SEX 30:70 and DTC: SIBX/SEX 10:90.

4.4.1 Cumulative solid and water recoveries

Figure 4.23, a graph of water and solids recovery for the best performing single collector (SIBX) and the best collector suites for DTP and DTC collector suites. For reference, the results obtained for collector-less flotation and as well as for pure DTP and pure DTC are also shown. The figure shows that the solids and water recoveries for SIBX were slightly higher than those for the DTC: SIBX/SEX 10:90. The water and solids recoveries for pure DTC and the DTC collector suite are very similar as shown in Table 4.12. The DTP mixture had the highest solids and water recoveries of all the collectors.

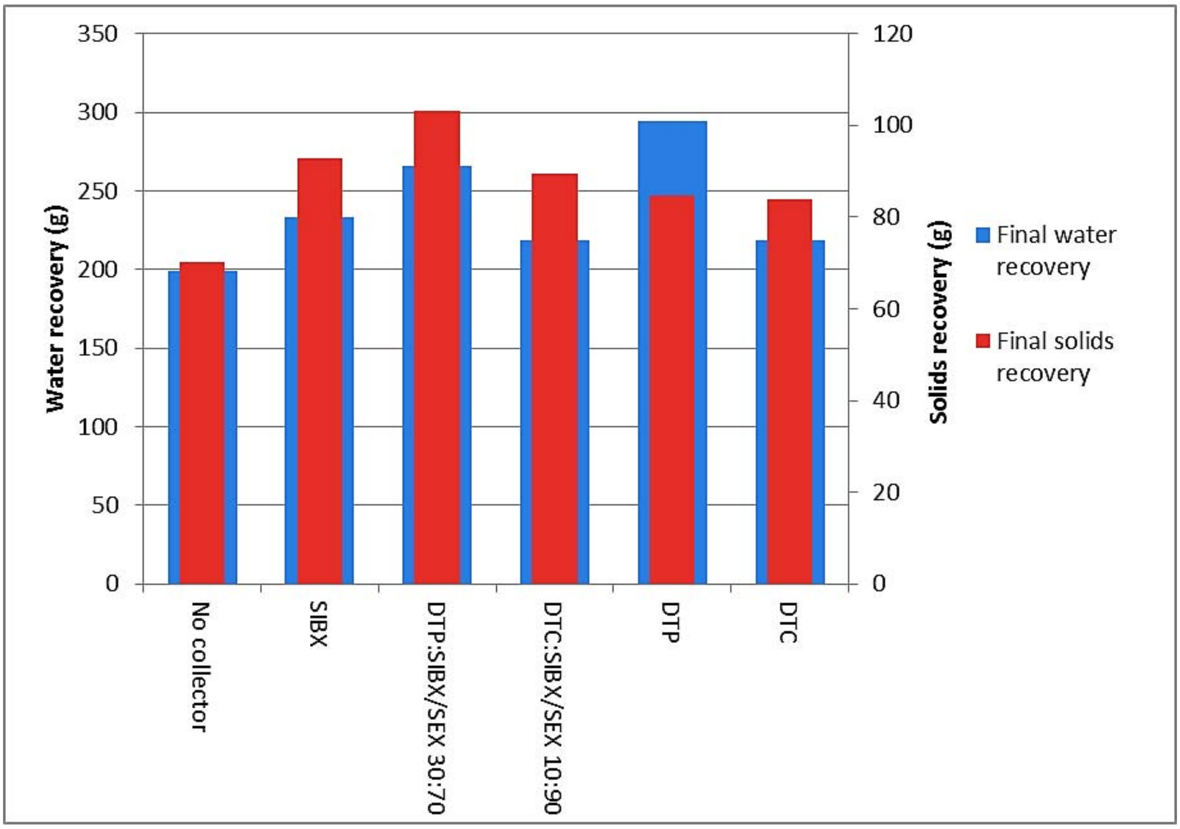

Figure 4.23 Final solids and final water recovery for the best collector suites

Table 4.12 Final water and solids recoveries for the best collector system

	Final water recovery (g)	**Final solids recovery (g)**
No collector	199.0	70.3
SIBX	233.2	92.9
DTP: SIBX/SEX 30:70	266.1	103.1
DTC: SIBX/SEX 10:90	218.8	89.3
DTP	294.2	84.7
DTC	218.4	83.9

The DTP collector suite showed 23% increase in solids recovery and a 12% increase in water recovery as compared to SIBX. The DTC collector suite gave lower final solids and water recoveries as compared to SIBX.

4.4.2 Comparison of cumulative nickel recoveries and grades for the best performing collector suites

The nickel recovery as function of time is shown in Figure 4.24. The DTP collector suite was the strongest collector system; it improved the flotation of nickel by over 40% as compared to collector-less flotation. This improvement in nickel recovery can be related back to the final solids recovery, where the DTP collector suite showed almost 30% increase in solids recovery (cf. Section 4.5.1) as compared to flotation without collector. The DTC collector suite collected about 10% less nickel than the DTP collector suite, with a slower recovery rate. SIBX collected slightly more nickel than the DTC collector suite; however the nickel recovery rate is much lower than that of the collector suites.

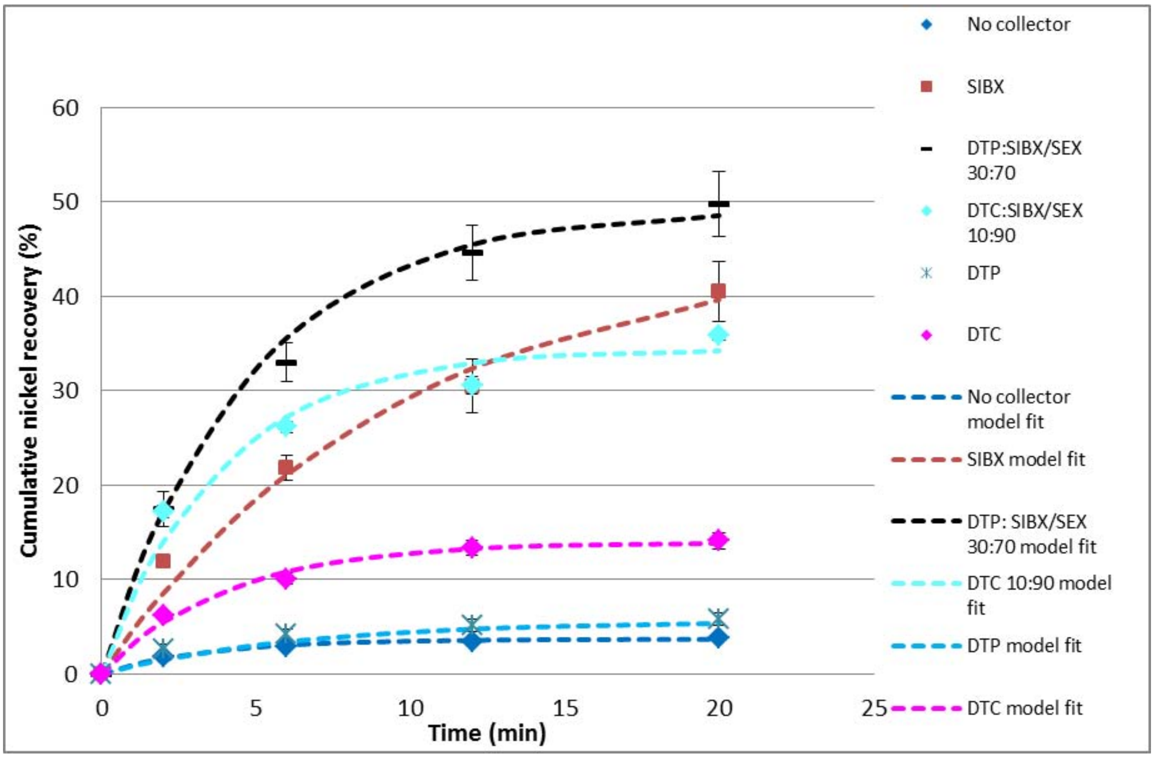

Figure 4.24 Cumulative recovery of nickel using the best performing collectors.

Table 4.13 The rate of flotation (k) and maximum recovery (Rmax) for nickel recovery using the best performing collector suites.

Collector	**Rate constants**	
	k **(min^{-1})**	**R$_{max}$ (%)**
No collector	0.08	3.7
SIBX	0.43	43.2
DTP: SIBX/SEX 30:70	0.86	78.9
DTC:SIBX/SEX 10:90	0.70	34.4

Error! Reference source not found. Figure 4.25 shows the grade recovery curves for the different collector systems. The best performance, as shown by the highest grade-recovery curve was obtained for the DTP collector suite. The copper grade for all four concentrates for DTC: SIBX/SEX 10:90 falls within a narrow range and it gives the highest nickel grade of 1.25%. The DTP: SIBX/SEX collector suite has the highest grade for its individual concentrates but has a final grade that is lower than for the DTC collector suites. This is probably due to entrained gangue which lowers the overall grade. Both collector mixtures performed better than SIBX which was the best single collector.

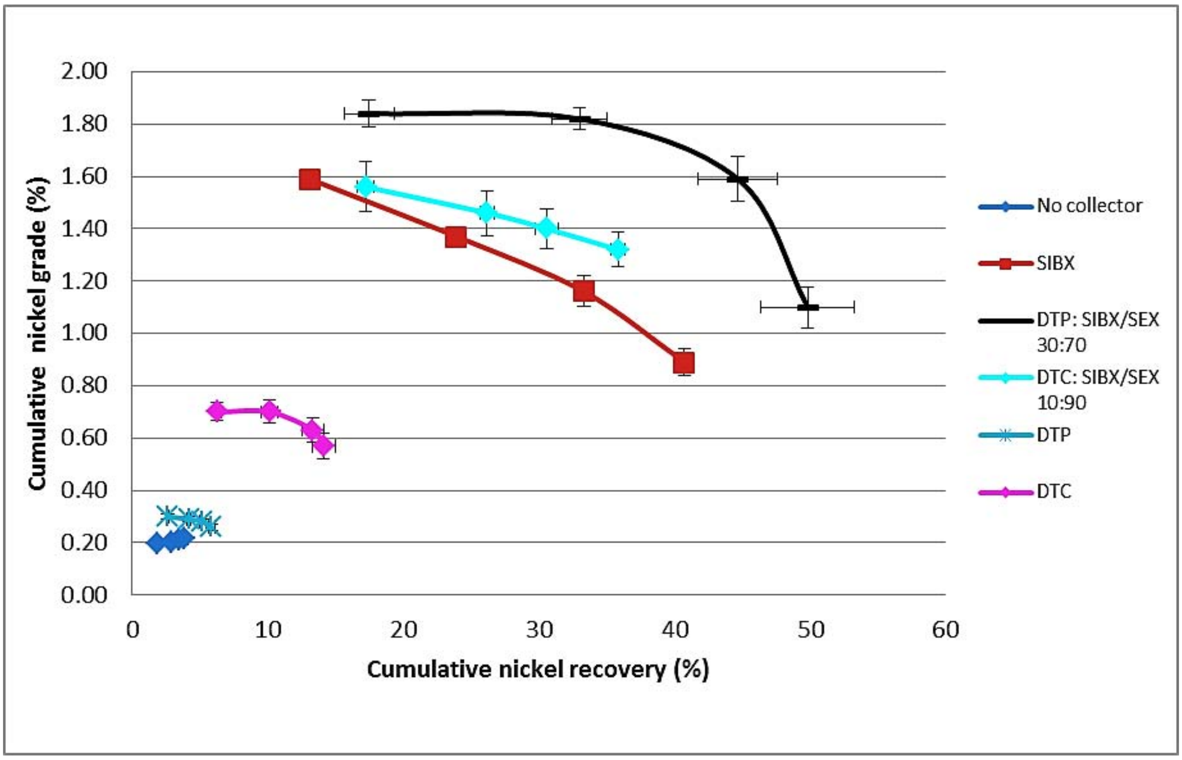

Figure 4.25 Cumulative nickel grade vs nickel recovery curves for the best performing collectors.

From these results it can be seen that the best collector suites have better selectivity as compared to their constituent collectors. The next section investigates the possible effects that the overall best performing collector suit has on the pulp phase.

4.5 Investigating the mechanisms by which the DTP: SIBX/SEX 30:70 collector suite enhances flotation performance

4.5.1 The effect of sequential addition when using collector mixtures

The results shown in this section are for flotation tests which were carried out to ascertain whether the sequence in which the collectors where added affected the flotation behaviour of the collector suite. These tests were carried out using the DTP: SIBX 30:70 mixture which will simply be referred to as DTP: SIBX/SEX. This was the best performing mixture for all the collector mixtures tested. The reagent sequence was either xanthates first or DTP first or both collectors were pre-mixed and added together. More details are given in the experimental section.

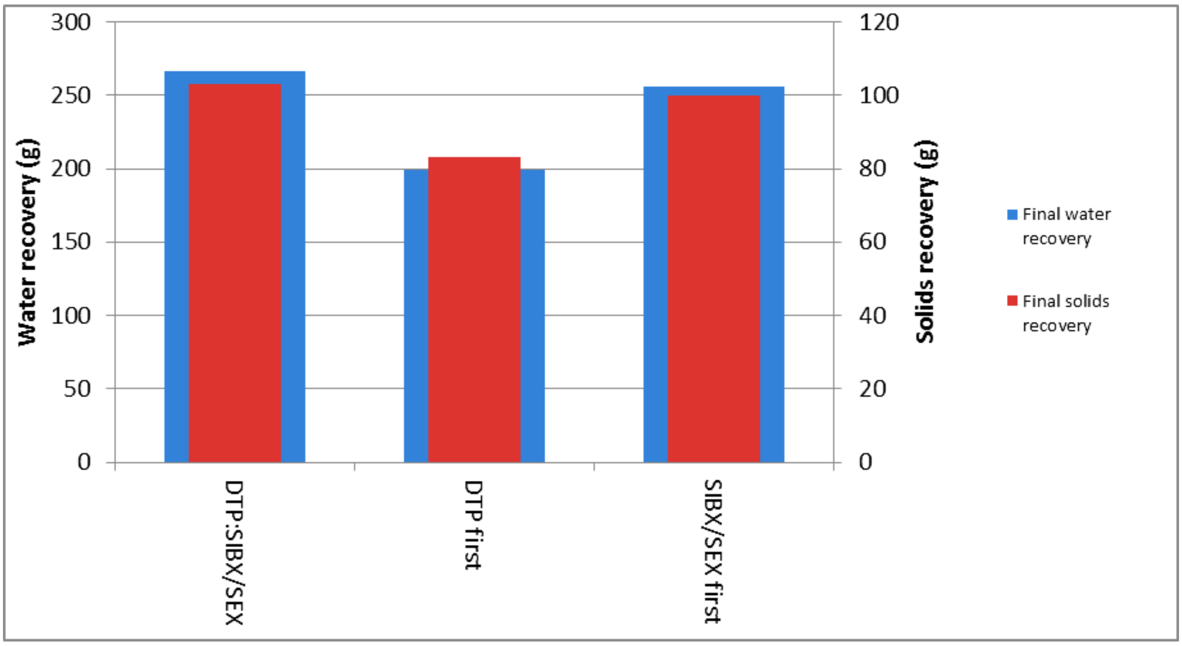

Figure 4.26 Water and solids recovery for sequential addition of DTP:SIBX/SEX 30:70.

Figure 4.26 shows adding DTP first yields solids and water recovery obtained were lower by roughly 35% when compared to adding both collectors together. On the other hand when SIBX/SEX was added first, almost identical results were obtained as adding pre-mixed collector.

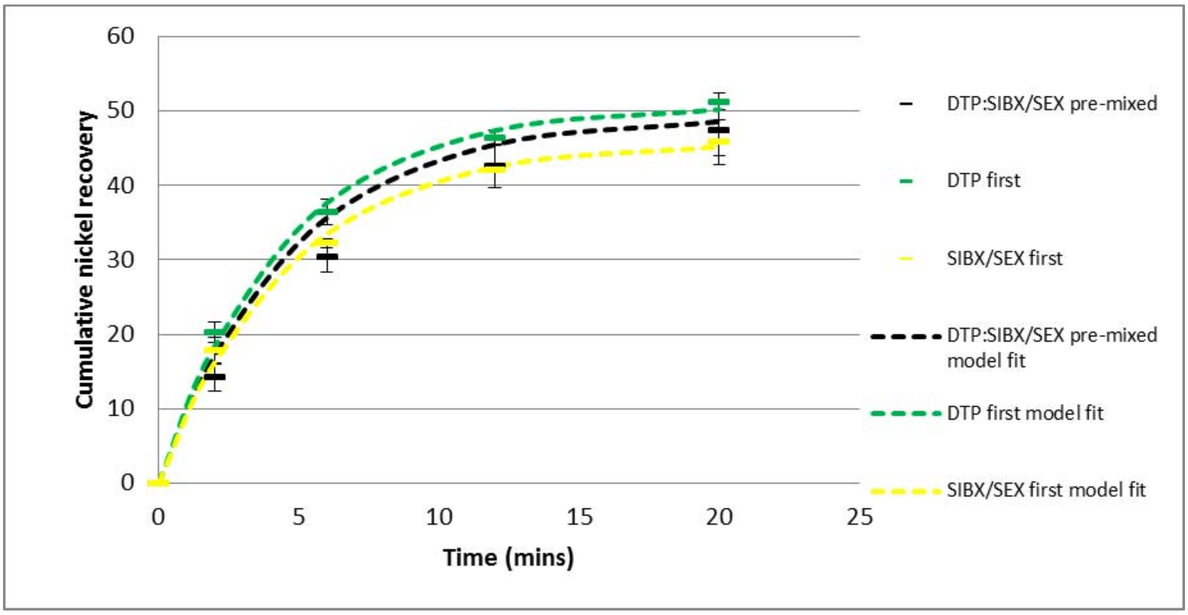

Figure 4.27 Cumulative nickel recovery vs time graphs using different sequences of addition for the DTP: SIBX/SEX collector suites. Error bars represent standard error between duplicate tests.

Table 4.14 The rate of flotation (k) and maximum recovery (Rmax) for nickel recovery for sequential addition.

Collector	**Klimpel constants**	
	k **(min^{-1})**	**R$_{max}$ (%)**
DTP: SIBX/SEX	0.86	49.3
DTP first	0.92	50.7
SIBX/ SEX first	0.81	45.8

Figure 4.27 shows the effect of order of addition of the DTP: SIBXSEX mixture on the cumulative recovery of nickel. Slightly higher recoveries were obtained when DTP was added first as compared to SIBX/SEX first or simultaneous addition; however there was an overlap of error bars which suggests that the ultimate nickel recovery was not significantly affected by the sequence of addition. Table 4.14 shows that the rate of recovery for DTP first was slightly higher than for the other sequences.

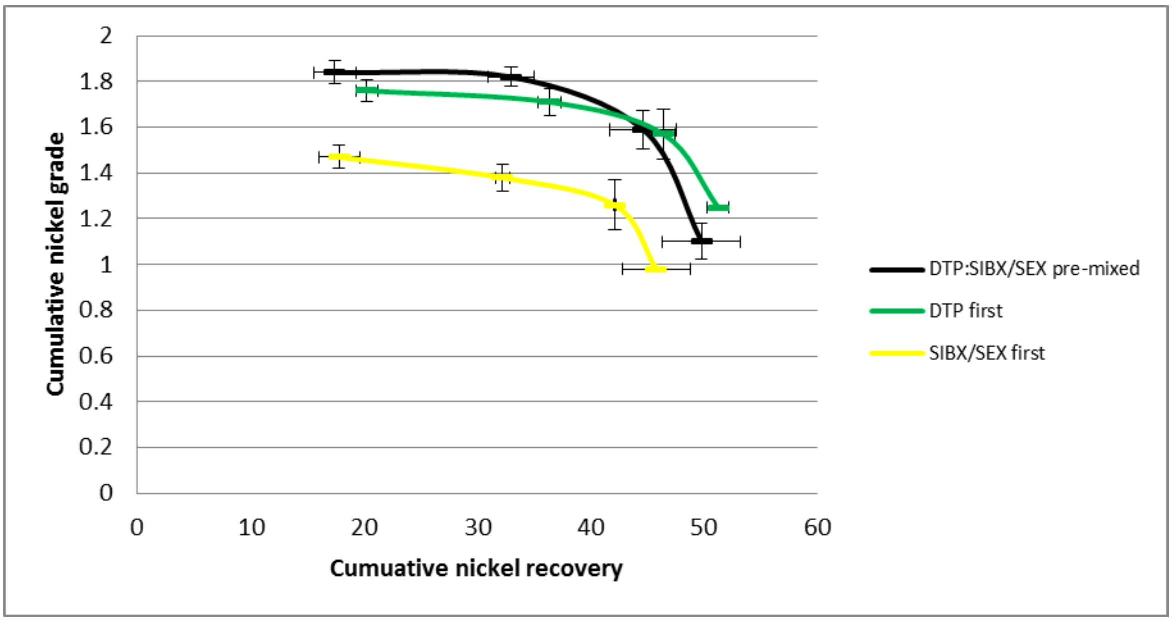

Figure 4.28 Nickel grade vs nickel recovery curve for different sequences of addition for the DTP: SIBX/SEX collector suites. Error bars represent standard error between duplicate tests.

Figure 4.28 shows the nickel- grade recovery curve obtained for different sequences of addition. The premixed collector and the “DTP first” result were almost identical, however, the grade was significantly lower when SIBX/SEX was added first.

4.5.2 Investigation into size class recovery

Particle size is an important flotation variable because particle sizes behave differently in flotation. The particle sizes are classified as shown in Table 4.15 below.

Table 4.15 Classification of particle sizes

Particle size range (µm)	**Description**
-10	ultrafine
-25 +10	fine
+25, -75	medium
+75	coarse

The distribution of particle sizes by volume percent is shown in Figure 4.29. A logarithmic scale was used for the x-axis (particle size) to accommodate the wide range of particle sizes and since the graph was heavily skewed to the left, it allowed for better resolution in the ultrafine to fine particle size range (Merkus, 2009).The feed distribution is shown in grey. The original feed size distribution was 60% passing 75 µm, and hence a higher proportion of particles fall within the coarse particle range. The particle size distribution curves shown below were plotted as multi-modal with more than one peak, rather than uni-modal where only the main peak is shown, in order to show more detail on the distribution of particles in the concentrates. The distribution exhibited distinct peaks for different size ranges (ultrafine, fine, medium and course), and these peaks became more defined as flotation time elapsed.

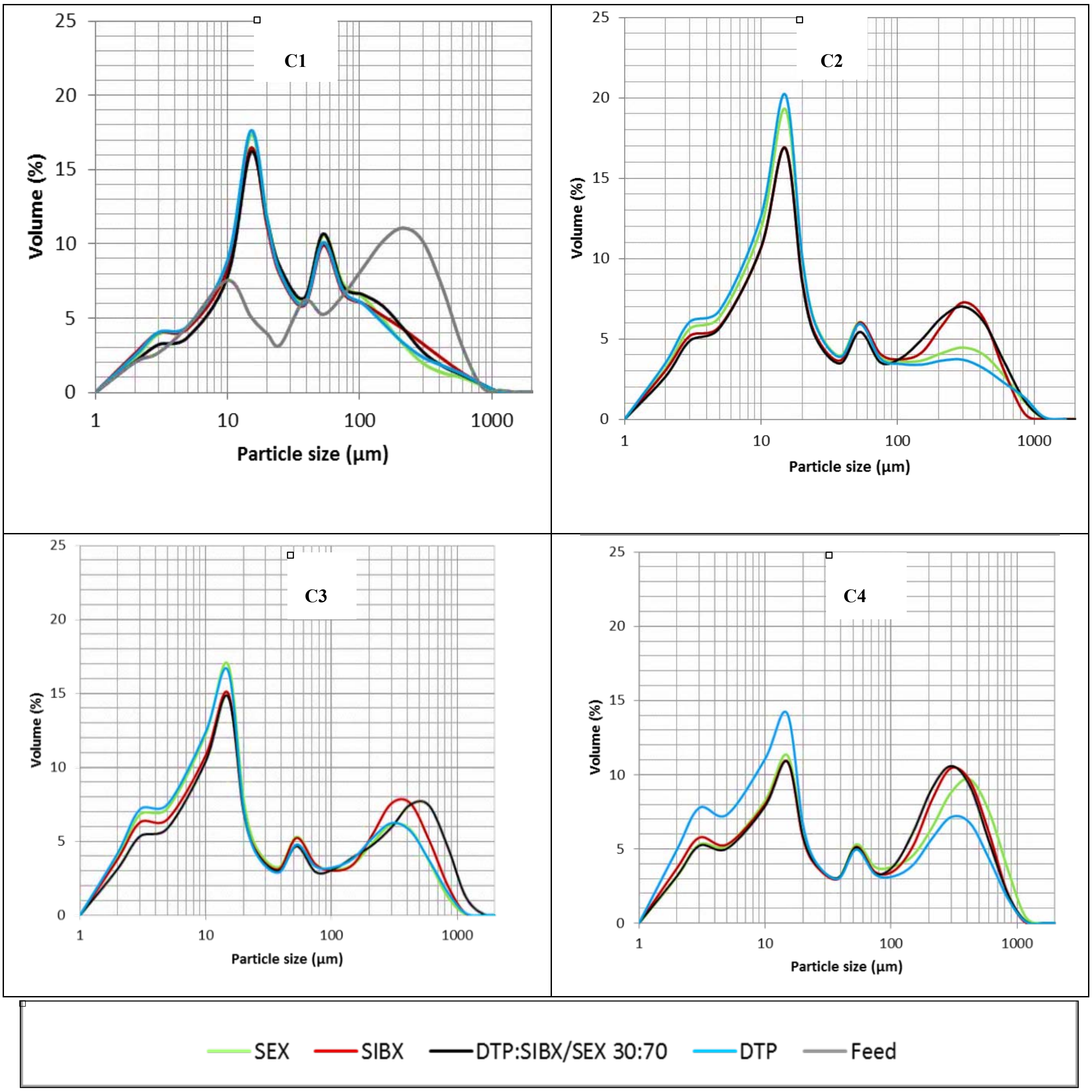

Figure 4.29 Particle size particle distribution of the concentrates after 2 minutes of flotation (C1), after 6 minutes of flotation (C2), after 8 minutes of flotation (C3) and after 12 minutes of flotation (C4) for DTP: SIBX/SEX 30:70 collector suite and its constituents. (SEX, SIBX, DTP). The feed size distribution is shown for reference.

The particle size distribution does not vary significantly in the first concentrate for different collector systems. The majority of particles recovered are within the fine to medium size range and two peaks appear at around 15 and 50 µm. Notably, the ultrafine and coarse particles were not well represented in C1. After 6 minutes of flotation, peaks begin to emerge in the coarse particle range for SIBX, SEX, and the DTP: SIBX/SEX 30:70 collector suite. These peaks appear at about 120 µm and SIBX and the DTP collector mixture peaks are larger than those for SEX and DTP. The same pattern is shown in C3; however it is interesting to note how the peak for the DTP collector suite shifts to the right from about 120 to 150 µm. When going from C3 to C4, there is an increase in the proportion of coarse particles, as shown by the last peak, from about 8% to11%.

5 Discussion

The aim of this study was to investigate effect of mixed collectors on the flotation of Nkomati sulfide ore. Tests on pure collectors were carried out to establish a baseline against which to assess the performance of collector mixtures. In this chapter, the results will be analysed in order to determine whether mixed collectors have superior metallurgical performance over single collectors as well as to try and ascertain the mechanism by which this enhancement occurs. Finally recommendations will be made for future work.

5.1 Single collectors

5.1.1 Assessment of the frothing properties of single collectors

The two phase tests showed that when collector was added to frother, the water recovery increased. The increase for the xanthates (SEX, SIBX and SIBX/SEX) was around 50%. DTC more than doubled the water recovery (111%) with DTP in the presence of a frother almost quadruple the mass of water recovered compared to using frother only. This increase in water recovery can be attributed to a relatively more stable froth being formed in the presence of both frother and collector. Frothers are surface active agents i.e. a hydrophilic head and hydrophobic tail. They stabilise bubbles by adsorbing at the air-water interface, forming an envelope around the bubbles which prevents bubble coalescence (Bulatovic, 2007). Since collectors are also polar molecules, they may behave in a similar manner. Hence, in the presence of both frother and collector, there is a higher concentration of surface active ingredients than in the presence of frother alone. The amount of floating gangue will be essentially constant for all collectors, since the amount of depressant used did not vary (0 g/t). Therefore, it is the collector itself that is contributing to the variations in froth stability (in the form of water recovered) and not varying amounts of floating gangue.

It is interesting to note that the xanthates all had similar water recoveries and DTC had a higher water recovery than the xanthates, while DTP gave the highest water recoveries even in the absence of frother. The observed effects may be due to the difference in structure of the collectors. The activity of the collectors appears to be influenced by molecular weight, the nature of the functional group as well as the length and shape of the hydrophobic chain .According to literature (Laskowski and Woodburn, 1998; Somasundaran, 2006) long, straight chains result in closer packing of the surfactant molecules at the interface. Introduction of bulky chains reduces the amount of lateral chain interaction which reduces the cohesive strength of the surfactant layer, making it more elastic and less likely to rupture. Interplay of all these factors might explain the observed order for water recovery for single a collector which was as follows:
DTP > DTC > SEX/SIBX > SEX

DTP has the largest molecular weight (cf. Table 3.4) and has a relatively bulky structure and the least electronegative functional group (phosphate). These combined factors possibly give DTP the required metastability to make it a relatively good surface active agent which in turn would account for the high water recovery observed with DTP even in the absence of a frother. Additionally, residual alcohol during the manufacture of DTP may contribute to the frothing properties observed. Furthermore, McFadzean and O'Connor (2013) showed that the enthalpy of dilution was much higher for DTP than other collectors. These workers postulated that this observation showed that there was a substantial rearrangement occurring when DTP molecules were solvated by water molecules. This interaction with water may also explain why DTP behaves as better froth modifiers than the other collectors.

In the three phase system, the water recovery observed for DTP was approximately 30% higher than for the "collector-less flotation". This was expected since DTP was shown to possess frothing capabilities in the two phase tests. However the frothing effects observed for the other collectors in the two phase system was not carried over into the three phase system. This may be due to the fact that the xanthates and DTC adsorbed onto the mineral surface in a three phase system and were no longer available to the air-water interface. Microcalorimetry studies have shown that DTP does not adsorb onto galena and chalcopyrite surfaces (McFadzean and O'Connor, 2013). If this is the case with Nkomati ore, then there would still be DTP available in solution, which accounts for the frothing effects observed in the three-phase system. Furthermore, the results of pulp potential experiments carried out in the present study (Figure 4.7) suggest that there was no net electron transfer in the presence of DTP as was the case with other collectors.

5.1.2 Nickel recoveries for single collectors

Nickel recovery and grade was highest for SIBX and lowest for DTP, which was only marginally higher than with no collector. The SIBX/SEX mixture showed recovery similar to that of SEX. DTC gave Ni recoveries higher than DTP but significantly lower than the xanthates. Collector strength and selectivity on a mineral surface depends on the nature of the functional group and the chain length. The following orders of collector strengths have been proposed by previous workers to be:

Collector strength DTC > X > DTP

Selectivity DTP > X > DTC (Bhaskar and Forsling, 1991).

SIBX has the longest hydrophobic chain hence it is expected to form more insoluble and strongly hydrophobic species on the mineral surface which result in superior recoveries and faster rates of flotation. This may, in some cases have adverse effect since it can result in particle hydrophobicity that exceeds the optimum for a stable froth (Ata et al, 2002).

DTC is classified as a strong collector (Lotter and Bradshaw, 2010) and based on this, it was expected that DTC would yield the highest nickel recovery. However, DTC gave relatively poor recovery of nickel. The observed result suggests that the theoretical affinity for the mineral surface does not always translate to good collecting properties. Findings from microcalorimetry and flotation showed that the hydrophobic character of the collector is a more decisive parameter in the flotation properties of a collector than the affinity for the mineral surface (Maier et al, 1996). Thus, DTC may be a stronger adsorbent onto the mineral particle surface, but that does not necessarily mean that the hydrophobicity is optimum for flotation performance. As mentioned previously, froth stability is sensitive to the hydrophobicity of particles that are recovered in the froth. Highly hydrophobic particles may destabilise the froth resulting in relatively poor grades and recoveries (Wiese et al, 2011).

The paymetal grades and recoveries observed for SIBX/SEX were higher than those obtained for SEX but were similar to those obtained for SIBX. It is possible that more even coverage of the mineral surface may have been obtained for SIBX/SEX, however, these effects may have been mitigated by the destabilising effect that highly hydrophobic particles have on the froth phase. Even though DTP was expected to give low final recoveries since it is classified as a weak collector, it was not expected that the collecting properties would be almost non-existent. This also can be explained by titration microcalorimetry experiments carried out by McFadzean and O'Connor (2013) which showed that the enthalpy of reaction for DTP was comparatively low in the presence of a mineral and the pulp potential experiments in this study which show that there extent of electron transfer reaction between DTP and the mineral surface was small.

5.1.3 Copper recoveries for single collectors

As expected, Cu recovery for all the collectors was similar. This was expected since chalcopyrite is highly floatable. As with the Ni results, DTP had the slowest flotation rate, followed by DTC and the xanthates had the highest final recovery. A possible explanation is the presence of galvanic interactions. Because of their electrochemical nature, when two sulfide minerals are in contact with each other, there is transfer of electrons from a less cathodic mineral to a more cathodic one (Bozkurt et al, 1998), Pentlandite (NiFeS) is less cathodic than chalcopyrite ($CuFeS_2$) hence pentlandite loses electrons which results in the oxidation of the sulfide. This oxidation at the mineral surface hindered the natural floatability of the mineral hence nickel did not float as rapidly as copper in the absence of a collector. In addition, sulphur is known to have a unique ability for catenation (forming bonds with itself). It is possible that adsorption of thiol collectors on sulfide minerals involves some catenation with sulphur atoms on the mineral surface (Bhaskar *et al*, 1984). If this is taken into account, then it is possible that chalcopyrite forms more bonds with the thiol collectors since it has twice as many sulphur atoms as compared to pentlandite, hence it would form more hydrophobic aggregates which float faster.

5.2 The effect of collector mixtures on copper and nickel recoveries

5.2.1 Solids and water recoveries for DTP collector suites

Figure 4.8 shows that in general the collector mixtures gave slightly higher solids recovery than their constituents' i.e. DTP and SIBX/SEX. The difference in solids recovery among the collector suites was only marginal. Of note is the high water recovery for DTP without a concomitant increase in solids recovery. Since it has been shown that DTP is a poor collector, the bulk of the solids recovered were likely due to entrainment. It has already been shown in Figure 4.4 and 4.5 that valuable mineral recovery and grade is lower for DTP than other collectors.

Generally, the differences in the cumulative mass and water recovery obtained with all DTP mixtures were only marginal. However Figure 4.9 shows that there was a correlation between the proportion of DTP in a collector suite and the solids: water ratio. The relationship between the proportion of DTP in the mixture and water recovery is approximately linear. As the proportion of DTP increases in the collector suites, the solids to water ratio (density) decreases. The grade of a PGM ore can be predicted using the density of the concentrate (Somasundaran, 2006). As the density decreases, there is more water present, which translates into greater recovery by entrainment and a lower grade. Thus, it is expected that, with the addition of DTP, lower grades would be observed unless there was an increase in true flotation.

5.2.2 Nickel recoveries and grades for DTP collector suites

It can be seen in Figure 4.10 and 4.11 that all substitutions of SIBX/SEX for DTP, except the DTP: SIBX/SEX 90:10 ratio, improved the recovery and grade of nickel as compared to the single collectors. Addition of all proportions of DTP gave between 8 and 20% improvement in recovery. The best recovery was obtained for the DTP 30:70 collector suite, which increased nickel recovery by almost 20% more than the SIBX/SEX collector mixture and a 10-fold improvement from using DTP only. Different responses with respect to total nickel recoveries were obtained for the same number of moles for each collector suite and approximately the same amounts of solids. This shows that the improved nickel recoveries were largely due to differences in true flotation rather than by increased entrainment.

Figure 4.12 compares the nickel grades and recoveries for the different collector suites. The highest nickel recovery of 49.3 % was obtained using the DTP: SIBX/SEX 30:70 collector mixture and the highest final grades obtained were for the DTP: SIBX/SEX 70:30 collector mixture. When going from the DTP: SIBX/SEX 30: 70 to the DTP: SIBX/SEX 70:30 collector suite there is a 10% drop in recovery and 0.2% increase in grade. This shows that overall the DTP: SIBX/SEX 30: 70 is a better collector suite as the increase in grade is very marginal when compared to the decrease in recovery. This is an expected result since the first suite contains more SIBX/SEX which is a stronger collector and the second suite has a larger proportion of DTP which is a more selective collector hence there is an expected trade-off between grade and recovery as you vary the proportions of collector. Of further interest is the fact that addition of 30% DTP to SIBX/SEX increases recovery by a factor of 8 and grade by a factor of 6 over as compared to 100% SIBX/SEX. This may suggest that DTP, in the presence of SIBX/SEX (in the correct proportions) may have some surface activity which results in enhanced selectivity. The trends in Figure 4.12 show, the effect is not linearly additive which further supports the idea that the metallurgical response was not directly related to the collector mixture content which may infer some level of synergism.

5.2.3 Copper recovery and grades for DTP collector suites

There are small, but definite differences in the grades and recoveries of copper although the differences are not nearly as marked as for the nickel recovery. Comparing the performance of the best collector (DTP: SIBX/SEX 90:10) and the weakest collector mixture (DTP: SIBX/SEX 70:30) Figure 4.13 shows that the there is a 7.5% difference in recovery. A 7.5% difference in recovery is certainly not insubstantial since a plant may change reagents on the basis of a 1% increase in recovery (Doucet et al, 2009). Also of note is the slower flotation rate of the DTP: SIBX/SEX 70:30 collector suite as compared to all the other collector suites. This was the best performing collector suite for nickel recovery. This shows that DTP collector suites react differently with different mineral surfaces. It is possible that the contact angle induced by the DTP: SIBX/SEX 70:30 ratio on the nickel surface may be optimal for nickel flotation but that the contact angle formed on copper may not be ideal for the flotation of copper.

5.2.4 Water and solids recoveries for DTC collector suites

Generally the water recovered for the DTP collector suites was higher than those for the DTC collector suites (cf. Table 4.6 and Table 4.9). It is interesting to note that although pure DTP recovered roughly 25 % more water than pure DTC, the solids recovery were almost identical (83.93 g and 84.67 g) respectively. This reiterates that although there was some level of entrainment when DTP was used, selective recovery played a large role in the recovery of solid material.

5.2.5 Nickel grade and recoveries for DTC collector suites

Figure 4.17, which shows that all substitutions of SIBX/SEX for DTC, except the DTC: SIBX/SEX 90:10 ratio, improved the recovery of nickel. This improvement can be attributed to the difference in the mode of action for the constituent collectors. Xanthates adsorb onto the mineral surface through charge transfer between the collector and the mineral surface and may also dimerize to form highly hydrophobic dixanthogen molecules. On the other hand dithiocarbamates, which can also dimerize (Finkelstein and Poling, 1971), have faster adsorption kinetics than xanthates and form a more stable metal-thiolate complex. This would result in a more even coverage of the mineral surface rendering it more hydrophobic and ultimately more floatable (Bradshaw, 1997; Makanza et al, 2008). It is also postulated that dithiocarbamates may, through a mechanism which is not yet clearly understood, catalyse the formation of dixanthogen molecules and provide anchors by which the dixanthogen molecules attach to the mineral surface (Bradshaw et al, 1995). This would also render the mineral surface more hydrophobic.

The poor performance of the DTC 90:10 and pure DTC may be due to the nature of the species formed during flotation which may have been too hydrophobic to allow for a stable froth (Ata et al, 2003). There was also an observed 0.5% improvement in grade for collector mixtures from the use of DTC alone, but not much improvement was made from the SIBX/SEX collector suite. This is an expected result since it is well known in literature that xanthates are more selective than dithiocarbamates.

5.3 Comparison of the best performing DTP and DTC collector suites

Results from the previous sections have shown that not all proportions of collector mixtures result in improved recoveries and grades or higher flotation rates when compared to single collectors. This section compares and discusses the differences between the performance of the best performing single collector (SIBX) and the best collector suites for DTP and DTC, namely, DTP:SIBX/SEX 30: 70and DTC:SIBX/SEX 10:90. Similar collector ratios have been reported by previous workers (Hangone et al, 2005; McFadzean et al, 2012; Ngobeni et al, 2013) as giving superior metallurgical performances when compared to other collector ratios.

A plot of percentage nickel recovery as a function of time (Figure 4.24) shows that the DTP: SIBX/SEX 30:70 mixtures gave the highest rate of nickel recovery and the highest final recovery of 78.9%. This was accompanied by a relatively high water and solids recovery which may have resulted in a lower than expected final grade as shown in Figure 4. 25. The DTC: SIBX/SEX 10:90 mixture gave a final recovery which was less than half of the DTP: SIBX/SEX 30:70 mixture but gave a final grade which was almost 0.15% higher than that of the DTP collector mixture. This higher grade was probably because there was less water recovery for the DTC collector suite hence less gangue reported to concentrate by entrainment.

It is interesting to note that although pure DTP has the highest water recovery, the DTP: SIBX/SEX 30:70 mixtures gives the highest solids recovery and the highest nickel grade. The same is observed for the DTC:SIBX/SEX 10:90 mixture which has similar water recoveries as DTC but the collector mixture recovers more solids and gives a better grade. Pure SIBX collects almost the same amounts of water and solids as the DTC collector suite, however, it recovers 26% more nickel than the DTC mixture, but at a slower rate with lower final grades. The improved grades obtained from collector mixtures in spite of increased mass and water recovery indicates that mixed collectors may have better froth drainage characteristics as well as a higher ability to selectively float valuable minerals.

The difference in the final recovery of nickel for the collector mixture can be attributed to interplay of several effects which are a result of the different characteristics of DTP and DTC as well as the different ways in which they interact with SIBX/SEX and the mineral surface. As mentioned previously, DTC is highly hydrophobic and may form highly hydrophobic aggregates. This may result in particle hydrophobicity that exceeds the optimum for a stable froth and result in paymetal draining back into the pulp (Ata et al, 2003). In contrast, DTP has been shown to have frothing properties and since it is relatively less hydrophobic, the species formed on the mineral surface would also be moderately hydrophobic which may result in a more stable froth.

Glembotskii (1958) postulated that the larger the difference in structure and composition of mixed collectors, the larger the effect of synergy. The xanthates and DTC have relatively straight chains with a carbon disulfide (CS_2) in their functional groups. On the other hand DTP is bulkier and has a phosphorous disulfide (PS_2) in its functional group. Hence there is a larger difference in structure between DTP and xanthates as compared to DTC and xanthates. This also, may account for the observed differences in the metallurgical performance of DTP: SIBX/SEX 30:70 and DTC: SIBX/SEX 10:90.

It is also interesting to note how a small amount of co-collector added to the primary collector produced more enhanced effects. The same effect is observed despite the DTP co-collector being weaker and more selective and the DTC being stronger and less selective.

5.4 Investigating the mechanism by which the DTP: SIBX/SEX 30:70 collector suite enhances flotation performance.

The effect of collectors and their mixtures on the froth phase has already been shown in previous sections. This section discusses the factors in the pulp zone which could have enhanced flotation for the collector mixture with the best overall metallurgical performance i.e. DTP: SIBX/SEX 30:70.

5.4.1 Sequential addition of components of the DTP: SIBX/SEX 30:70 collector mixture.

Sequential addition tests were carried out to investigate the theory that the mineral surface is heterogeneous and may contain areas of different degrees of oxidation and metal/sulphur ratios (Plaskin and Zaitseva, 1960; Bradshaw and O'Connor, 1993). It is predicted that when a mixture of selective and non-selective collectors is used, each collector adsorbs on the most suitable site for its polar group.

The results in Figure 4.27 show that when SIBX/SEX, a stronger, less selective collector, is added first it may occupy both strong weak and strong sites. Although it is thought that very little DTP adsorbs on the mineral surface, these results seem to suggest that there is some adsorption and that, when SIBX/SEX is added first, it displaces even the small amount that was adsorbed on the strong sites. This in turn results in lower recovery and grade of nickel as shown in Figures 4.27 and 4.28. A second effect is that there is more DTP remaining in solution and therefore there is more frothing compared to when DTP is added first. The observed effect is high water recovery and solids recovery as shown in Figure 4.26, which can also account for lower grade observed when SIBX/SEX is added first. The opposite effect is expected when DTP is added first. After adsorption of the more selective collector i.e. DTP on the stronger, less oxidised active sites, the stronger less selective collector (SIBX/SEX), will attach to the residual weak, more oxidised sites. This means amount of collector adsorbed on the mineral surface increases resulting in more even coverage of the mineral surface making the mineral surface more hydrophobic and more readily floatable. This effect would result in a higher grade and recovery as shown Figure 4.27 and 4.28. However, it is important to note that the effects of sequential addition are not very pronounced as shown by the overlap of error bars in Figure 4.27. This may be due to the low concentration of the collectors as well as the time between additions of collectors.

5.4.2 DTP: SIBX/SEX 30:70 collector mixture: particle size distribution of the concentrate

The ultrafine and coarse particles were not well represented in C1 and this is expected since very fine particles show poor flotation kinetics due to their poor collision efficiency and coarser particles float slowly due to detachment forces (Pearse et al, 2006). The majority of particles recovered are within the fine to medium size range and two peaks appear at around 15 and 50 µm. The particle size distribution does not vary significantly in the first concentrate for different collector systems. This is probably due to the fact that intermediate, fast floating particles are collected during the first two minutes hence the size of particles recovered is independent of the collector type.

After 6 minutes of flotation, peaks begin to emerge in the coarse particle range for SIBX, SEX, and the DTP: SIBX/SEX 30:70 collector suite. These peaks appear at about 120 µm and the SIBX and DTP collector mixture peaks are larger than those for SEX and DTP alone, showing a greater efficiency in collecting coarse particles. The same pattern is shown in C3; however it is interesting to note how the peak for the DTP collector mixture shifts to the right from about 120 to 150 µm. This shows that in this instance the collector mixture was collecting, on average, coarser particles than SIBX and the other collectors. When going from C3 to C4, there is an increase in the proportion of coarse particles, as shown by the last peak, from about 8% to11%. This is evident for all collectors except DTP, suggesting that the coarser fractions benefited more from the presence of xanthates than the fine particles.

6 Conclusions

It has been shown in this study that all collectors have froth modifying properties. DTP had the highest water recoveries for both the two phase tests and the standard batch flotation tests. It has also been observed that DTP has almost no activity on the mineral surface. This was illustrated by the fact that relatively few electron transfer reactions occurred when DTP was added to the pulp as shown by the Eh profile. It has also been seen that collectors that are theoretically expected to have strong bonding properties with metals do not always give the best recoveries in the flotation cell. This observation is mainly true for DTC which has a positively inductive functional group and, by inference, a strong thiol-metal bond. The xanthates were more efficient than both DTC and DTP since they gave higher cumulative grades and recoveries.

The flotation experiments have shown that mixed collectors offer some important advantages over single collectors in Nkomati sulfide ore beneficiation. It has been shown that not all collector constituents are compatible for formulation of mixed collectors. However, when collectors that are compatible are mixed at their optimum ratio, they yield higher valuable mineral recoveries than their individual constituents. Generally it was shown that the addition of a small ratio of co-collector to the main collector was beneficial. This was best illustrated by the DTP: SIBX/SEX 30:70 and the DTC: SIBX/SEX 10:90 mixtures, which improved nickel recovery and grade. Furthermore, there were no significant differences in cumulative mass and water recoveries for different collector suites and therefore, the differences in nickel recovery can mainly be attributed to the difference in selectivity of the collectors.

With respect to the mechanism by which the DTP: SIBX/SEX 30:70 mixtures enhance recovery, no solid conclusions can be drawn from the sequential addition experiments since there was an overlap in error bars. However, investigations in the particle size recoveries showed that the collector suite was more efficient in recovering coarse particles.

6.1 Recommendations for future work.

Recommendations for future test work, based on the findings from this study are listed as follows;

1) Microflotation test work must be carried out with the pure collectors and collector mixtures in order to decouple froth phase effects and pulp phase effects.
2) Microcalorimetry tests should be done to try and ascertain the mechanism by which both single and mixed collectors interact with the mineral surface as well as the interaction between collectors.
3) Mineralogical assays must be carried out on the feed and concentrate samples in order to determine mineralogical association between collector type and recovery.
4) Further batch flotation test work should be carried out at increased dosages in order to determine if the effects observed at lower concentration can also be observed at higher concentrations, or if the benefits of collector mixtures are overridden at higher dosages.

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8 Appendices

Appendix A: Summary of batch Flotation tests

SIBX/SEX collector dosage optimisation

Reagents	Sample	Time,	Ave cum	Ave cum water	Cu	Ave	Ave	Ni	Ni	Ni	Ave	Ave	Sulphur	S	S	Average
		min	Mass, g	Rec, g	%	Cu grade	Cu rec	%	Grade	Rec	Ni grade	Nil rec	%	Grade	Recovery	S grade
SIBX/SEX						%	%		%	%	%	%		%	%	%
No collector		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	C1	2	37.22	94.85	0.75	0.71	7.11	0.55	0.38	2.87	0.39	2.92	1.01	1.01	1.74	0.94
	C2	6	55.67	148.31	0.98	0.66	9.84	0.51	0.40	4.53	0.41	4.52	1.57	1.20	3.12	1.10
	C3	12	64.70	188.75	0.88	0.67	11.58	0.43	0.42	5.51	0.43	5.53	1.53	1.25	3.80	1.16
	C4	20	70.33	199.09	0.67	0.67	12.60	0.38	0.43	6.17	0.44	6.13	1.40	1.26	4.18	1.18
	F				0.17			0.52					2.41			
	T															
	T2				0.64			0.52					2.35			
	T3				0.10			0.55					2.42			
	C1				0.68			0.61	0.40	2.97			0.88	0.88	1.35	
	C2				0.10			0.60	0.41	4.51			1.24	0.99	2.25	
	C3				0.54			0.52	0.44	5.54			1.57	1.07	2.80	
	C4				0.69			0.43	0.44	6.10			1.46	1.10	3.13	
	F				0.20			0.40					1.96			

	T2				0.67			0.52					2.78			
	T3				0.09			0.55					2.58			
30g/tonne																
		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	C1	2	44.90	102.58	2.16	2.08	42.28	1.80	0.87	7.03	0.92	6.72	6.89	6.89	11.90	6.48
	C2	6	65.17	155.56	0.33	1.53	45.18	1.34	0.79	9.22	0.78	11.00	5.39	6.43	16.07	5.85
	C3	12	76.19	192.89	0.13	1.33	46.01	0.87	0.93	12.67	0.69	12.09	4.97	6.22	18.11	5.80
	C4	20	83.20	199.50	0.23	1.24	46.85	0.60	0.97	14.44	0.55	13.58	3.63	5.99	19.13	5.65
	F				0.19			0.53					2.45			
	T															
	T2				0.09			0.53					2.35			
	T3				0.19			0.55					2.42			
	C1				2.00			2.00	0.97	6.41			6.06	6.06	10.52	
	C2				0.30			1.24	0.85	8.17			5.94	5.28	13.35	
	C3				0.20			0.97	1.02	11.50			4.39	5.38	15.95	
	C4				0.30			0.58	1.04	12.73			3.57	5.30	17.10	
	F				0.21			0.59					2.45			
	T															
	T2				0.12			0.53					2.35			
	T3				0.13			0.79					2.42			
50g/tonne	C1	2	46.38	157.78	2.24	2.27	69.52	3.10	0.08	1.28	1.66	18.82	8.64	8.64	14.48	8.60
	C2	6	79.52	241.26	0.27	1.44	75.79	0.08	1.24	30.54	1.57	30.00	8.32	8.52	23.13	8.41
	C3	12	113.00	347.25	0.23	1.08	80.59	0.30	0.96	33.68	1.16	36.54	7.80	8.30	32.19	8.21
	C4	20	149.38	409.10	0.16	0.85	84.36	0.04	0.76	34.11	0.88	37.16	6.07	7.82	38.71	7.71
	F				0.20			0.57					2.27			
	T															
	T2				0.02			0.23					1.53			

	T3				0.02			0.24					2.42			
					0.02			0.23					1.53			
					0.02			0.24					2.42			
	C1				2.30			3.23	3.23	36.36			8.56	8.56	11.46	
	C2				0.30			0.08	1.90	39.14			8.00	8.30	20.30	
	C3				0.20			0.30	1.35	39.39			7.68	8.12	28.08	
	C4				0.16			0.03	1.01	40.21			6.23	7.61	36.04	
	F				0.28			0.70					2.27			
	T															
	T2				0.02			0.20					1.53			
	T3				0.02			0.24					2.42			
70g/tonne																
		0	0	0	0	0	0	0	0	0	0	0				
	C1	2	40.26	110.61	2.37	2.35	68.15	2.36	2.36	23.55	2.41	30.91	9.82	9.82	13.23	9.82
	C2	6	82.80	159.62	0.36	1.30	78.48	0.50	1.21	31.73	1.41	37.31	8.10	8.75	31.04	8.93
	C3	12	106.88	283.37	0.28	1.07	83.48	0.49	1.06	35.20	1.19	40.81	7.19	8.42	37.91	8.54
	C4	20	122.08	319.21	0.17	0.96	85.27	0.28	0.95	36.60	1.12	43.82	7.82	8.34	43.17	8.45
	F				0.18			0.54					2.26			
	T															
	T2				0.03			0.20					1.30			
	T3				0.02			0.19					1.30			
	C1				2.34			2.45	2.45	38.27			9.82	9.82	23.12	
	C2				0.26			0.42	1.62	42.89			8.10	9.11	36.47	
	C3				0.28			0.43	1.33	46.41			7.19	8.66	45.43	
	C4				0.15			0.98	1.29	51.04			7.82	8.56	51.00	
	F				0.18			0.34					2.26			

	T															
	T2				0.02			0.20					1.30			
	T3				0.02			0.19					1.30			
1100g/tonne																
		0	0	0	0	0	0	0	0	0	0	0				
	C1	2	51.51	133.99	2.15	2.16	72.13	1.47	1.47	25.93	1.50	26.57	10.10	10.10	23.72	9.89
	C2	6	84.17	224.20	0.34	1.46	79.82	0.79	1.22	34.28	1.20	34.70	8.97	9.68	36.35	9.34
	C3	12	109.30	340.96	0.23	1.18	83.56	0.54	1.05	39.06	1.04	39.14	7.68	9.20	45.40	8.95
	C4	20	129.01	404.67	0.13	1.02	85.18	0.41	0.96	41.54	0.95	41.88	6.68	8.85	50.79	8.61
	F				0.17			0.54					2.34			
	T															
	T2				0.02			0.19					1.17			
	T3				0.03			0.18					1.20			
	C1				2.17			1.53	1.53	27.20			9.68	9.68	22.58	
	C2				0.39			0.67	1.19	35.11			8.01	9.01	35.10	
	C3				0.23			0.49	1.03	39.23			7.57	8.69	43.46	
	C4				0.13			0.40	0.93	42.22			6.81	8.38	50.18	
	F				0.17			0.40					2.34			
	T															
	T2				0.02			0.20					1.17			
	T3				0.03			0.16					1.20			

Mixed Collector suites

Run no.	Reagents	Sample	Time,	Ave cum	Ave cum w	Cu	Ave	Ave	Ni	Ave	Ave	Su	Average	Average
	DTP:SIBX/SEX		min	Mass, g	Rec, g	%	Cu grade	Copper rec	%	Ni grade	Ni rec	%	S grade	S recovery
							%	%		%	%		%	%
1	DTP only													
		C1	2	44.32	153.59	0.90	1.08	35.52	0.22	0.30	2.61	2.39	1.79	2.60
		C2	6	65.25	218.56	1.24	1.08	58.17	0.33	0.29	4.16	2.56	1.78	4.14
		C3	12	77.25	270.46	1.16	1.04	71.19	0.35	0.28	5.19	2.94	1.75	5.21
		C4	20	84.67	294.20	0.92	0.90	77.65	0.37	0.26	5.86	3.12	1.63	5.92
		F				0.12			0.46			3.66		
		T												
		T2				0.02			0.52			3.71		
		T3				0.02			0.52			3.73		
		C1				0.98			0.29			1.70		
		C2				1.29			0.32			2.62		
		C3				1.40			0.40			3.31		
		C4				1.14			0.42			3.72		
		F				0.14			0.41			2.77		
		T												
		T2				0.04			0.40			3.62		
		T3				0.04			0.42			3.77		
	DTP:SIBX/SEX 10:90													
1		C1	2	50.06	108.54	1.69	1.67	70.29	1.00	1.73	13.38	4.83	5.20	10.78
		C2	6	73.27	174.87	0.43	1.28	79.30	1.88	1.54	23.65	5.93	4.80	17.16
		C3	12	88.06	217.74	0.25	1.09	81.02	2.54	1.35	32.38	5.79	4.26	21.00

		C4	20	100.15	256.50	0.30	1.02	86.08	3.03	1.13	41.45	6.16	4.20	24.29
		F				0.16			0.47			2.21		
		T												
		T2				0.02			0.28			2.27		
		T3				0.02			0.28			2.01		
2		C1				1.64			1.25			4.84		
		C2				0.49			1.81			6.42		
		C3				0.03			2.39			5.85		
		C4				0.70			3.24			6.07		
		F				0.15			0.46			2.30		
		T												
		T2				0.02			0.32			1.92		
		T3				0.02			0.31			2.05		
	DTP: SIBX/SEX 30;70													
		C1	2	55.71	120.60	1.89	1.99	69.14	1.35	1.84	17.45	5.72	6.04	14.98
		C2	6	81.46	187.12	0.43	1.50	76.10	2.24	1.82	33.00	6.35	5.89	22.48
		C3	12	97.39	231.32	0.23	1.35	79.00	2.62	1.59	44.66	4.88	5.89	26.26
		C4	20	105.58	284.56	1.82	1.30	88.62	2.62	1.10	49.82	5.34	5.85	28.29
		F				0.15			0.46			2.28		
		T												
		T2				0.02			0.20			1.92		
		T3				0.02			0.22			1.58		
2		C1				2.09			1.25			6.05		
		C2				0.43			2.82			6.35		
		C3				0.37			3.56			5.46		
		C4				1.94			2.60			5.50		

		F				0.14			0.46			2.45		
		T												
		T2				0.02			0.25			1.79		
		T3				0.02			0.25			1.60		
	DTP: SIBX/SEX 50:50													
1		C1	2	52.17	131.74	1.94	1.84	71.67	1.06	1.49	13.78	5.27	5.15	11.72
		C2	6	77.52	209.84	0.48	1.39	80.67	1.83	1.40	24.92	5.29	5.09	17.23
		C3	12	92.20	255.71	0.28	1.22	83.96	2.08	1.28	32.54	3.91	4.91	19.60
		C4	20	102.02	291.87	0.24	1.13	85.85	2.17	1.05	38.22	5.31	4.87	21.86
		F				0.15			0.41			2.31		
		T												
		T2				0.02			0.26			1.97		
		T3				0.02			0.23			1.90		
2		C1				1.74			1.04			5.02		
		C2				0.47			1.65			4.67		
		C3				0.32			2.04			3.48		
		C4				0.27			2.42			5.22		
		F				0.16			0.41			2.51		
		T												
		T2				0.02			0.22			1.68		
		T3				0.02			0.33			2.02		
	DTP 70:30													
1		C1	2	49.65	130.36	1.88	1.88	70.09	1.28	2.11	12.95	4.16	5.15	11.53
		C2	6	72.65	200.63	0.58	1.46	79.86	2.49	1.88	24.10	5.91	5.01	18.45
		C3	12	87.67	258.35	0.37	1.28	84.13	2.36	1.62	32.10	5.56	4.89	22.82
		C4	20	99.21	307.28	0.27	1.17	86.83	2.47	1.28	39.01	5.47	4.49	26.55
		F				0.37			0.53			2.11		

		T												
		T2							0.30			1.64		
		T3				0.02			0.30			1.46		
2		C1				1.88			1.27			4.82		
		C2				0.55			2.22			5.62		
		C3				0.39			2.94			5.51		
		C4				0.38			3.69			7.38		
		F				0.19			0.51			2.48		
		T												
		T2				0.03			0.42			1.75		
		T3				0.03			0.37			1.67		
	DTP 90:10													
1		C1	2	49.83	129.82	2.05	2.03	72.64	1.02	1.18	10.08	4.16	3.78	8.40
		C2	6	71.22	199.80	0.53	1.59	81.17	1.70	1.17	16.30	2.48	3.39	10.75
		C3	12	83.23	242.03	0.40	1.42	84.63	1.46	1.13	19.71	2.77	3.28	12.17
		C4	20	90.92	264.38	0.27	1.32	86.38	1.25	1.00	21.76	2.62	3.20	12.99
		F				0.18			0.52			2.18		
		T												
		T2				0.03			0.46			2.11		
		T3				0.03			0.43			2.23		
2		C1				2.01			0.98			3.40		
		C2				0.58			1.17			2.46		
		C3				0.40			1.35			2.56		
		C4				0.36			1.38			2.12		
		F				0.18			0.54			2.60		
		T												
		T2				0.03			0.46			2.46		
		T3				0.00			0.46			2.38		

	SIBX/SEX first	C1	2	45.32	105.76	1.84	1.87	58.43	1.35	1.47	17.84			
1		C2	6	64.28	155.28	0.53	1.48	65.84	2.24	1.38	32.26			
		C3	12	75.03	187.38	0.35	1.32	68.69	2.62	1.26	42.15			
		C4	20	82.44	216.51	0.33	1.24	70.38	2.62	0.98	45.82			
		F				0.15			0.46					
		T												
		T2				0.05			0.18					
		T3				0.05			0.21					
2		C1				1.89			1.25					
		C2				0.60			2.82					
		C3				0.42			3.56					
		C4				0.33			0.38					
		F				0.15			0.46					
		T												
		T2				0.05			0.20					
		T3				0.05			0.25					
	DTP first													
1		C1	2	47.41	118.17	1.91	1.98	59.08	1.24	1.76	20.28			
		C2	6	67.88	175.36	0.68	1.56	66.93	2.29	1.71	36.43			
		C3	12	79.40	202.79	0.53	1.41	70.72	2.52	1.57	46.45			
		C4	20	85.05	221.40	0.44	1.35	72.29	2.52	1.25	51.28			
		F				0.15			0.99					
		T												
		T2				0.05			0.15					
		T3				0.05			0.19					
2		C1				2.04			1.26			0.00		
		C2				0.53			2.32			0.00		
		C3				0.50			2.56			0.00		

		C4				0.44			2.48			0.00		
		F				0.15			0.86			0.00		
		T												
		T2				0.05			0.17			0.00		
		T3				0.05			0.14			0.00		
1	**DTC only**													
		C1	2	45.97	115.68	1.65	1.64	58.62	0.60	0.70	6.25	4.99	4.58	7.89
		C2	6	66.42	176.25	0.70	1.36	70.51	0.85	0.70	10.12	4.08	4.44	11.02
		C3	12	78.52	208.50	0.47	1.23	75.27	1.13	0.63	13.32	4.28	4.41	12.96
		C4	20	83.93	218.42	0.42	1.18	77.00	0.67	0.57	14.11	1.65	4.23	13.29
		F				0.14			0.40			2.55		
		T												
		T2				0.03			0.37			2.33		
		T3				0.04			0.41			2.33		
2		C1				1.62			0.53			4.17		
		C2				0.79			0.72			4.16		
		C3				0.54			1.06			4.27		
		C4				0.40			0.54			1.70		
		F				0.17			0.40			2.65		
		T												
		T2				0.03			0.40			2.77		
		T3				0.03			0.39			2.90		
	DTC:SIBX/SEX 10:90													
1		C1	2	50.94	116.77	1.69	1.97	75.75	1.22	1.56	17.21	5.87	6.38	15.07
		C2	6	72.52	176.36	0.50	1.52	83.58	1.55	1.46	26.17	3.09	5.76	19.36
		C3	12	81.72	204.84	0.29	1.38	85.52	1.92	1.40	30.57	5.85	5.73	21.73
		C4	20	89.33	218.88	0.24	1.29	87.00	2.67	1.32	35.82	7.00	5.85	24.26

		F				0.15			0.43			2.50		
		T												
		T2				0.02			0.28			2.00		
		T3				0.02			0.28			1.85		
2		C1				2.25			1.41			6.89		
		C2				0.44			1.68			5.52		
		C3				0.27			1.83			5.33		
		C4				0.27			2.67			7.34		
		F				0.16			0.42			2.26		
		T												
		T2				0.02			0.31			1.84		
		T3				0.02			0.31			2.02		
	DTC:SIBX/SEX 30:70													
1		C1	2	47.72	115.65	1.83	1.91	66.42	1.02	1.49	12.33	6.36	5.99	12.23
		C2	6	73.22	181.61	0.58	1.44	77.24	1.85	1.42	24.37	4.01	5.34	16.73
		C3	12	85.38	213.73	0.45	1.30	81.16	1.92	1.31	30.62	5.26	5.33	19.48
		C4	20	92.37	224.41	0.40	1.23	83.20	2.41	1.02	34.85	5.19	5.30	20.97
		F				0.19			0.41			2.53		
		T												
		T2				0.03			0.28			2.05		
		T3				0.02			0.28			1.97		
		C1				1.98			1.02			5.61		
		C2				0.58			1.88			4.25		
		C3				0.43			2.14			5.30		
		C4				0.40			2.36			4.76		
		F				0.18			0.42			2.80		
		T												

		T2				0.03			0.28			2.05		
		T3				0.02			0.28			1.97		
	DTC:SIB/SEX 50:50													
1		C1	2	48.58	120.79	1.90	1.90	62.72	1.06	1.91	9.33	5.58	5.39	12.55
		C2	6	73.56	183.78	0.74	1.51	75.44	2.78	1.78	21.90	5.20	5.18	18.27
		C3	12	85.93	213.01	0.51	1.37	79.86	3.03	1.57	29.10	4.78	5.23	21.55
		C4	20	92.80	225.35	0.40	1.30	81.75	3.52	1.01	33.65	4.91	5.22	23.23
		F				0.20			0.59			2.67		
		T												
		T2				0.03			0.38			1.87		
		T3				0.03			0.38			1.78		
2		C1				1.90			0.96			5.19		
		C2				0.76			2.51			4.36		
		C3				0.54			3.09			6.14		
		C4				0.41			3.45			5.29		
		F				0.18			0.53			2.60		
		T												
		T2				0.03			0.41			1.89		
		T3				0.03			0.39			1.61		
	DTC:SIBX/SEX 70:30													
1		C1	2	47.62	116.59	2.00	1.92	62.80	1.02	1.50	12.83	4.66	4.61	10.87
		C2	6	71.82	183.34	0.79	1.52	74.94	1.85	1.43	24.75	1.69	4.61	16.41
		C3	12	86.59	218.83	0.62	1.36	80.88	1.92	1.30	32.68	7.29	5.04	21.63
		C4	20	93.57	243.91	0.19	1.28	82.40	2.41	1.02	37.07	2.36	4.94	22.95
		F				0.45			0.41			5.12		
		T												
		T2				0.03			0.28			1.95		

		T3				0.03			0.28			1.83		
2		C1				1.83			1.02			4.56		
		C2				0.67			1.88			7.46		
		C3				0.55			2.14			7.00		
		C4				0.41			2.36			5.01		
		F				0.18			0.42			2.49		
		T												
		T2				0.03			0.28			1.72		
		T3				0.03			0.28			1.81		
	DTC:SIBX/SEX 90:10													
			0	0	0	0	0	0	0	0	0	0	0	0
1		C1	2	46.81	134.26	1.94	1.88	59.57	0.87	1.53	8.40	5.20	4.87	10.84
		C2	6	68.33	188.48	0.77	1.52	70.38	1.19	1.32	13.68	5.72	5.02	16.34
		C3	12	82.62	218.28	0.67	1.37	76.73	3.20	0.96	22.71	5.87	5.19	20.46
		C4	20	90.56	229.73	0.51	1.29	79.40	3.74	0.86	28.87	4.65	5.16	22.34
		F				0.21			0.52			2.81		
		T												
		T2				0.04			0.35			2.01		
		T3				0.04			0.35			2.24		
2		C1				1.82			0.85			4.53		
		C2				0.71			1.19			4.97		
		C3				0.64			2.87			6.11		
		C4				0.48			3.73			5.15		
		F				0.19			0.56			3.06		
		T												
		T2				0.03			0.46			1.97		
		T3				0.03			0.42			1.27		

Appendix B: Analysis of Float Data

Experimentally determine the mass of the Concentrates (Conc), Feed (F) and Tails (T) as well as the mass of the recovered water.

Copper:
% given by analysis
Cu Mass = % x Mass of Conc
Cu Grade = (Cum mass of Cu) / (Cum mass of Conc)
Cu Recovery = [(Cum mass of Cu) / (Mass of Cu in Conc + Tails)] x 100
Mass of Cu in Conc + Tails = [(Cum Mass of Cu) + (%T2 + %T3) / 2] x (T1 + T2 + T3)

Nickel:
% given by analysis
Ni Mass = % x Mass of Conc
Ni Grade = (Cum mass of Ni) / (Cum mass of Conc)
Ni Recovery = [(Cum mass of Ni) / (Mass of Ni in Conc + Tails)] x 100
Mass of Ni in Conc + Tails = [(Cum Mass of Ni) + (%T2 + %T3) / 2] x (T1 + T2 + T3)

Sulphur:
% given by analysis
S Mass = % x Mass of Conc
S Grade = (Cum mass of S) / (Cum mass of Conc)
S Recovery = [(Cum mass of S) / (Mass of S in Conc + Tails)] x 100
Mass of S in Conc + Tails = [(Cum Mass of S) + (%T2 + %T3) / 2] x (T1 + T2 + T3)

Plots:
Cum mass of Conc vs. Cum mass of Water recovered
Grade vs. Recovery
Recovery vs. Cum mass of Water recovered

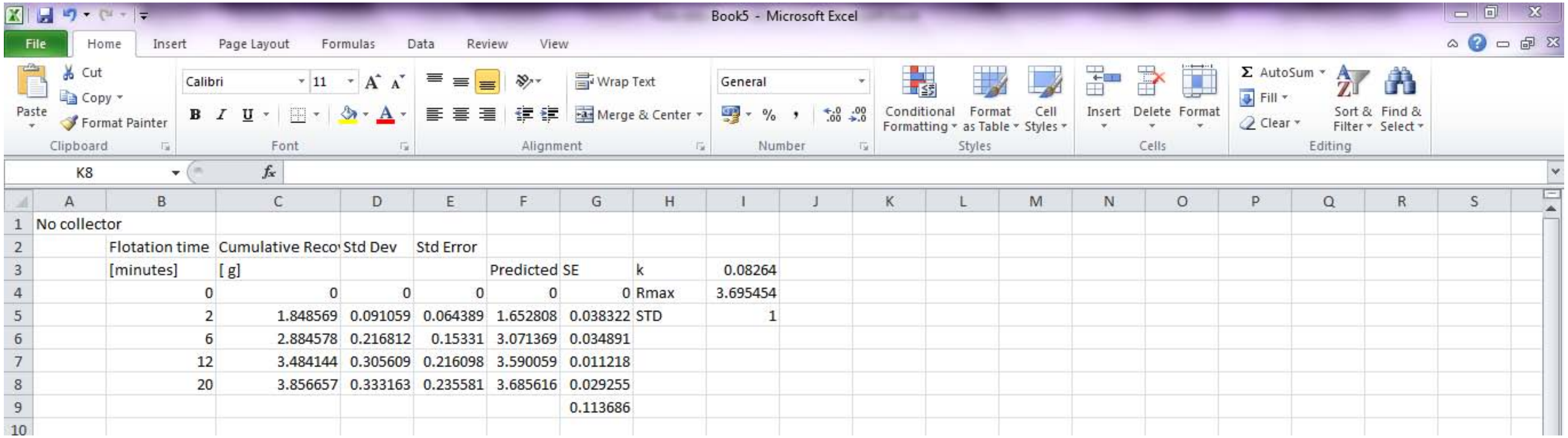
Appendix C: Determination of the parameters of the flotation rate equation

The flotation first order rate constant (*k*) and the infinite time recovery (*Rmax*) were calculated using Klimpel's equation (Klimpel, 1984) and Excel's solver function. The Klimpel equation is given as:

$R = Rmax[1- 1/(kt)\{1 - exp\text{-}kt\}]$

where *Rmax* is the recovery achieved at infinite flotation time and *k* is the first order rate constant. The procedure followed is explained below.

Figure A1: An example of recovery modelling using the Klimpel model and Excel's solver function



	A	B	C	D	E	F	G	H	I
1	No collector								
2		Flotation time	Cumulative Reco	Std Dev	Std Error				
3		[minutes]	[g]			Predicted	SE	k	0.08264
4		0	0	0	0	0	0	Rmax	3.695454
5		2	1.848569	0.091059	0.064389	1.652808	0.038322	STD	1
6		6	2.884578	0.216812	0.15331	3.071369	0.034891		
7		12	3.484144	0.305609	0.216098	3.590059	0.011218		
8		20	3.856657	0.333163	0.235581	3.685616	0.029255		
9							0.113686		
10									

The procedure was as follows:

1. Enter the values for cumulative time and cumulative recovery in columns A and B respectively.
2. Enter the Klimpel equation labels *Rmax* and *k* in cells I3and I4 respectively.
3. Rename Cell I4 to Rmax, i.e. position cursor in cell I4 and click the tab “Formulas”; click the tab “Define Name” and rename Cell B9 to Rmax
4. Similarly, rename cell I3 to “k”.
5. Guess initial values of *Rmax* and *k*.
6. Enter the Klimpel recovery equation in column C using the guessed values of *Rmax* and *k*.
7. In column D, calculate the difference between the actual recovery and the calculated recovery and square the difference.
8. Sum the square of the differences between the actual recovery and the calculated recovery in cell G9. The ultimate aim of this exercise is to minimise the value in cell G9.
9. Rename cell D9 as “SS”.
10. Activate the Solver function in Excel
11. In the “Set Target Cell” box, enter SS or choose cell G9 (this is the cell that needs to be minimised).
12. Select the “Min” option box where it says “Equal To”
13. Select cells I3 and I4 in the “By Changing Cells” box; alternatively type Rmax, k in the box “By Changing Cells”.
14. Select the “Solve” button

The optimisation program in Excel will now change the values *Rmax* and *k* until the minimum value of SS is obtained.