



**FROTH FLOTATION OF A MERENSKY PLATINUM BEARING ORE WITH VARIOUS
THIOL COLLECTORS AND THEIR MIXTURES**

by

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PUBLICATIONS AND PRESENTATIONS

Kloppers, L., Maree, W., Hangone, G. and Oyekola, O. 2015. Froth flotation of a Merensky Reef platinum bearing ore using mixtures of SIBX with a dithiophosphate and a dithiocarbamate. Presented at *Minerals Engineering Conference Precious Metals '15*, Falmouth.

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DECLARATION

I, Lourens Marthinus Kloppers, hereby declare that I have developed and written the enclosed thesis by myself and have not used any sources or means without any appropriate referencing. Any thoughts and quotation that were inferred from such sources have been clearly acknowledged. This thesis was not submitted in the same or in a substantially same version, not even partially to any other academic institution to achieve academic grading. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

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ABSTRACT

The Bushveld igneous complex in northern South Africa has the largest deposit of platinum group elements (PGE) in the world. In trace amounts, these are closely associated with base metal sulphides (BMS). Froth flotation is used to beneficiate these PGE ores. The process constitutes a bulk sulphide recovery. Improvement of recovery of the BMS is required to maximise the recovery of PGEs. The performance of the froth flotation process is largely dependent on the chemical additives used and these chemicals have been extensively studied. Mixtures of collectors are widely used in the flotation of sulphide and platinum group mineral (PGM) ores. A range of performance benefits for the use of mixtures over pure collectors have been observed on many systems. These include improved valuable metal grades and recoveries, lower reagent dosage requirements, improved rates of flotation and enhanced recovery of coarse particles. Improvements observed with mixtures of chemical reagent have been attributed to synergism; defined as the interaction of two or more agents to produce a combined effect greater than the sum of their individual effects. Synergism is highly desired in froth flotation.

For this study, mixtures of thiol collectors were used in batch froth flotation tests in an attempt to identify synergism between the different collectors on flotation performance of a typical platinum ore from the Merensky reef. Flotation performance was evaluated in terms of grades and recoveries of copper and nickel, and the rate of metal flotation. Single thiol collectors of xanthate (SIBX), a dithiocarbamate (DTC) and a dithiophosphate (DTP) were evaluated to determine the effect of functional group on flotation performance. SIBX was then used in mixtures with both DTC and DTP at various molar ratios to establish whether synergism occurs between these collectors on this particular platinum ore. Molar ratios of 90:10, 80:20, 70:30 60:40 and 50:50 were considered with SIBX being the major component. Further tests were conducted with the addition of a carboxymethyl cellulose depressant to the collector mixtures.

With the use of all DTP mixtures, an overall increase in metal recovery and flotation rate of 4 – 11% and 15 – 40% respectively over that of pure SIBX was observed however the grade decreased by 15 – 48%. This was attributed to the frothing properties associated with DTP and no synergism was observed. The frothing properties observed were proportional to the concentration of DTP in its mixture with SIBX. Mixtures of SIBX with DTC improved metal recoveries by 5 – 8% with a decrease of 5 – 10% in grades. Here, synergism was unlikely due to increased froth stability.

Although synergism was not observed, the addition of either DTC or DTP to SIBX in the mixtures resulted in improved nickel recoveries over pure SIBX. The rates of flotation for both copper and nickel were improved with the use of the collector mixtures.

The use of a depressant suppressed the flotation of talc and decreased froth stability. This resulted in improved grades over the tests without added depressant. An overall decrease in recoveries was observed with the addition of depressants. No synergism was observed for mixtures of thiol collectors when depressant was added.

Coarser particle flotation was favoured during the first concentrates for all tests. The finer particles reported more notably to the concentrate in the remaining three concentrates. The addition of DTC or DTP to SIBX resulted in more coarse particles reporting to the concentrates.

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GLOSSARY OF TERMS

- **Ore** is the mined rock body that contains minerals with significant economic value.
- **Grade** is the mass percentage of a particular pay-metal in an ore body.
- **Recovery** is the mass percentage of a particular material that reports to the concentrates.
- **Concentrate** is the high grade portion of desired minerals from the ore collected from the beneficiation process.
- **Tailings** the undesired portion of the ore after beneficiation that contains the gangue.
- **Gangue** is the undesired minerals that constitutes the majority of an ore.
- **Collectors** are chemical reagents added to flotation systems to impart hydrophobicity on the surfaces of desired minerals.
- **Hydrophobic** is a property of mineral surfaces where they have little affinity towards water. A hydrophobic surface would not easily be wetted.
- **Pulp** or slurry, is the homogeneous mixture of a crushed ore and water.
- **Froth** is a collection of small water bubbles containing mineral particles above the pulp.

LIST OF ABBREVIATIONS

| | |
|------------------|--|
| C1 | First concentrate, collected from 0 th to 2 nd minute |
| C2 | Second concentrate, collected from 2 nd to 6 th minute |
| C3 | Third concentrate, collected from 6 th to 12 th minute |
| C4 | Fourth concentrate, collected from 12 th to 20 th minute |
| k | Flotation rate constant |
| XRF | X-ray fluorescent spectrometry |
| R | Percentage recovery |
| R _{max} | Infinite time recovery |
| rpm | Revolutions per minute |
| SIBX | Sodium Isobutyl Xanthate |
| DTC | Sodium di-ethyl Dithiocarbamate |
| DTP | Sodium di-ethyl Dithiophosphate |
| CMC | Carboxymethyl Cellulose |
| BMS | Base metal sulphides |
| PGE | Platinum group elements |
| PGM | Platinum group minerals |
| BIC | Bushveld Igneous Complex |
| PSD | Particle Size Distribution |

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CHAPTER 1

1. Introduction

1.1 Background

South Africa has the largest deposits of platinum group elements (PGE) in the world. These deposits are located in the Bushveld igneous complex (BIC) in the north of the country and have been commercially mined since 1925 (Matthey, 2014). Statistics indicate that South Africa produced 133 000 kg platinum in 2012 which accounted for 73% of the world's production and largely contributed to the country's commodity based economy (Loferski, 2012). The Merensky reef, together with the Upper Group 2 (UG2) chromitite and the Platreef make up the deposits within the BIC that are commercially mined (Vermaak, 2005).

Froth flotation is the primary process used to beneficiate valuable PGE bearing minerals from the host rock. The flotation process relies on the differences in mineral surface properties. Conventional separation occurs when the valuable minerals are rendered hydrophobic and report to the concentrate while the gangue which makes up the bulk remain hydrophilic. The PGE deposits of the Merensky Reef are sulphide dominant deposits due to their strong association with base metal sulphide (BMS) minerals present in the reef. Effective recovery of the sulphide minerals is vital for PGE recovery.

Chemical reagents are essential for effective flotation and consists of collectors, frothers and modifiers (Wills and Napier-Munn, 2006). Collectors selectively render the surfaces of particular desired minerals hydrophobic and has been the subject of various studies. Urbina (2003) stated that there may be numerous collectors available for the flotation of particular minerals, but that the discovery of new collectors is unlikely due to patent laws and ownership. It is suggested that the flotation performance can be improved by mixing different collectors at various ratios and dosages to facilitate synergism. The quest for synergism has led to various studies of collector mixtures on particular ore deposits. These have resulted in conclusions of lower collector dosage requirements, improved pay-metal recovery, concentrate grade and rate of flotation, and the preferential flotation of different particle sizes (Bradshaw et al., 1998).

Current Merensky reef operations make use of two thiol collectors; xanthate, in particular sodium isobutyl xanthate (SIBX), as primary collector and dithiophosphate (DTP) as co-collector. Other reagents employed in these operations include frothers, depressants and activators; collectively known as a reagent suite. The ratios and dosages of these reagent suites depends on the operation (Bulatovic, 2010). Improved paymetal recovery from a reagent

suite change may result in higher rates of return on processing operations as no further capital investments would be required (Woods, 2004).

The current study investigates the metallurgical performance of three thiol collectors on the froth flotation on a Merensky PGE ore in terms of copper, nickel and sulphur grades and recoveries, solids and water recoveries and rate of flotation. The thiol collectors employed are: sodium isobutyl xanthate (SIBX), sodium diethyl dithiophosphate (DTP) and sodium diethyl dithiocarbamate (DTC). The DTP and DTC collectors are then respectively used in mixtures with SIBX to evaluate if synergism exists.

1.2 Scope of project

This thesis investigated how the metallurgical performance of collector mixtures compared to the respective single collectors, by analysing for copper, nickel and sulphur recovery and grade. The size distribution and rate of flotation of the concentrates recovered from batch flotation tests on a Merensky Reef ore sample were also studied. The results were analysed to determine whether the mixtures of collectors resulted in any synergism.

Initial tests were conducted without the addition of a depressant to evaluate how different mixtures and ratios of thiol collectors affect metallurgical performance. Selected tests were then repeated with the addition of a depressant to simulate mining operation conditions.

The chemical reagents for the batch flotation tests were limited to collectors, a frother, a pH modifier and a depressant. The collectors were sodium isobutyl xanthate (SIBX), sodium diethyl dithiophosphate (DTP) and sodium di-ethyl dithiocarbamate (DTC) and the frother was Senfroth 200. Calcium hydroxide was used as pH modifier and the depressant was a carboxymethyl cellulose.

Statistical analyses of the results obtained are shown as error bars on all figures which represent standard deviation between duplicate tests.

1.3 Research Objectives

The objectives of this thesis are to:

1. Evaluate and compare the metallurgical performances in terms of nickel and copper grades and recoveries, and rate of flotation; achieved in the batch flotation of the Merensky Reef ore by the respective pure thiol collectors (SIBX, DTC and DTP).
2. Investigate collector synergism for mixtures of SIBX and DTC in the flotation of a Merensky Reef ore. The constituent ratios of SIBX to DTC investigated are 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, and 20:80.
3. Investigate collector synergism for mixtures of SIBX and DTP in the flotation of a Merensky Reef ore. The constituent ratios of SIBX to DTP investigated are 90:10, 80:20, 70:30, 60:40, and 50:50.
4. Investigate impact of depressant addition on collector synergism.
5. Investigate the effect of collector suites on different particle size classes recovered in the concentrate.

CHAPTER 2

2. Literature Review

2.1 Bushveld Igneous Complex

The Bushveld Igneous Complex in northern South Africa covers an area of 65 000 km², of which approximately 550 km² contains the valuable platinum group element (PGE) bearing ore (Figure 1) (Royal Bafokeng Platinum, 2015). The complex contains the world's most important PGE reserves and mining operations here account for more than half of the world's PGE production (Cawthorn, 1999; Loferski, 2012; Vermaak, 2005). The complex consists of a series of regular and distinct layers that contain various ore bodies; three of which contain PGE concentrations high enough for economic extraction. These are the Merensky reef and the Upper Group 2 (UG2) chromitite layer found on the eastern and western sides of the complex and the Platreef located towards the north (Figure 1) (Matthey, 2014). Each of these ore bodies have their own distinctive mineralogy (Jones, 1999; Osbahr, 2012). The ore deposits in the Bushveld complex are PGE dominant and are exploited primarily for their PGE content.

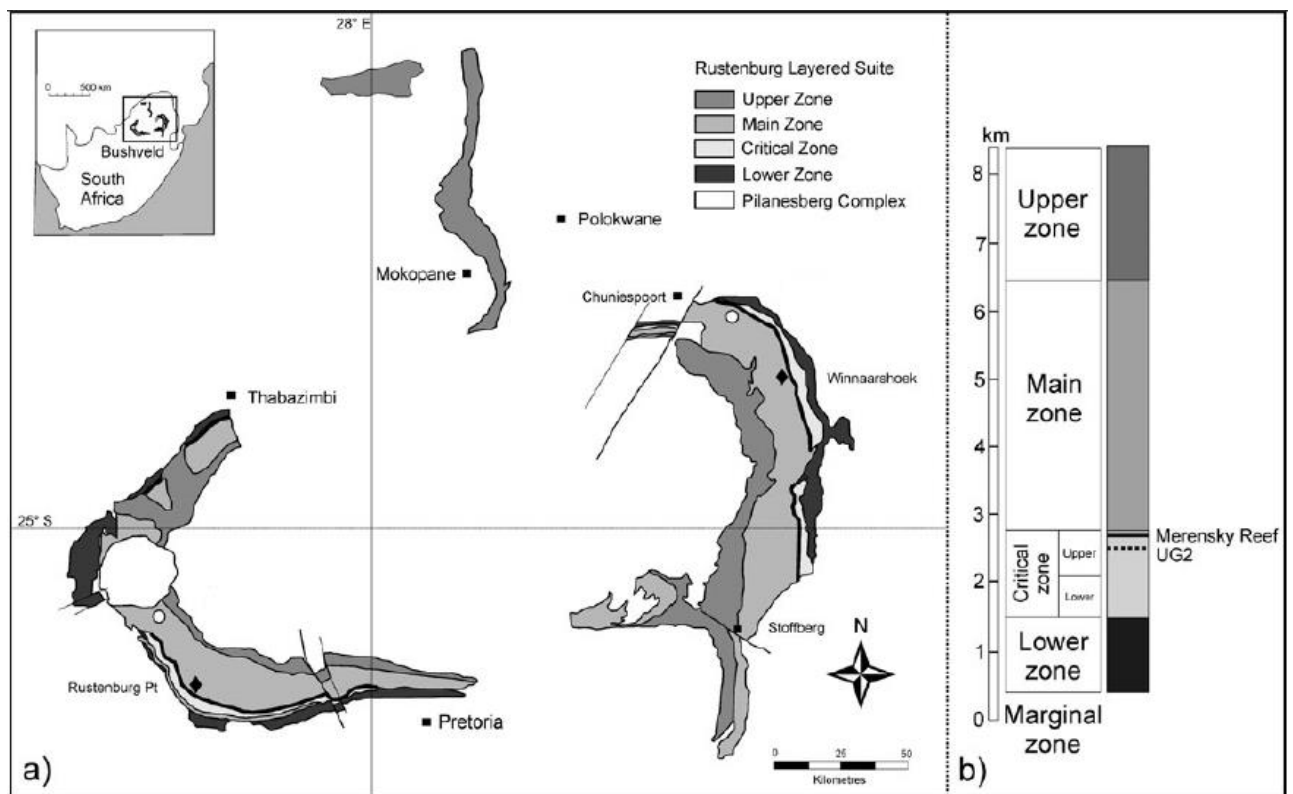


Figure 1: a) A simplified geological map of the Bushveld Complex in South Africa, indicating the eastern and western limbs which hosts the Merensky Reef and UG2, and the northern limb which hosts the Platreef. b) Simplified stratigraphy of the Bushveld Complex indicating the position of the Merensky Reef in the Upper Critical Zone (Osbaahr, 2012).

2.2 Merensky Reef

In 1924, Dr Hans Merensky discovered the Merensky reef, which is characterised as a pegmatoidal pyroxenitic layer lying between two thin chromitite layers. The thickness of the pyroxenite layer varies between 4 cm and 4 m across the Merensky Reef and mining of the reef is generally done at 80 cm (Osbaahr, 2012). The Merensky Reef is characterized as being well mineralised with large sulphide deposits (up to 3%) that contain significant concentrations of PGE; particularly platinum, palladium and rhodium and trace amounts of gold (Cawthorn, 1999; Loferski, 2012; Osbaahr, 2012). Although ores from the Merensky Reef exhibit the same characteristics, the composition is known to vary depending on the geographical location of its origin.

2.3 Merensky Reef Mineralogy

Commercial exploitation of the Merensky reef began soon after its discovery. It was made possible as the PGMs were hosted in relatively coarse-grained base metal sulphide (BMS) minerals which allowed for the beneficiation of the valuable minerals using the conventional sulphide flotation process (Vermaak, 2005). The process of beneficiation has not changed much since then and numerous operations collectively produce over 127 tonnes of platinum annually from the Merensky reef (Newell, 2008).

2.3.1 Valuable Minerals

The Merensky Reef ore sample that was used for this study was sourced from the western limb of the Bushveld Complex near Rustenburg. The base metal sulphide (BMS) content of the Merensky reef in this region is about 1-2%; distributed as 45% pyrrhotite, 32% pentlandite, 16% chalcopyrite and small amounts of pyrite (Jones, 1999; Wiese, 2006). PGE within the reef are closely associated with these BMS; present either as discrete PGM or in solid solution with the BMS. The majority of the PGMs are most closely associated with pentlandite, either as fine inclusions within pentlandite grains or as intergrowths at the pentlandite-gangue grain boundary (Bulatovic, 2010; Jones, 1999; Osbaahr, 2012). The exact mechanism responsible for the formation and accumulation of PGE in the reef remains unclear. However it is clear that the contribution of BMS to the total PGM content of the reef is significant.

Table 1 shows the distribution of PGM in the Merensky reef. Although, only 36% of the PGM distribution is sulphide based, all the PGMs are associated with the BMS (Shamaila and O'Connor, 2008). The PGE content in the Merensky reef is directly proportional to BMS

content, and BMS response is used as proxy for PGE recovery (Kinloch 1982; Schouwstra et al., 2000).

Table 1: Summary of the bulk mineralogy and PGM distribution of the Merensky reef (Shamaila and O'Connor, 2008)

| | |
|------------------|----------------------|
| Bulk mineralogy | Pyroxene |
| | Feldspar |
| | Base Metal Sulphides |
| PGM Distribution | Tellurides ≈ 30% |
| | Arsenides ≈ 7% |
| | Alloys ≈ 7% |
| | Sulphides ≈ 36% |
| | Rest ≈ 20% |

Copper is present in the Merensky reef only as chalcopyrite. The majority of nickel is present as pentlandite. Pentlandite is the only sulphide nickel present in the reef, thus nickel recovery is considered to represent pentlandite recovery in flotation. The significant non sulphide nickel found in the reef is present in the silicate minerals, olivine and orthopyroxene. Trace amounts of nickel can be present as solid solution in pyrrhotite (Brough, 2008; Osbahr, 2012).

Sulphide minerals in the reef have a lattice crystal structure. Grinding breaks the bonds of the crystal structure and fresh mineral surfaces are exposed. These surfaces are highly reactive and readily oxidises on exposure to air and water. Collectors used for sulphide flotation and oxide flotation differ due to variation in the interactions between collectors and different surfaces. The degree of sulphide surfaces that have been oxidised thus affects the floatability of the minerals. The effects of oxidation depends on the time between the production of freshly milled sulphide surfaces and the time that surface reacts with a collector molecule (Wills and Napier-Munn, 2006).

2.3.2 Gangue Minerals

The bulk of Merensky ores consist of undesired silicate minerals. These major rock forming silicate minerals make up most igneous rocks. The amounts and composition of the silicate minerals differ along the reef, however the major silicate minerals are orthopyroxene (50-70%), plagioclase (11-25%) and clinopyroxene (2-27%) (Table 2) (Liddell et al., 1986). The reef contains a small amount of the naturally floatable gangue silicate and talc (0.5-5%). Talc is the only naturally floatable silicate in Merensky reef ores and is known to have negative effects on flotation. It may report to the concentrate via true flotation which may decrease concentrate

grades. Talc may form partial rims and coatings around pyroxene particles that allow them to collect in the concentrate by true flotation (Becker et al. (2006) and Jasieniak and Smart (2009)). It also has froth stabilising effects which may increase water recovery and entrainment in the froth. Depressants have been added to the flotation pulp of Merensky reef ores to negate the froth stabilising effects and depress the talc.

Table 2 shows the classification and composition of minerals commonly present in the Bushveld Complex. Silicate gangue minerals dominate the complex, with small amounts of oxides and the desired base metal sulphides.

Table 2: Minerals common to the Bushveld Complex (Schouwstra et al., 2000)

| Mineral group | Mineral | Composition |
|---------------|--------------|------------------------------|
| Pyroxene | Enstatite | Mg, Fe silicate |
| | Augite | Mg, Fe, Ca silicate |
| Feldspar | Plagioclase | Ca, Na, Al silicate |
| Mica | Phlogopite | K, Mg, Al silicate |
| | Biotite | K, Mg, Fe, Al silicate |
| Chlorite | Chlorite | Hydrated Mg, Fe, Al silicate |
| Clay | Talc | Hydrated Mg silicate |
| Serpentine | Serpentine | Hydrated Mg, Fe silicate |
| Spinel | Chromite | Cr, Fe, Mg oxide |
| Sulphide | Pentlandite | Ni, Fe sulphide |
| | Chalcopyrite | Cu, Fe sulphide |
| | Pyrrhotite | Fe mono-sulphide |
| | Pyrite | Fe di-sulphide |

2.4 Platinum beneficiation

The processing chain of PGE beneficiation is similar for all ore types in the Bushveld Complex. Each flow-sheet will however have a slightly different processing route, dictated by the ore mineralogy. Every step in the processing of PGE ores is designed to increase the concentration of the Platinum Group Minerals (PGM) by reducing the bulk of the unwanted products.

Run-of-mine ore is of low grade and large range in particle size distribution. Comminution i.e. crushing and grinding, is used to reduce the average particle size and thereby liberate the desired minerals present. The sulphides that contain the PGM, are concentrated by froth flotation. Dry flotation concentrate, rich in PGM, is the final product of minerals processing and further processing is referred to as refining. Refining utilises smelting, converting and various hydrometallurgical processes to separate and purify the different metals (Othmer, 2006).

2.5 Principles of froth flotation

Froth flotation is one of the most important separation processes in the minerals processing industry and has allowed economic beneficiation of low grade and complex ores. It is a physico-chemical process that utilises differences in mineral surface properties to separate valuable from unwanted gangue minerals (Wills and Napier-Munn, 2006). The flotation process consists of two phases that allow separation to occur. The pulp phase contains the bulk of the ore where mineral recovery occurs and the froth phase rests above the pulp phase where the desired minerals are concentrated and separated from the bulk (Figure 2) (Rao, 2004).

Froth flotation generally occurs in a cuboid or cylindrical tank that is fitted with a stirrer to agitate the pulp and some form of gas/air disperser. During normal operation, bubbles of air are introduced into the bottom of the tank or cell and are distributed into the pulp as they rise. Hydrophobic mineral particles, either natural or induced by the addition of chemicals called collectors, within the pulp may then attach to the rising air bubbles when successful collisions occur (Figure 2). The particles attached to the air bubbles rise through the pulp and collect as a concentrate in the froth phase on the surface of the pulp phase. The froth phase occurs as a result of the addition of chemicals called frothers that reduce the surface tension of the water in the pulp. The hydrophobic particles are suspended above the pulp phase in the froth phase. This allows hydrophilic particles that reported there by mechanisms other than by true flotation to fall back into the pulp phase. The froth phase, concentrated in the valuable minerals, is recovered from the cell either by mechanical scraping or the froth migrates unassisted over the lip of the vessel (Wills and Napier-Munn, 2006).

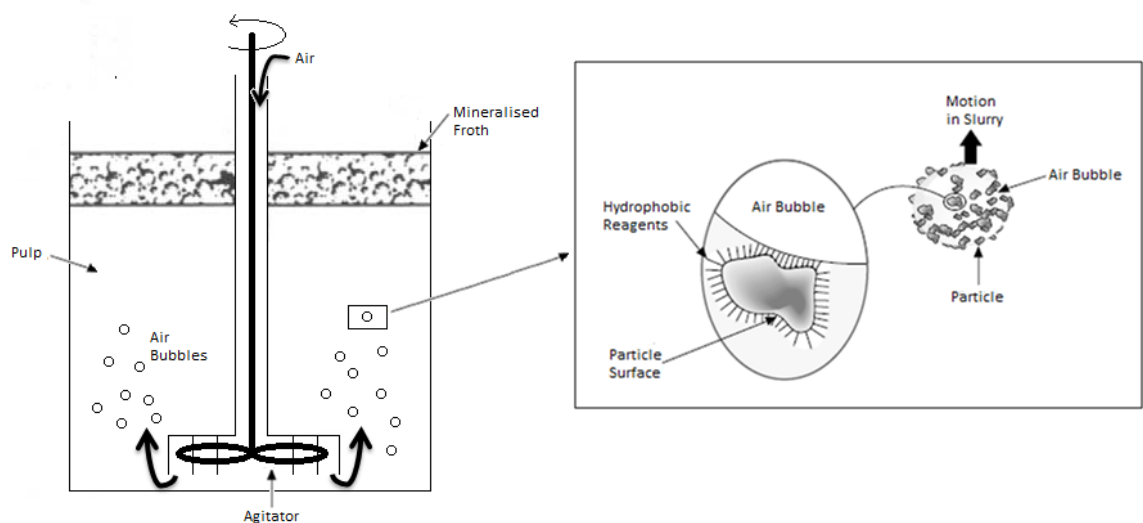


Figure 2: Schematic illustration of the flotation process and the attachment of hydrophobic particles to a rising air bubble (adapted from Rehmann, 2007)

The flotation process depends on various sequential sub-processes which all contribute to the success of the separation of valuable minerals from the gangue. Sweet (1999), summarised the processes as follows:

1. Collector(s) attach to the surface of the valuable minerals which renders them hydrophobic.
2. Air is introduced into the cell, which results in a vast amount of bubbles to rise through the pulp.
3. The rising bubbles collide with minerals particles in the pulp. Particles attach and detach from the bubbles as they rise.
4. Loaded bubbles are transported to the pulp-froth interface.
5. Loaded bubbles are transferred to the froth phase where the hydrophobic particles are suspended. Particles that reported here other than by true flotation are allowed to drain and report back to the pulp phase.
6. The loaded bubbles are transferred and collected from the froth phase.

These sub-processes describe the selective mechanism for particle recovery known as true flotation. However, two unselective mechanisms also exist. Entrainment recovers both valuable and gangue particles by the upward flow of air bubbles and associated water to the froth; while aggregated and composite particles are recovered via entrapment. The sub-processes of true flotation rely on the success of the preceding processes e.g., if the collector does not attach and render the surfaces of desired minerals hydrophobic, the particles will not successfully attach to the bubbles and ultimately not be collected from the froth phase. Each of the sub-processes may be further divided into more intricate micro-processes; each with its own distinct effects.

2.5.1 Rate of Flotation

The kinetics involved in froth flotation provides an indication for the rate of mineral flotation. This information may be used to ensure adequate residence time in the flotation cell or to optimise the flotation process.

The flotation of minerals can be described as a first order rate process. Klimpel (1984) proposed that the flotation process is a function of both flotation rate and ultimate recovery using the following equation:

$$R = R_{max} [1 - \{1/(kt)\}(1 - \exp^{-kt})] \quad (1)$$

Where R is the cumulative recovery after time t , R_{max} is the maximum recovery after infinite time, k is the flotation rate constant and t is the cumulative flotation time.

2.6 Important parameters in froth flotation

The froth flotation process is complex and relies on successful interaction between various parameters. There are over 25 equally important and interactive known parameters that, either independently or in combination with other parameters, influence flotation performance (Klimpel, 1984). These parameters are divided into three major groups which corresponds with the physical, chemical or operational nature of the process (Figure 3).

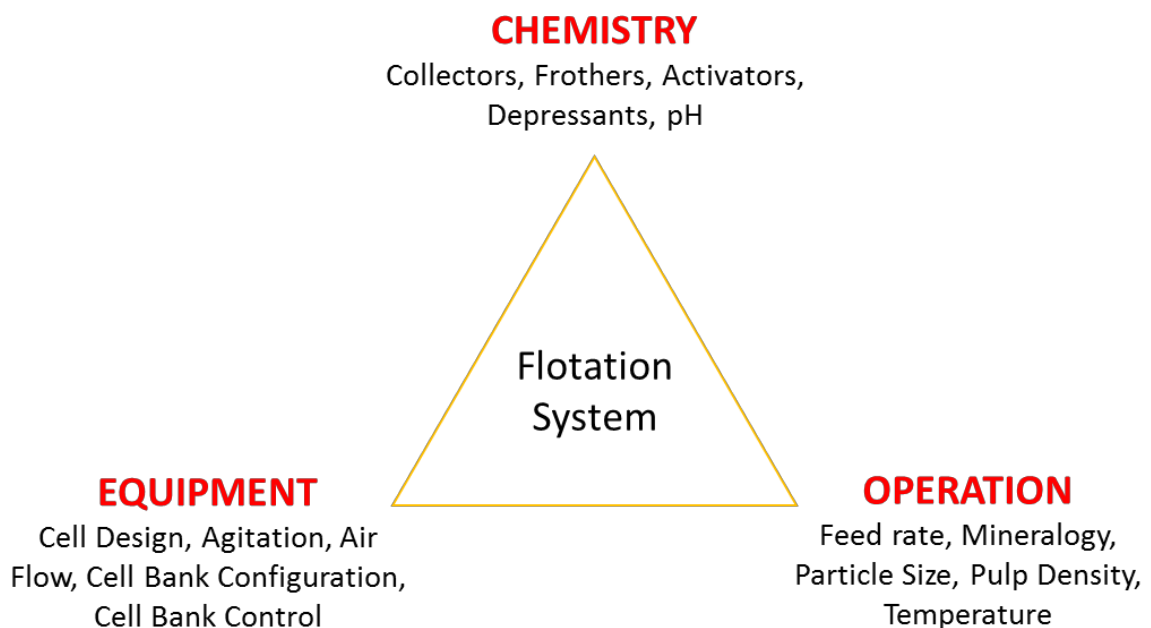


Figure 3: Summary of the interrelated variables of froth flotation (Klimpel, 1984)

2.6.1 Equipment Parameters

The role of the equipment parameters in froth flotation is to create and control a favourable hydrodynamic environment for successful particle-bubble interaction. This will govern flotation performance. Cell bank design and configuration is determined during the plant design phase and is largely dependent on equipment manufacturers (Matis and Mavros, 1991). The cell design must allow for the transportation of particles (both froth concentrate and pulp tailings), have an area of low turbulence for the froth layer and avoid sedimentation to occur. Once the

plant has started up, only the air flow, rate of agitation and control system can be easily altered to maintain suspension of particles in the pulp and disperse the air bubbles throughout the cell.

2.6.2 Operational Parameters

The operational parameters are non-chemical variables which can affect flotation performance. Mineralogy is dependent on the ore that is mined, while temperature depends on the weather. Feed rate, feed particle size and pulp density may be adjusted to meet operational requirements by increasing production, altering grinding conditions or increasing the make-up water in the flotation cells (Ucurum and Bayat, 2007).

2.6.2.1 Particle Size

The size distribution of particles fed to a flotation system has a significant effect on the grade and the recovery of the flotation system. It is considered that there is a size range where mineral recovery is optimum and that recovery decreases drastically above or below this range (Figure 4). This size range differs for various minerals and flotation systems. The general size range for optimum flotation recovery is between 10 and 100 μm (Kawatra, 1995).

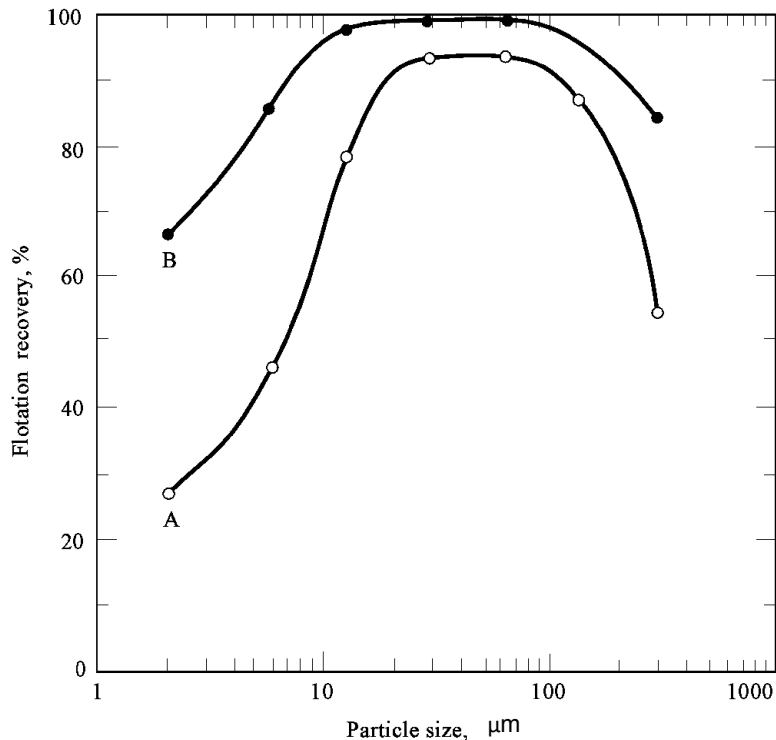


Figure 4: Recovery as a function of particle size curves for different minerals. (Othmer, 2006)

Larger or coarser particles have a greater inertia than smaller particles and subsequently higher probability of successful collisions and attachment to rising air bubbles. This results in higher rates of flotation compared to smaller or finer particles. However larger particles have higher rates of detachment from the froth due to their large mass (Tao, 2004). Particles that are too large may however not be sufficiently buoyant which results in low recoveries. The surfaces of finer particles are more easily oxidized and require a larger collector dosage due to the larger surface area.

Goncalves et al, 2003, found that a finer feed grind will yield a higher recovery and a coarser feed grind will result in a higher grade.

2.6.3 Chemical Parameters

The many chemical parameters involved in froth flotation are interactive and the resulting complexity provides ample opportunity for research. Chemical additives to the flotation process alters the pulp conditions and may allow the desired minerals to be successfully recovered. These additives may increase the hydrophobicity of the desired minerals, control selectivity, enhance recovery and grade, and improve the kinetics of the flotation system. The major chemicals in froth flotation are classified according to the role they fulfil in the process. These may be collectors, frothers, activators, depressants or modifiers. These chemicals are however not confined to their intended purpose, and may fulfil more than one role within the flotation system (Bradshaw, 1997). Collectors prepare the surfaces of the desired minerals for attachment to air bubbles by rendering them hydrophobic. Modifiers, activators and depressants ensure that only the desired mineral surfaces are rendered hydrophobic. The air bubbles with attached particles rise through the pulp where the frother stabilises the bubbles in the froth on the pulp surface. The addition of chemical reagents allows for successful processing of complex ores by flotation.

2.6.3.1 Frothers

The froth flotation process relies on the formation of a stable froth above the pulp phase. Frothers are chemical reagents that are added to the pulp to allow the formation of this froth. The functions of the froth layer are (i) to further upgrade the desired hydrophobic minerals by

allowing hydrophobic particles to drain by gravity and (ii) to transport the mineral loaded bubbles from the pulp-froth interface to a concentrate (Bulatovic, 2007).

Frother molecules are heteropolar; which consist of a non-polar hydrocarbon chain and a polar functional group (Wills and Napier-Munn, 2006). The hydrocarbon chain can be straight, branched or cyclic while the functional group can be a hydroxyl, carboxyl, carbonyl, amino or a sulpho group. The heteropolar structure of the molecules allows it to absorb at the air-water interface and reduces the surface tension of the water. The non-polar end of the molecule is directed at the air while the polar functional group prefers the water-side where it can form hydrogen bonds with water molecules. This prevents the air dispersion of bubbles or their coalescence (Othmer, 2006). A frother should exhibit no collecting properties, be soluble in water to effectively distribute its surface acting properties evenly and be stable over a wide range of pH (Wills and Napier-Munn, 2006).

2.6.3.2 Depressants

Depressants are used in Merensky reef processing to reduce the recovery of naturally floatable gangue material. The depressants suppress the mostly silicate gangue by adsorbing onto their surfaces which allows for adequate upgrading of the desired minerals (Wiese, 2006). Depressants used in Merensky reef ore processing are the polysaccharide depressants of guar gum and carboxymethyl cellulose (CMC) (Bradshaw et al., 2005). Although these depressants are different in their structure and effects on froth stability, they exhibit similar efficiencies in gangue suppression (Wiese, 2009). CMC ionises in solution which produces a negative charge on the gangue while guar gums are only slightly charged.

The function of depressants in flotation systems are described as being opposite to that of collectors (Bulatovic, 2007). Depressants inhibit the flotation of given minerals by preventing collectors from adsorbing onto hydrophilic mineral surfaces or by adsorbing onto the surfaces of gangue minerals and thus rendering them hydrophilic. Successful suppression of gangue in flotation requires that, depressants have a functional group with high affinity for the gangue minerals, have strong hydrophilic character in the molecule structure and should not compete with the collectors for the surfaces of the desired minerals (Fuerstenau et al., 2007).

The froth phase is affected by the addition of depressants to flotation systems, particularly at high dosages. Depressants have been found to reduce the stability of froths due to the

suppression of the froth stabilising talc and due to the nature of the polymers (Bradshaw et al., 2005). At high depressant dosages it has been found that polysaccharide depressants co-absorb onto sulphide mineral surfaces and depress them resulting in lower recoveries (Steenberg and Harris, 1984; Morris, 1997). In the absence of a depressant, maximum recoveries of sulphide minerals were obtained as collectors could attach on the surfaces without competition (Vianna, 2004).

2.6.3.3 Collectors

For successful recovery of desired minerals by froth flotation it is required that the surfaces of these minerals be rendered hydrophobic. This achieved by the addition of collectors into the pulp. There are various collectors available, and their application is dictated by its interactions with the minerals present in the ore. Collectors are heteropolar organic reagents that concentrate at the mineral-water interface and renders the surfaces of these particles water-repellent. A schematic diagram of sodium ethyl xanthate (SEX), illustrates the heteropolar structure of collectors (Figure 5).

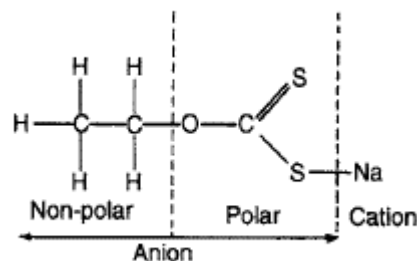


Figure 5: Schematic diagram representing the general structure of a SEX collector molecule

The polar functional group chemisorbs onto mineral surfaces while the non-polar group renders the particles hydrophobic and allows them to attach to a passing air bubble (Figure 6).

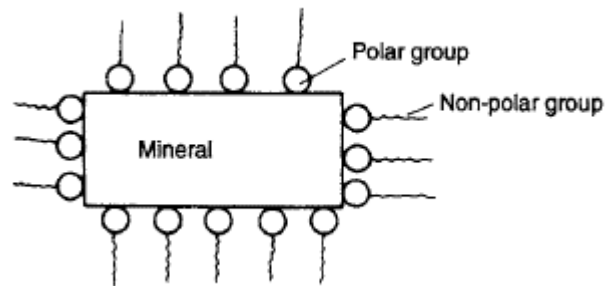


Figure 6: Schematic diagram of collector adsorption on a mineral surface (Wills and Napier-Munn, 2006)

Collectors can be divided into two types: ionising and non-ionising. Ionising collectors are further subdivided into anionic or cationic, depending on the ion the exhibits the water repellent effect in solution. Cationic collectors are used in the flotation of oxides, carbonates, silicates and alkali earth metals (Wills and Napier-Munn, 2006). The anionic group of collectors consists of either oxyhydal or sulphydryl functional groups and are most commonly used in froth flotation. Sulphydryl collectors, also referred to as thiol collectors, have a bivalent sulphur atom attached to either a carbon or a phosphorous atom in the functional group and are used in the flotation of sulphide minerals (Bulatovic, 2007; Lovell, 1982). Xanthates, dithiophosphates and dithiocarbamates are commonly used sulphydryl collectors in sulphide flotation.

Nagaraj (1988) identified the order of collector strength with sulphide minerals as: dithiocarbamate > xanthate > dithiophosphate. Collector strength and selectivity are influenced mainly by the functional group and to a lesser extent by alkyl chain length. It has been found that the effects of increasing the length of the nonpolar alkyl chain of the collector molecule increases the hydrophobicity of mineral surfaces and enhances flotation recovery at the expense of selectivity (Ackerman et al., 1987).

This thesis focusses on the recovery of sulphide minerals, thus only these collectors will be discussed further.

2.6.3.3.1 Xanthates

Xanthates are the most common collector used in the flotation of sulphide ores. Their popularity is due to their strong collecting power and relative low cost. Xanthates are formed when an alkali hydroxide is reacted with an alcohol and carbon bisulphide (Wills and Napier-Munn, 2006). The carbon chain length of the alcohol used in the production dictates the xanthate alkyl

chain length, and the alkali metal in the hydroxide dictates whether the cation is sodium or potassium (Figure 7).

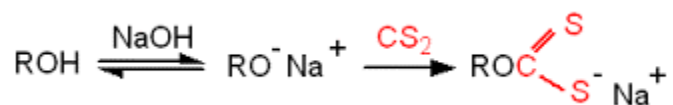


Figure 7: Chemical reaction for the production of a generic sodium xanthate molecule, R = hydrocarbon chain group

The length of the hydrocarbon chain determines the strength of the attachment between collector and mineral. Longer chain lengths have greater intermolecular forces and form stronger adsorption on mineral surfaces. The smaller surface area of shorter hydrocarbon chained xanthates allows higher adsorption densities on sulphide mineral surfaces (Wakamatsu, 1968). The chemistry of xanthates makes them susceptible to decomposition, either by atmospheric oxygen or in the presence of acidic pulp. Xanthates are therefore used in weakly alkali pulps (Bulatovic, 2007).

Sodium isobutyl xanthate was used in this study. It has a branched hydrocarbon chain comprised of four carbon atoms. It is the xanthate of choice in platinum processing. The branched chain gives it the activity associated with shorter chained xanthates and the strength of longer chains (Wills and Napier-Munn, 2006).

2.6.3.3.2 Dithiocarbamates

Dithiocarbamates are less common than xanthates due to their higher cost. However they have stronger collecting properties than xanthates (Jiwu et al., 1984, Lotter and Bradshaw, 2010). The stronger collecting power is due to the lone pairs of electrons on both sulphur and nitrogen. They are also similar to xanthates in structure. Dithiocarbamates are synthesised then an amine is reacted with carbon bisulphide and sodium hydroxide. (Figure 8).

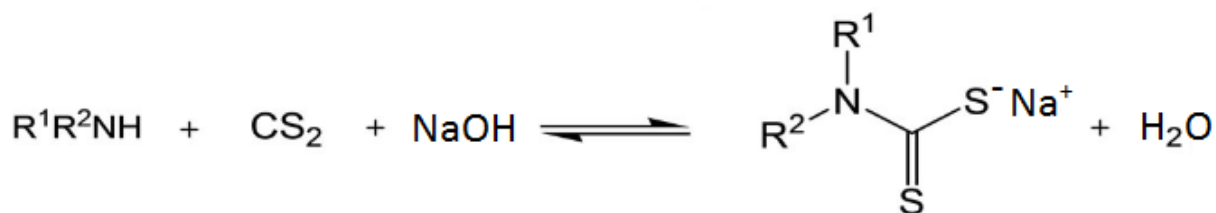


Figure 8: Chemical reaction for the production of a generic dithiophosphate molecule, R^1 , R^2 = hydrocarbon chain groups

Dithiocarbamates have high affinity towards precious metals and are often used in selective flotation. Apart from the stronger collecting properties over xanthates, dithiocarbamates also adsorb more rapidly onto mineral surfaces and are stable over a wider range of pH (Adkins and Pearse, 1992). Dithiocarbamates are salts with alkyl groups ranging from one to six carbons. However, as collectors they are generally found commercially in clear to yellow solutions (Bulatovic, 2007).

Sodium diethyl dithiocarbamate was used in this study. It has a total of four carbon atoms arranged as two ethyl hydrocarbon chains. It is often used as co-collector with xanthates.

2.6.3.3.3 Dithiophosphates

Dithiophosphate collectors, the second most popular thiol collector after xanthates, are widely used in sulphide mineral flotation (Bulatovic, 2007; Mingione, 1984). They are produced by neutralising dithiophosphoric acid with an organic or organic base like sodium hydroxide or zinc oxide. The dithiophosphoric acid is the reaction product of pentasulphide (P_2S_5) and phenols or alcohols. The general structure of a dithiophosphate molecule is shown in Figure 9.

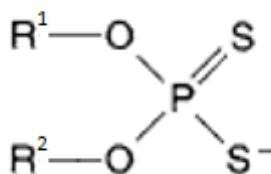


Figure 9: Generic structure of a dithiophosphate molecule, R^1 , R^2 = alkyl chain

The donor atom, phosphorus, in dithiophosphate molecules is more electropositive than the carbon in xanthate molecules. This makes dithiophosphate collectors weaker, but more selective than xanthates (Adkins and Pearse, 1992; Bradshaw, 1997; Lotter and Bradshaw,

2010). Stamboliadis (1976) reported that a wide range of sulphide minerals may be selectively floated with dithiophosphates, with the exception of the nickel minerals pentlandite and millerite. Adkins and Pearse (1992) reported that the length of the alkyl group affects the flotation response with dithiophosphates. Stamboliadis (1976) found that dithiophosphates with longer chain lengths exhibited frothing properties in addition to their selective collecting abilities and attributed the frothing properties to the excess alcohol the collectors are stored in. Lovell (1982) however suggested that the frothing properties are due to the decomposition of the alcohols used in the manufacturing process, while Mingione (1984) suggested that the salt form of the dialkyl dithiophosphates increases the frothing properties.

Dithiophosphates are more resistant to hydrolysis and oxidation than corresponding xanthates (Sutherland and Wark, 1955). Metal-dithiophosphate salts have been found to be more soluble than those of corresponding metal-xanthates (Fuerstenau, 1982). They are commonly used as co-collectors with xanthates to improve flotation performance.

Sodium diethyl dithiophosphate was used in this study. It has two ethyl chains which equals a total of four carbon atoms. It is often used as co-collector with xanthates to improve the recovery of fine particles in platinum processing.

2.7 Interaction of thiol collectors with sulphide minerals

It is well known that thiol collectors adsorb onto sulphide minerals by a mixed potential mechanism (Yoon and Basilio, 1993). Other mechanisms that have been proposed include the chemical and the ion exchange mechanisms (Taggart, 1955; Cox and Wark, 1934). The chemical mechanism was based on the theory where insoluble metal-collector compounds are formed. The model for this system however proved inconsistent (Sutherland, 1955). The ion exchange mechanism suggested that the thiol collector displaced OH⁻ ions on the surface of minerals which allowed for direct adsorption of collector on minerals. The resultant mineral surface formed by this mechanism would however be too charged to be hydrophobic (Sutherland, 1955).

2.7.1 Mixed Potential Mechanism

The mixed potential mechanism involves electron transfer from the collector to the mineral. More specifically the anodic oxidation of collectors at the mineral surface and the cathodic reduction of oxygen (Yoon and Basilio, 1993). The anodic and cathodic reactions may occur

simultaneously to give a single electrode potential. This mixed potential theory has overcome the short-comings of other mechanisms that have been proposed. Three classes of electrochemical reactions are reported to be possible that depend on the minerals involved, their pre-treatment and the collector used. These are chemisorption, catalytic oxidation and metal-thiol formation (Yoon and Basilio, 1993).

Chemisorption involves the formation of a monolayer of the thiol oxidation product at potentials below thermodynamic potential for the formation of the metal thiol compound. Here the collector interacts with the mineral surface while metal ions are not removed from their lattice sites. The chemisorption interaction is covalent and depends on collector coverage. The chemisorbed layer of collector may induce flotation of affected minerals. The anionic oxidation of the collector at the mineral surface is (Woods, 1984):



where X^- is a xanthate anion and X_{ads} is the chemisorbed xanthate on the mineral surface.

Metal ions may be removed from their lattice sites and multilayers may form. In such cases a hydrophobic surface will only be established if there is bulk precipitation on the mineral surface (Bradshaw et al, 1998). The chemisorption of xanthate on many mineral surfaces has been confirmed (Yoon and Basilio, 1993). If monolayer coverage is not achieved, the chemisorbed thiol species may transform into dithiolates or metal compounds.

Catalytic oxidation is a kinetically slow process where the thiol compound is transformed to its dithiolate. During this transformation, electrons are transferred through the mineral from the site where the collector is oxidised to the site where oxygen is reduced. The mineral does not participate in the reaction and its surface remains unchanged. The dithiolate that forms is only weakly attached to the mineral surface by physisorption. This mechanism is most common in minerals with electron deficiency (Lotter and Bradshaw, 2009; Yoon and Basilio, 1993). The oxidation of the thiol ion to the corresponding dithiolate is:



where X_2 is the dithiolate.

The oxidation of xanthate, dithiophosphate and dithiocarbamate yield the dithiolates: dixanthogen, dithiophosphatogen and thiouram disulphide respectively (Fuerstenau, 1990). The formation of dithiolates on the mineral surface occurs when the rest potential of the mineral in the solution with the collector is greater than the reduction potentials of the dithiolate (Allison et al., 1972).

The metal-thiol formation or electrochemical mechanism is where a metal-thiol compound is formed on the surface of the mineral which participates in the adsorption process. This mechanism occurs when the mineral surface is easily oxidised and involves an electrochemical and a chemical reaction (Yoon and Basilio, 1993). The electrochemical metal-thiol formation is controlled by the electrochemical potential and can be represented by the following reaction:



This is followed by a chemical reaction of the metal ion with the thiol collector that is controlled by the stability constant of the metal-thiol compound:



The overall metal-thiol adsorption mechanism is as follows:



2.7.2 Collector Adsorption on Mineral Surfaces

The largest classification of mineral ores treated by froth flotation are sulphide ores. Consequently thiol collectors account for over 80% of collector usage (Fuerstenau, 1995). Sulphide minerals are easily collected with thiol collectors because the sulphur atom on the collectors have accessible and vacant d-orbitals that readily accepts electrons to form π - and σ - bonds (Bhaskar and Khangaonkar, 1984). Sulphur also has the ability to form bonds with itself (catenation) which may allow the sulphur of the thiol collectors to bond with the sulphide minerals.

The interactions among thiol collectors and the desired minerals of platinum group element (PGE) flotation are discussed in the following sections.

2.7.2.1 Adsorption on Chalcopyrite

Chalcopyrite is the most abundant copper mineral. It has a tetragonal crystal structure which, by weight, consists of 30.43% iron, 34.63% copper and 34.94% sulphur. It has a chemical formula of CuFeS_2 , thus copper and iron are present as Cu(I) and Fe(III) respectively (Pearce et al., 2006). Chalcopyrite has been found to float without the addition of collector as a result of surface oxidation. The oxidation may cause iron atoms to migrate from the mineral lattice and leave a hydrophobic metal-deficient layer on the mineral surface or lead to the formation of hydrophobic elemental sulphur (Woodcock et al., 2007). The natural floatability of chalcopyrite makes it difficult to examine the effect of collectors on its hydrophobicity. Flotation of chalcopyrite is however conducted with the addition of moderate amount of collector as the natural floatability of chalcopyrite deteriorates by the formation of surface precipitates and oxidation products.

It has been proposed that the mechanism that allows for the flotation of chalcopyrite with xanthates is due to the formation of cuprous xanthate and dixanthogen (Woodcock et al., 2007). Allison et al. (1972) suggested that the flotation of chalcopyrite is reduced when dixanthogen does not form. The relatively high solubility of Cu^{2+} from the mineral surface promotes the oxidation to dixanthogen (Ackerman et al., 1987). However Yoon and Basilio (1993) found that both metal xanthates and dixanthogens co-existed on the surface at higher potentials.

Finkelstein and Goold (1972) reported that cuprous dithiophosphate formed on the surface of chalcopyrite under alkali conditions. The oxidation product for dithiophosphates on chalcopyrite is dependent on pulp pH (Grano et al., 1997). Dithiophosphate collectors are often used in cleaning circuits for copper sulphide processes under alkali conditions as they are more selective towards the chalcopyrite as compared to xanthates (Woodcock et al., 2007).

The reaction product between chalcopyrite and dithiocarbamate has been reported to be due to the formation of cuprous dithiocarbamate (Finkelstein and Goold, 1972). It has also been reported that dithiocarbamates adsorb on the surface of chalcopyrite via chemisorption (Mangalam and Khangoankar, 1985).

The hydrophobic species responsible for the flotation of chalcopyrite is dixanthogen with xanthate, Cu(DTP)_2 with dithiophosphate and Cu(DTC) or Cu(DTC)_2 with dithiocarbamate.

2.7.2.2 Adsorption on Pentlandite

The nickel-iron sulphide mineral, pentlandite, is the main source of nickel in the world. It has a general formula of $(\text{Fe,Ni})_9\text{S}_8$ with almost equal amounts iron and nickel. The metal ions are both in tetrahedral and octahedral arrangement with sulphur atoms in its complex face centred cubic structure. Surface oxidation and the formation of passive layers on the surface of pentlandite have been attributed for its poor recoveries by flotation (Nyambayo, 2014).

Xanthate is known to chemisorb on the surface of pentlandite (Hodgson and Agar, 1989). The adsorbed xanthate oxidises and form dixanthogen. Both chemisorbed xanthate and the dixanthogen enhance the hydrophobicity of pentlandite.

Dithiophosphates are incapable of forming insoluble nickel compounds required for flotation of pentlandite (Stamboliadis, 1976). Both the polar and non-polar alkyl chain of the reagent are responsible for its apparent inability to float pentlandite. It has been reported that with dithiophosphates the metal-thiolate formation mechanism imparts hydrophobicity on pentlandite (Lotter & Bradshaw, 2010).

Dithiocarbamate forms a stable metal-thiolate with pentlandite (Lotter & Bradshaw, 2010).

The hydrophobic species responsible for the flotation of pentlandite are NiX with xanthate, Ni(DTP)_2 with dithiophosphate and Ni(DTC)_2 with dithiocarbamate.

2.7.2.3 Adsorption on PGMs

Platinum group minerals (PGMs) can be classed as sulphides, tellurides, arsenides, alloys and oxides. The vast amount of PGMs present in the Bushveld complex and their low concentration has limited the identification of the mechanisms responsible for hydrophobicity. Vermaak (2005) performed studies on a synthetic telluride where it was reported that chemisorbed xanthate forms at short contact time on the mineral surface and that the chemisorbed xanthate converts to dixanthogen when the contact time is increased. It was also reported that the pH

of the pulp affected the formation of dixanthogen and that a more alkaline pulp favoured dixanthogen formation. Shackelton et al. (2007) similarly reported that thiol collectors achieved favourable PGM recovery.

Industrial flotation plants often report that PGMs are lost to the tailings. Vermaak (2005) reported that these minerals are present as fine and ultrafine particles and that they have been fully liberated from their sulphide hosts. This suggests that not all PGM minerals respond favourably to thiol collectors.

2.8 Collector Mixtures and Synergism

It has been shown that the use of collector mixtures may have benefits over the use of pure collectors, and the practice of using collector mixtures is well established in the mineral processing industry (Bradshaw et al., 1998; Bradshaw, 1997; Hangone, 2004; Ngobeni and Hangone, 2013; Lotter and Bradshaw, 2009; Wiese et al., 2005). The interest in mixtures of collectors may be due to the shortcomings of single collectors during treatment of complex ores. Increase in global metal demand has resulted in the treatment of many poly-sulphide ores and the use of a single collector has been found not to react favourably with all sulphide minerals present (Nagaraj and Ravishankar, 2007). These shortcomings may be overcome by using mixtures of collectors. The use of properly considered mixtures of collectors may increase the range of sulphide minerals in the ore with which the collector suite will interact and increase mineral recovery. Mixtures of collectors have also shown enhanced metallurgical performance over the respective collectors in the flotation of various sulphide ores (Table 3) (Bradshaw, 1997; Heilbig et al., 2000; McFadzean et al., 2012).

The use of mixtures of collectors are often more effective than their respective pure collectors. The increase in effectiveness may be attributed to the sum of the contribution from each of the respective collectors or to synergism between the respective collectors. In synergism, the combined effect of the collectors exceeds the sum of the individual collectors. Synergism has been found to occur in collector-collector, collector-frother and frother-frother interactions. The interactions between reagents that result in synergism are complex and depend upon their chemical nature and their adsorption properties (Bradshaw and O'Connor, 1994).

Table 3 summarises various cases of synergism between xanthate, dithiocarbamate and dithiophosphate collectors in batch flotation tests performed on various sulphide mineral ores. Increased metal recoveries were the most frequently observed metallurgical benefit when mixtures of thiol collectors were used over the respective pure collectors. Higher rates of flotation were also observed in some studies. However, significantly increased grades were not observed.

Table 3: The effects of mixing reagents in flotation (adapted from Bradshaw and O'Connor, 1998; Castelyn, 2011)

| Reagents (Ratios tested) | Mineral System | Benefit of Mixture | Reference |
|---|--|---|------------------------------|
| Ethyl X: amyl X (2:1, 1:2 mass) | Arsenopyrite | Higher rates of recovery | Plaskin et al. (1954) |
| Ethyl X: diethyl DTP (1:1 mass) | | | |
| n-propyl DTC: n-hexyl DTC: cyclohexyl DTC: dipropyl DTC (10:90; 50:50; 90:10) | Pyrite with quartz gangue | Increased recoveries for all mixtures | Bradshaw and O'Connor (1994) |
| Isopropyl DTC: isopropyl X (1:2 mass) | Chalcopyrite ore | Better results with DTC: X mixture than with pure DTC | Falvey (1969) |
| Di-isobutyl DTP: isobutyl X (30:70; 50:50; 70:30 mass) | Platinum group mineral (PGM) ore | Recovery improved by 7% with 70:30 mixture | Mingione (1984) |
| Isobutyl X: cyano diethyl DTC (12:44 mass) | Chalcopyrite/pyrite with quartz gangue | Improved chalcopyrite recovery | Jiwu et al. (1984) |
| Ethyl X: diethyl DTC (80:20; 66:33; 50:50; 33:66; 20:80) | Hazelwoodite | Increased recovery in microflotation | Critchley and Riaz (1991) |
| Isopropyl X: dicresyl DTP (95:5) | Mixed copper sulphide/oxide ore | Enhanced rate and recovery with mixture | Adkins and Pearse (1992) |
| n-butyl X: cyclohexyl DTC (95:5; 90:10; 85:15; 50:50) | Pyrite with quartz gangue | Recovery increased with all mixtures | Bradshaw and O'Connor (1997) |
| Ethyl X: Ethyl DTP (10:90; 50:50; 90:10) | Galena and pyrite | Recovery improved with 17% for 10:90 ratio | McFadzean et al. (2012) |
| Ethyl X: Ethyl DTC (10:90; 50:50; 90:10) | | Recovery increased by 29% with 90:10 ratio | |

The benefits of using a collector mixtures over a single collector reagent suite may include lower dosage requirements, improved selectivity and recovery, higher rate of flotation, and improved coarse particle recovery. Often there is an optimum ratio of constituents in a synergistic collector mixture. Collector-frother interactions have also given decreases in frother dosage requirements. Corin et al. (2012) reported that a dithiophosphate mixture with xanthate on a PGM ore did not create collector-collector synergism, but rather modified the froth. The

addition of DTP stabilised the froth which resulted in an increase in the recovery of fine particles.

Hangone (2004) reported the collector-collector synergistic effects may have occurred when a xanthate-DTC mixture was used on a chalcopyrite ore. Furthermore, it was reported that collector-frother synergism may have occurred when a xanthate-DTP mixture was used on a similar ore. Nyambayo (2014) reported that synergistic effects may have been observed with the use of a ternary mixture composed of short and long chained xanthates with either DTP or DTC on the flotation of a pentlandite mineral ore.

2.8.1 Adsorption Mechanism for Collector Mixtures

As discussed above, synergism has been well reported, however the mechanism by which synergism is achieved remains unclear. There are two dominant theories proposed to be responsible for synergism: strong and weak adsorption sites and catalysed formation of dixanthogens.

Bradshaw and O'Connor (1994) proposed that the surfaces of sulphide minerals are not uniform and rather consists of sites with different activities. More oxidised areas on the mineral surface are weak sites while the less oxidised areas are strong sites. Collectors with different activities would respond to these areas differently. The weaker, more selective collector in the mixture would preferentially adsorb onto the stronger active sites, while the stronger, less selective collector adsorbs onto the remaining weak sites. The xanthates, dithiocarbamates and dithiophosphate classes of collectors have different selectivity and collection activity which may explain synergism in their mixtures by this mechanism. It is proposed that sequential addition of collectors may affect this mechanism (Nyambayo, 2014).

Bradshaw et al. (1995) and Bacgi et al. (2007) reported that dithiocarbamates and dithiophosphates would preferentially adsorb onto the surfaces of sulphide minerals. They would then catalyse the formation of hydrophobic xanthate dimers that attach to the dithiocarbamate or dithiophosphate through van der Waals forces and form a hydrophobic multilayer on the mineral surface.

CHAPTER 3

3 Methodology

3.1 Introduction

Laboratory froth flotation tests accurately simulate commercial plant conditions and provides an easier, more cost effective alternative to optimise industrial flotation processes. Optimisation results from laboratory tests are easily incorporated into industrial flotation processes.

Flotation tests were conducted using standard batch laboratory bench scale tests to investigate the effects of pure SIBX, DTP and DTC collectors as well as mixtures of SIBX:DTP and SIBX:DTC on the metallurgical performance of a typical Merensky Reef PGE ore. Flotation performance was evaluated from the grades and recoveries of copper, nickel and sulphur, mass of solids and water recoveries and rate of flotation. Initial tests of pure SIBX were conducted to determine the optimum collector dosage to be used for all tests.

All tests were conducted in duplicate and error bars on figures represent standard deviation between subsequent tests.

3.2 Characterisation of ore sample

A bulk Merensky ore sample from the southern section of the western limb of the Bushveld Igneous Complex, South Africa was received from the Centre for Minerals Research (CMR) at the chemical engineering department of Cape Peninsula University of Technology (CPUT) on the Bellville Campus for test work.

An 80 kg ore sample was received crushed. It was screened to confirm the particle size distribution of 100% passing 3 mm. The sample was then blended, riffled and split into representative 1 kg samples using a rotary splitter. The mean copper, nickel and sulphur values from all tests were calculated from the feed and tailing samples (Table 4). The PGE in the ore sample were only present in trace amounts which fall at the lower level of equipment detection. Therefore, no analysis for PGE was conducted.

Table 4: Mean calculated feed values of the ore

| Compound | wt % |
|----------|-------|
| Copper | 0.041 |
| Nickel | 0.096 |
| Sulphur | 0.205 |

The Merensky ore is classed as a PGE dominant ore where the PGMs associate with the small amount of disseminated sulphides present in the layered reef structure. The three main sulphide minerals associated with the PGMs are chalcopyrite, pentlandite and pyrrhotite (Xiao and Laplante, 2004). QEMSCAN analysis of the feed samples presents modal composition of gangue and BMS minerals in the ore (Table 5). Table 5 illustrates that the major gangue minerals in the ore are plagioclase and pyroxene.

Table 5: Modal composition of sulphide and gangue minerals present in the Merensky ore sample as determined by QEMSCAN (Wiese, 2009).

| Mineral | Feed Ore (%) |
|-----------------|--------------|
| Pentlandite | 0.31 |
| Chalcopyrite | 0.25 |
| Pyrrhotite | 0.44 |
| Pyrite | 0.08 |
| Other Sulphides | 0.02 |
| TOTAL Sulphides | 1.09 |
| Plagioclase | 43.38 |
| Orthopyroxene | 32.60 |
| Clinopyroxene | 7.48 |
| Talc | 3.51 |
| Olivine | 0.59 |
| Serpentine | 0.80 |
| Chlorite | 0.83 |
| Phlogopite | 0.46 |
| Quartz | 0.67 |
| Calcite | 0.18 |
| Oxides | 8.10 |
| Other | 0.32 |
| TOTAL | 100.00 |

3.3 Ore milling

Milling was conducted in a 200 mm diameter stainless steel laboratory rod mill produced by SMC. The mill was charged with 20 stainless steel rods. All rods were 300 mm long; of which twelve were 25 mm and eight were 15 mm in diameter. Water was added, and wet milling was conducted at 60% solids by mass at a mill speed of 90 Hz. No reagents were added to the mill.

A milling curve was constructed by milling three separate samples at 10, 15 and 20 minutes (Figure 10). The milling time to obtain a feed grind of 60% passing 75 μm was determined to be 17 minutes and was confirmed by milling another sample for that time.

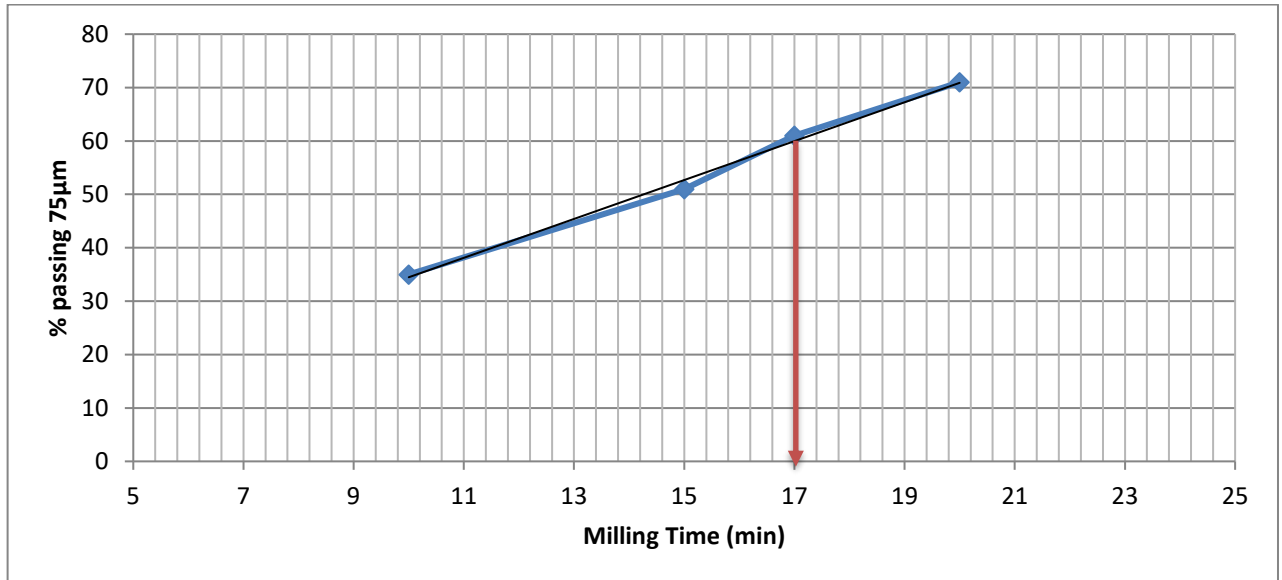


Figure 10: Milling curve for ore

3.4 Flotation reagents

The frother, depressant and all collectors used in this study was supplied by Senmin (Pty) Ltd South Africa. Standard solutions of all reagents were prepared prior to each test with distilled water to avoid decomposition. All reagents were added to the flotation cell.

3.4.1 Collectors

The collectors used in the flotation tests were sodium isobutyl xanthate (SIBX), sodium di-ethyl dithiophosphate (DTP) and sodium di-ethyl dithiocarbamate (DTC). SIBX was received as a yellow powder while DTC and DTP were received as clear yellow solutions. The molar masses and purity of each collector used is summarised in Table 6. All collectors were stored in a refrigerator at approximately 3°C. SIBX was selected as it is the primary collector used in platinum processing operations. Sodium di-ethyl dithiocarbamate and sodium di-ethyl dithiophosphate was selected so that they have the same cation as SIBX. The hydrocarbon chain length in the structure of the molecules for the selected DTC and DTP were also the same. Collector preparation is given in *Appendix A*.

Table 6: Specifications of collectors used in this study

| Collector | Abbreviation | Molecular structure | Molar mass (g/mol) | Purity (wt. %) |
|---------------------------------|--------------|----------------------|--------------------|----------------|
| Sodium Isobutyl Xanthate | SIBX | $C_4H_9OCS_2Na$ | 172 | 97 |
| Sodium di-ethyl Dithiocarbamate | DTC | $C_5H_{10}NS_2Na$ | 171 | 45 |
| Sodium di-ethyl Dithiophosphate | DTP | $C_4H_{10}NaO_2PS_2$ | 208 | 46 |

3.4.2 Frother

The study made use of the polyglycol ether frother, Senfroth 200, at a dosage of 40 g/t for all batch flotation tests.

3.4.3 Depressant

Initial tests were conducted without the addition of a depressant. However, later repeat tests were conducted with the carboxymethyl cellulose (CMC) depressant, Norilose 8058, at a dosage of 100 g/t. Depressant solutions were prepared by slowly adding the powdered depressant into the vortex that formed from the agitation of water in a beaker by a magnetic stirrer. Once all the depressant was added, the solution was allowed to agitate for 2 hours, until the solution was homogenous.

3.5 Collector dosage

In order to quantify differences in metallurgical performance between collectors, it was necessary to determine an appropriate collector dosage that would ensure that the same amount of collector is added to the ore regardless of purity or molar mass. A dosage that is too low might not render the mineral surfaces sufficiently hydrophobic, and a dosage that is too high might remove any observable metallurgical differences between different collectors. Tests were performed at dosages of 0 g/t, 50 g/t, 100 g/t, 150 g/t and 200 g/t to determine the optimum dosage of SIBX required on the ore by analysing nickel, copper and sulphur recoveries. SIBX was selected as baseline in this study as it is the primary collector used in platinum processing. The results from these tests are illustrated in Figure 11. It is illustrated that copper recovery was not a function of collector concentration, but that the addition of collector does improve recovery. Nickel and sulphur recovery was a function of collector concentration until 100 g/t, after which the recovery decreased. The dosage of 50 g/t was selected as the most appropriate dosage since it showed to sufficiently render the minerals surfaces hydrophobic without over-dosing. The 50 g/t dosage was equivalent to a molar dosage of 282 mmol/t and all subsequent tests were conducted to at this dosage.

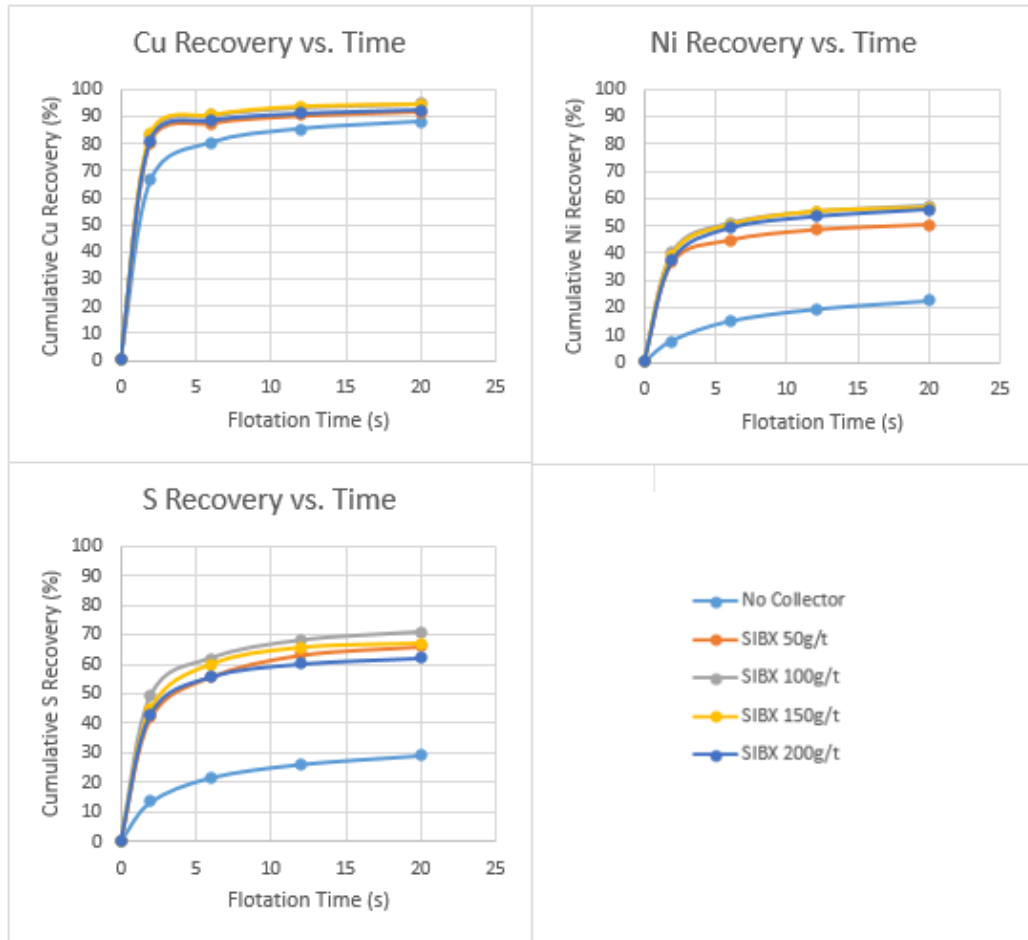


Figure 11: Graphs of cumulative copper, nickel and sulphur recoveries for SIBX collector at different dosages.

The molar ratios for the mixtures of SIBX with DTC and DTP were varied as shown in Table 7. The xanthate, SIBX, was maintained as the major component in all mixtures. All mixtures were premixed and added into the flotation cell.

Table 7: Molar ratios used in mixed collector suites

| | Mole ratio | | | | | | |
|------------|------------|----|----|----|----|----|-----|
| SIBX | 100 | 90 | 80 | 70 | 60 | 50 | 0 |
| DTC or DTP | 0 | 10 | 20 | 30 | 40 | 50 | 100 |

Table 8 shows the molar ratios employed to evaluate the effect of depressant on the mixtures of SIBX with DTC and DTP.

Table 8: Molar ratio used for tests with depressant

| | Mole ratio | | | | |
|------------|------------|----|----|----|-----|
| SIBX | 100 | 90 | 70 | 50 | 0 |
| DTC or DTP | 0 | 10 | 30 | 50 | 100 |

3.6 Apparatus

3.6.1 Rod Mill

The ore sample was received crushed and subsequently milled to the required size for flotation in a stainless steel rod mill. Figure 12 is a photograph of the rod mill used in this study.



Figure 12: Image of the rod mill used for grinding the ore samples

3.6.2 Flotation Cell

The flotation cell used was a Leeds laboratory cell with a 3 L capacity (Figure 13). The impeller was fitted with a speed controller and the air flow rate was adjustable. The pulp level was maintained by the manual addition of water into the cell to have a froth height of 2.0 cm. The slurry density in the cell was approximately 35% solids.



Figure 13: Image of the Leeds flotation cell used in the batch flotation tests

3.6.2.1 Flotation procedure

After wet milling the ore sample to the desired size, the sample was transferred into a 3 L flotation cell. The impeller speed was adjusted to 1200 rpm and water was added to the cell until the pulp level allowed a froth height of 2 cm. Slaked lime was added to increase the slurry pH to 10. A 25 ml feed sample was taken from the stirred slurry. The collector was then added under the surface of the slurry and conditioned for two minutes after which the frother was added in the same manner and conditioned for one minute. The air was switched on and maintained at a flow rate of 7 l/min. This signalled the start of flotation and the froth was scraped into the concentrate collection dishes every 15 seconds. Cumulative concentrate samples were collected after 2, 6, 12 and 20 minute of flotation time. The pulp level was maintained throughout by the manual addition of water into the cell. After the flotation time elapsed the air was switched off and a 25 ml tailing sample was collected from the pulp. The tailings was removed from the cell and were pressure filtered and dried. The feed, tailings and concentrates collected were filtered and dried in a low-heat oven at 60°C. Dried samples were weighed and analysed for copper and nickel. Table 9 summarises the experimental flotation procedure.

Table 9: Summary of batch flotation procedure

| Action | Reagent suites without depressant | Reagent suites with depressant |
|---|-----------------------------------|--------------------------------|
| | Time (min) | Time (min) |
| pH adjusted | 0 | 0 |
| Collection of feed sample | 4 | 4 |
| Addition of depressant | - | 5 |
| Addition of collector | 5 | 7 |
| Addition of frother | 7 | 9 |
| Air turned on | 8 | 10 |
| C1 | 10 | 12 |
| C2 | 14 | 16 |
| C3 | 20 | 22 |
| C4 | 28 | 30 |
| Air turned off and collection of tailing sample | | |

The tests that involved the addition of depressant had an added step where the depressant was added prior to the collector and conditioned for two minutes. All tests conditions for subsequent tests were maintained and tests were conducted in duplicate. Copper and nickel analysis were conducted by XRF spectrometer and sulphur analysis by LECO analysis. Particle size distribution (PSD) was established by Malvern analysis. XRF analysis was carried out by the Central Analytical Facilities at the University of Stellenbosch and Axis House. The results from both facilities corresponded. LECO analysis and PSD was conducted by the Analytical Laboratory at the chemical engineering department of the University of Cape Town.

XRF and LECO data was used to calculate metal grade and recoveries. See Appendix B for calculation details.

CHAPTER 4

4 Results and Discussion

This chapter discusses the results from batch froth flotation tests conducted to investigate the effect of collector type and ratio within a mixture on the performance of a Merensky Reef ore. The conditions for the tests were:

- Pure SIBX collector at various dosages to determine an optimum molar dosage for all batch froth flotation tests.
- Pure sodium diethyl dithiophosphate and sodium diethyl dithiocarbamate at an equal molar dosage, as determined by pure SIBX. These results provided characteristics of each collector's effect on the flotation performance for the particular ore. These results served as the baseline for comparison of flotation performance.
- Collector mixtures with DTP and DTC as respective co-collectors with SIBX at various ratios.
- Collector mixtures with DTP and DTC as respective co-collectors with SIBX at various ratios in the presence of a depressant.

The mass and water recoveries, recoveries and grades of copper and nickel and the rate of flotation were used to evaluate the performance of each collector and collector mixture. Further analyses were conducted to characterise the differences in flotation behaviour of the different collectors. These tests were:

- LECO sulphur analysis of concentrates for the estimation of sulphur recoveries
- Malvern particle size analysis of concentrates for the evaluation flotation behaviour on different size classes.

4.1 Reproducibility

In systems where the effect of a single variable are evaluated, meaningful conclusions may only be drawn if the contributions from the other variables in the system are negligible (Chhabra, 2014). Furthermore, the results need to be reproducible within a certain level of confidence. Batch flotation tests were conducted in duplicate to determine the standard error associated with a particular test result. The standard error was calculated by dividing the standard deviation by the square root of the sample size, and used as a guide to evaluate the reproducibility of the data. The results were considered reproducible when the standard error was below 5% for all data evaluated.

4.1.1 Feed Characterisation

In order to conduct substantial comparisons among the performances of the various collector investigated, the feed samples for all tests needed to be analogous in terms of mass and particle size distribution. Each individual sample was handled and processed in the same manner. To determine whether the feed samples for subsequent tests were comparable and consistent, four random samples of feed material used in the flotation tests were analysed for particle size distribution (PSD) using a Malvern analyser. Each random feed sample was taken from the pulp of the flotation cell. The results of the analysis (Figure 14) show that the samples had reproducible particle size distributions of $P_{60} 75 \pm 5 \mu\text{m}$, which confirms consistency of feed composition between different tests and correct milling time of 18 minutes.

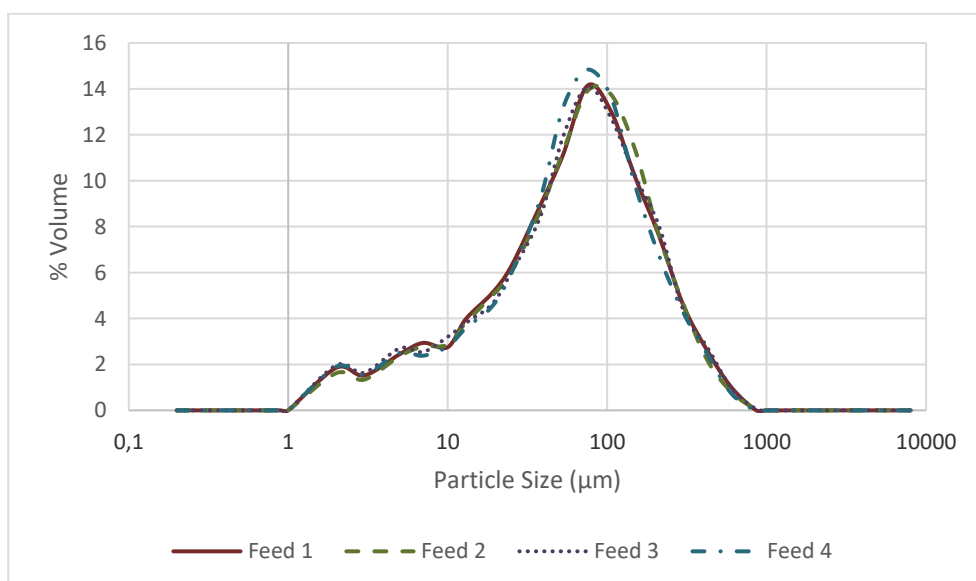


Figure 14: Particle size distribution of four randomly chosen samples

The mean copper, nickel and sulphur grades for all ore samples prior to testing were determined from the feed, concentrate and tailing samples (Table 10). The negligible standard error for the feed composition further confirms consistency of the sampling process of the feed samples. No analysis for PGE was conducted. The composition of the ore used in this study is similar to that used by Wiese (2009).

Table 10: Mean calculated feed values for the ore

| | Average, wt % | Standard Error |
|---------|---------------|----------------|
| Copper | 0.06 | 0.01 |
| Nickel | 0.14 | 0.01 |
| Sulphur | 0.28 | 0.02 |

4.1.2 Batch Froth Flotation Tests

Batch froth flotation tests were conducted in duplicate with the exceptions of the no-collector test and tests with added depressant. The standard deviations of the means from these tests are presented as error bars on graphs throughout this thesis. The standard deviation was divided by the square root of the sample size to determine the standard error. The results for the tests were considered reproducible when the standard error fell within a particular range. Bezuidenhout (2011) suggested that a general rule of thumb for standard error between duplicate batch flotation tests performed in a 3 L cell charged with a 1 kg ore sample, is that the difference in water recovery and concentrate mass between the tests may not exceed 50 g and 5 g respectively. This corresponds to a standard deviation of 2% for water recovery and 1% for mass recovery when the recoveries are considered as a percentage of the original content present in the cell (1 kg sample and 3 L cell with pulp density of 35%). All tests conducted fall within these error limits and the results from this point of view may be regarded as reproducible and within standard error.

4.2 Single Collectors

This section describes the results of batch froth flotation tests conducted to investigate the response of various pure collectors at equivalent dosages in terms of mass and water recoveries, copper and nickel grades and recoveries and the rate of flotation on the platinum ore.

4.2.1 Introduction

The cation for all thiol collectors used in this study is the same. The hydrocarbon chain length between the DTC and DTP collectors was also the same. Variations in flotation responses between the different collectors will therefore be due to the different properties associated with the functional group of each collector and its interactions with the minerals' surfaces.

Table 11 summarises the final recoveries and grades obtained with tests of the various collectors and will be used in this section for quantitative comparisons.

Table 11: Final grades and recoveries obtained for pure collectors

| | Final Cumulative Concentrate Mass Recovery (%) | Final Cumulative Water Recovery (%) | Final Cumulative Copper Recovery (%) | Final Cumulative Copper Grade (%) | Final Cumulative Nickel Recovery (%) | Final Cumulative Nickel Grade (%) |
|--------------|--|-------------------------------------|--------------------------------------|-----------------------------------|--------------------------------------|-----------------------------------|
| No Collector | 5.87 | 14.4 | 88.0 | 0.43 | 22.5 | 0.32 |
| SIBX | 8.98 | 22.2 | 90.0 | 0.41 | 53.8 | 0.58 |
| DTC | 10.1 | 40.5 | 89.6 | 0.38 | 59.3 | 0.55 |
| DTP | 22.6 | 84.5 | 95.7 | 0.14 | 64.4 | 0.30 |

4.2.2 Water and Mass Recovery

A froth should be stable enough to allow for concentrate transfer into a launder, while still allowing for the drainage of entrained hydrophilic particles. Without sufficient drainage, the levels of entrainment are high, resulting in low concentrate grades. Water recovery is a strong indicator of entrainment due to froth stability. To investigate these phenomena, the cumulative concentrate mass recoveries and cumulative water recoveries for no collector, pure SIBX, DTC and DTP are presented (Figure 15).

The cumulative water recoveries decreased in the following order; DTP (84.5%) > DTC (40.5%) > SIBX (22.2%) > no collector (14.4%). The cumulative mass recoveries followed the

same trend and the numerical values were 22.6%, 10.1%, 8.98% and 5.87% respectively (Table 11).

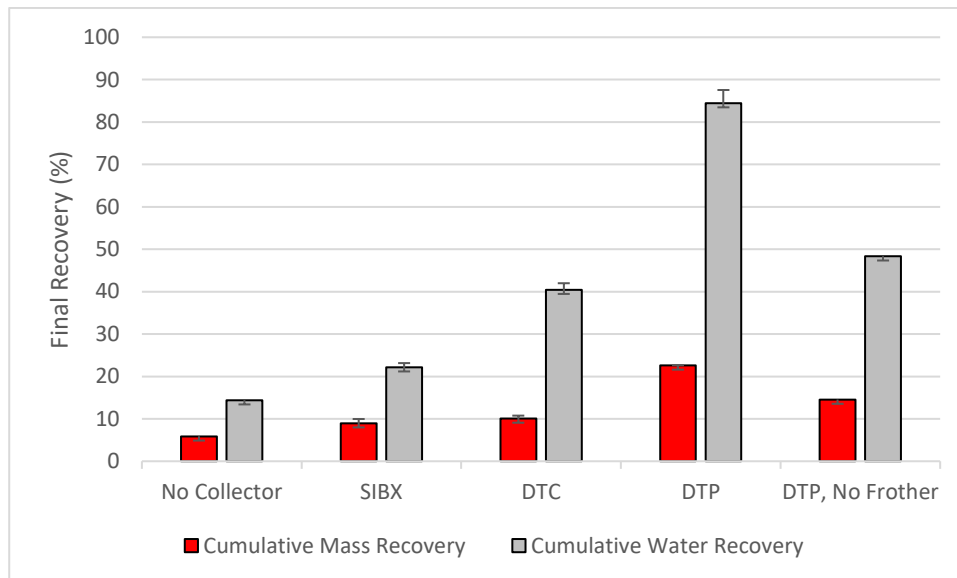


Figure 15: Cumulative mass and water recovery obtained with no collector, SIBX, DTC, DTP and DTP without frother

Addition of both SIBX and DTC increased both the mass and water recoveries compared to no collector (Figure 15). The increased water recoveries suggests that both SIBX and DTC may have increased the froth stability. Two phase tests conducted by Nyambayo (2014), illustrated that SIBX and a dithiocarbamate increased water recoveries over that of no collector by 52% and 111% respectively. Further, three-phase tests showed minimal increase in water recovery over no collector. The increased mass recoveries may have been due to the increased hydrophobicity imparted to the surfaces of the sulphide mineral particles with the addition of collectors. The increased hydrophobicity and subsequent mass recoveries may have contributed to the froth stability. The fact that no depressant was used may suggest that the collectors affected the floatability of the talc within the ore which, when floated, stabilised the froth.

The higher mass and water recoveries observed with DTP over pure SIBX, DTC and no collector suggest that it contributed to the formation of froth and its stability (Stamboliadis, 1976). The high mass and water recoveries achieved with DTP in the absence of a frother confirmed that it promoted froth stability. The higher froth stability decreased the rate of bubble breakage in the froth phase which increased the froth height and decreased the rate of water drainage (Aktas et al., 2008).

The froth stabilising effects of dithiophosphates have been reported (Corin et al., 2012). This was confirmed by a test conducted with DTP in the absence of a frother (Figure 15). The test with no collector was used to establish the natural flotability of minerals within the ore and any mass recovered was either due to the natural hydrophobicity of the mineral surfaces in the ore or due to entrainment of particles in the froth phase. As no depressant was used in this section of the work, either of the mechanisms may have been responsible for the particles that reported to the concentrates.

Theoretically xanthate and dithiocarbamate collectors have insignificant frothing properties. The production of dithiophosphates however uses an alcohol as reactant during synthesis and the DTP is subsequently stored in excess alcohol that may act as a frother and increase froth stability (Stamboliadis, 1976). This effect is most prevalent in longer chained DTP's.

4.2.3 Copper Grade and Recovery

Grade recovery curves are used to display the metallurgical performance of the flotation process. Increased metallurgical performance is represented by a point furthest from the origin, i.e. towards the top right of the curve. It is desired to collect as much of the desired pay-metal as possible at an economically viable grade.

The cumulative grade vs. recovery curves for the flotation of copper with the single collectors are presented in Figure 16. The final cumulative copper recoveries displayed the following trend; DTP (96%) > SIBX (90%) = DTC (90%) \approx no collector (88%). The cumulative copper grades displayed the following trend; no collector (0.43%) \approx SIBX (0.41%) \approx DTC (0.38%) > DTP (0.14%).

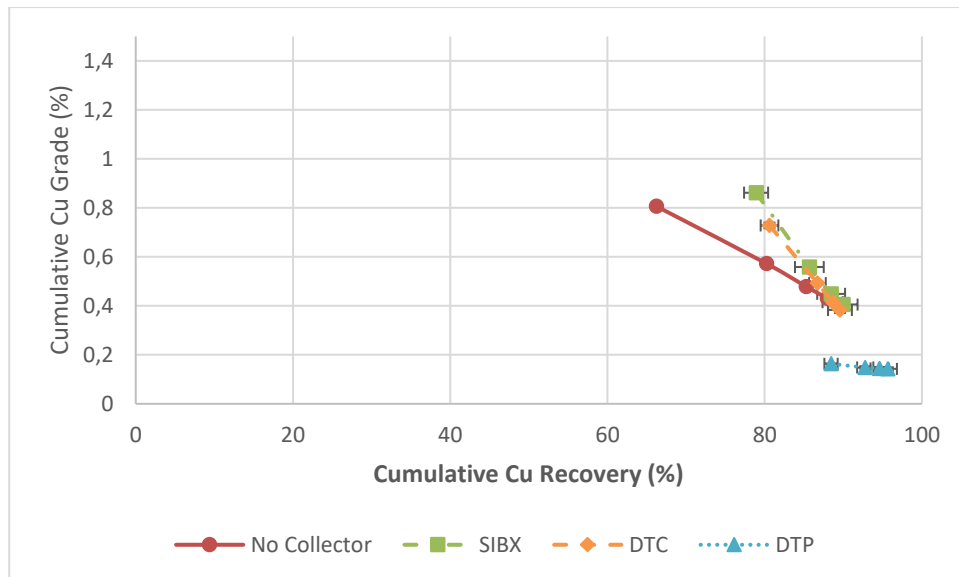


Figure 16: Percentage cumulative copper grade versus cumulative copper recovery for the single collectors.

Previous studies have shown that the decreasing order of collector selectivity, of which grade was an indicator, has DTC > Xanthate > DTP > no collector (Ngobeni and Hangone, 2013; Bulatovic, 2010). However, in this study it was observed that the absence of a collector produced a final copper grade and recovery not significantly different from those obtained with DTC and SIBX (Figure 16). This may have been due to the natural hydrophobicity and floatability of chalcopyrite; the only copper mineral present in the ore. The low water recovery with no collector indicated that the froth was sufficiently unstable to allow for adequate drainage of the entrained hydrophilic minerals while keeping the chalcopyrite which may have contributed to the higher copper grade. Hydrophobic talc may have been responsible for low grades achieved with SIBX and DTC. DTP collected 96% of the copper present, but at a very low grade. This indicated that the copper may not only have floated by true flotation, but in addition reported to the concentrate via entrainment.

4.2.4 Nickel Grade and Recovery

The majority of the PGEs in the Merensky Reef are associated with pentlandite (Bulatovic, 2010; Jones, 1999). Therefore an increase in nickel recovery is desirable. Pentlandite is not sufficiently naturally hydrophobic and the addition of collectors is required for its recovery by froth flotation.

Figure 17 shows the cumulative nickel grades vs. recovery curves for the flotation of nickel with the single collectors. The final cumulative nickel recoveries obtained decreased in the

order DTP (64.4%) > DTC (59.3%) > SIBX (53.8%) > no collector (22.5%). The final cumulative nickel grade decreased in the order SIBX (0.58%) \approx DTC (0.55%) > DTP (0.32%) \approx no collector (0.30%).

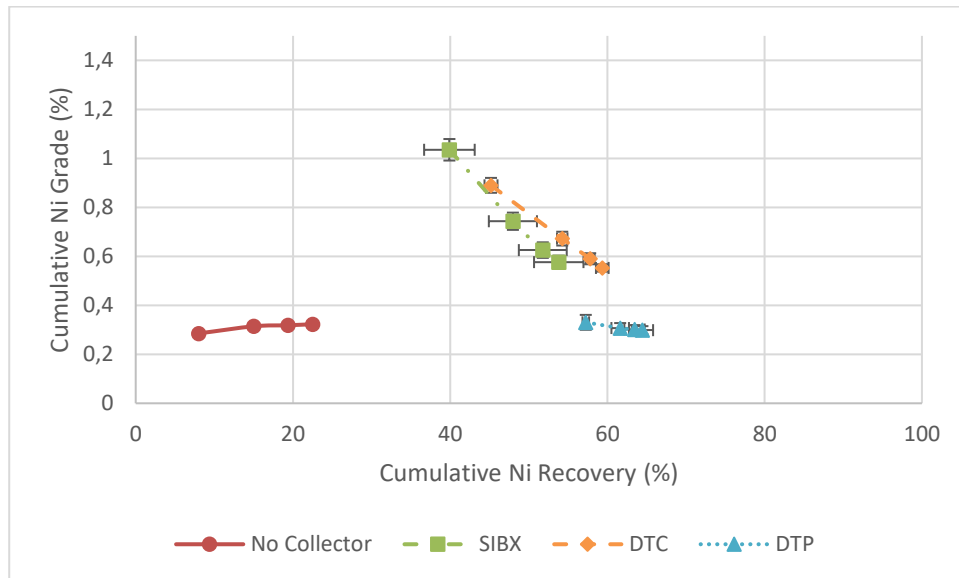


Figure 17: Percentage cumulative copper grade versus cumulative copper recovery for the single collectors.

The addition of a collector produced significant increases in both nickel recoveries and grades except for DTP, which increased only the nickel recovery. The frothing property of DTP, evident from the higher water and mass recoveries over that obtained with SIBX and DTC, led to the higher nickel recovery at a lower nickel grade. The low grade with DTP may confirm the claim that dithiophosphates do not form insoluble nickel compounds and are thus not rendered hydrophobic (Stamboliadis, 1976). The increased nickel recovery with DTC compared to SIBX may have been due to its greater selectivity as the larger water recovery obtained was not accompanied by a significantly larger mass recovery than obtained with SIBX (Figure 15). The increased nickel recovery obtained with DTC may also suggest that the metal-thiolate formation with DTC was preferred to the formation of dixanthogen with SIBX. DTP showed no interaction with the nickel (pentlandite).

4.2.5 Froth Flotation Kinetics

Chalcopyrite was the only copper mineral present in the platinum ore used in this study. Chalcopyrite is naturally hydrophobic with a high rate of flotation (Wills and Napier-Munn, 2006). The highest copper recovery was achieved with DTP, while the recoveries obtained with DTC and SIBX were comparable, but 6% lower than with DTP (Figure 18). The results

also show that the majority of the copper was recovered within 2 minutes, after which the curves flattened, which supports theory that the chalcopyrite was fast floating.

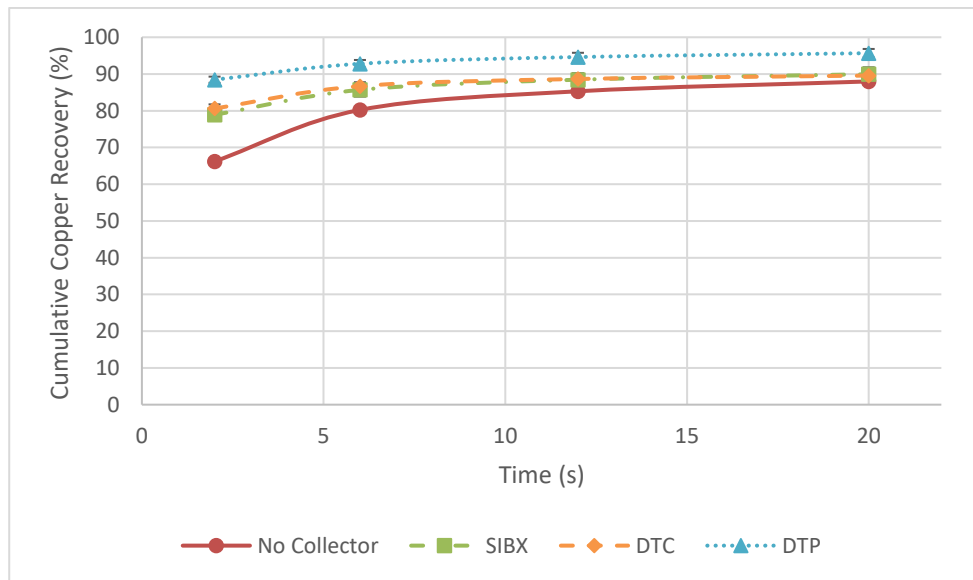


Figure 18: Cumulative copper recovery vs. flotation time for pure collectors.

Figure 19 shows the recovery of nickel as a function of time for the different pure collectors. The results indicate that, as with copper, DTP produced the highest nickel recovery. There was more variation in the recoveries of nickel between the different pure collectors as compared to copper recovery. The cumulative nickel recoveries obtained decreased in the order DTP > DTC > SIBX > no collector. The results indicate that the addition of a collector doubled the recovery of nickel. This suggests that the surfaces of the nickel minerals are not sufficiently hydrophobic and require collectors to alter their hydrophobicity and consequent flotability. The percentage of nickel recovery observed (50-65%) was less than the recovery of copper (90%). This may be attributed to the significant amount of non-sulphide nickel minerals present in the Merensky ore, whereas copper was only present as the sulphide, chalcopyrite. Pentlandite is considered to be a slow floating mineral (Fuerstenau, 2007). This would imply that recovery versus time curves for nickel recovery should only plateau after a substantial period of time. This trend was observed with no collector, SIBX and DTC. DTP, even though it recovered the largest cumulative nickel, recovered only 7% of its cumulative nickel in the final 18 minutes of flotation. This would suggest that the recovery of the nickel with DTP was not via true flotation and further confirms its froth stabilising effects which may have caused entrainment of non-sulphide nickel minerals to the concentrates.

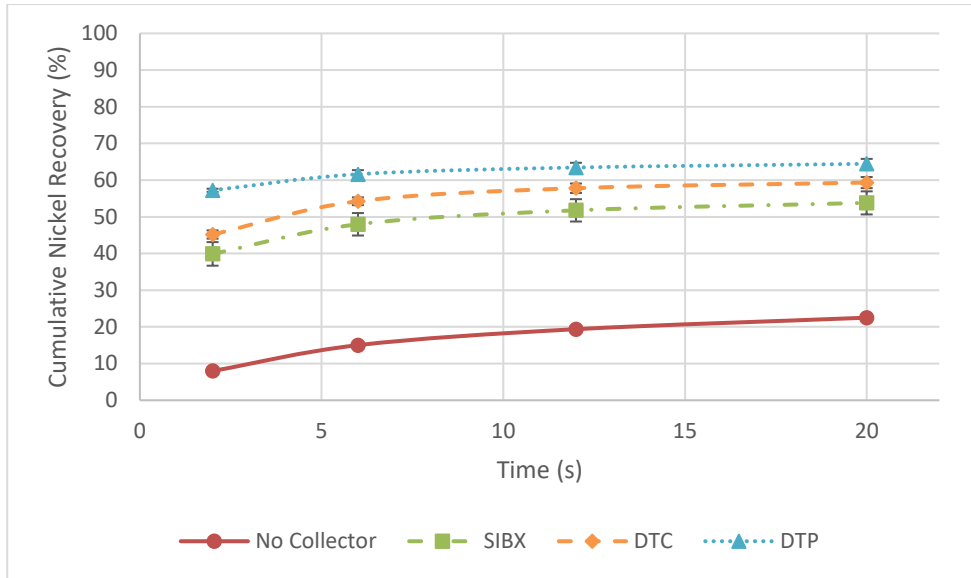


Figure 19: Cumulative nickel recovery vs. flotation time for pure collectors.

Table 12 shows the maximum copper and nickel recoveries as well as the first order rate constants obtained with the various pure collectors. R_{max} was calculated as the infinite time maximum recovery using first order kinetics while the actual recovery was the recovery obtained from the flotation tests. The table shows that for both the copper and nickel recoveries, the actual recovery is not significantly lower than the infinite time recovery. This suggests that the residence time for both copper and nickel flotation was sufficient.

Table 12: The rate of flotation (k) and maximum recovery for copper (R_{max}) with pure collectors

| Collector | Max Copper Recovery (%) | | Max Nickel Recovery (%) | | Rate Constant, k (min^{-1}) | |
|--------------|-------------------------|---------------|-------------------------|---------------|--|--------|
| | Actual | R_{max} (%) | Actual | R_{max} (%) | Copper | Nickel |
| No Collector | 88 | 89.5 | 22.5 | 25.5 | 1.85 | 0.37 |
| SIBX | 90 | 90.5 | 53.8 | 54.4 | 3.84 | 1.78 |
| DTC | 89.6 | 90.3 | 59.3 | 60.4 | 4.63 | 1.91 |
| DTP | 95.7 | 95.9 | 64.4 | 64.8 | 6.27 | 4.29 |

The rate constants calculated for copper are higher than for nickel for each of the tests performed. DTP yielded the highest rate constants for both copper and nickel recovery. Tests conducted by Bezuidenhout (2011) also indicated that diethyl DTP yielded higher copper and nickel flotation rates than SIBX. In PGE flotation, nickel recoveries are often used as proxy for pentlandite flotation (Wiese, 2009). The rate constant for nickel recovery with DTP, at more than double that of any other collector, is significantly higher than for the other tests. This indicates that DTP may have improved the rate of flotation for the slow floating pentlandite. The lack of adsorption affinity between DTP and pentlandite however makes this improbable. DTC and SIBX form adsorption species with pentlandite and their recoveries and rates

achieved for nickel may more accurately describe those for pentlandite in the ore. The high nickel recovery and rate of flotation with DTP may represent those of nickel, but not pentlandite. The higher rates achieved for copper and nickel with DTC over SIBX may suggest that the metal-thiolate species form faster than the dixanthogen species.

4.3 Collector Mixtures of SIBX and DTC

This section describes the results of batch froth flotation tests conducted to investigate the response of SIBX mixtures with DTC at varying ratios on mass and water recoveries, copper and nickel grades and recoveries and the rate of flotation on the platinum ore.

The flotation procedure for this section of the work was the same as for the pure collectors. The total collector concentration used was 282 mmol/t per flotation test.

The naming convention for the mixtures is such that SIBX and its molar contribution is mentioned first, followed by the molar ratio of DTC. For example, SIBX 70:30 DTC represents a mixture that contains 70 mol% SIBX and 30 mol% DTC. The collectors were premixed and added to the flotation cell.

Table 13 summarises the final recoveries and grades obtained with tests of the various collector mixtures of SIBX with DTC and will be used throughout this section for quantitative comparisons.

Table 13: Final grades and recoveries obtained for mixtures of SIBX with DTC at various ratios

| | Cumulative Concentrate Mass (%) | Cumulative Water Recovery (%) | Cumulative Copper Recovery (%) | Cumulative Copper Grade (%) | Cumulative Nickel Recovery (%) | Cumulative Nickel Grade (%) |
|----------------|---------------------------------|-------------------------------|--------------------------------|-----------------------------|--------------------------------|-----------------------------|
| Pure SIBX | 8.98 | 22.2 | 90.0 | 0.41 | 53.8 | 0.58 |
| SIBX 90:10 DTC | 12.2 | 48.0 | 91.0 | 0.38 | 62.9 | 0.53 |
| SIBX 80:20 DTC | 10.3 | 40.0 | 89.0 | 0.37 | 59.2 | 0.54 |
| SIBX 70:30 DTC | 10.7 | 40.2 | 90.8 | 0.38 | 61.2 | 0.52 |
| SIBX 60:40 DTC | 10.6 | 39.8 | 91.2 | 0.35 | 61.2 | 0.53 |
| SIBX 50:50 DTC | 11.1 | 44.2 | 90.0 | 0.35 | 61.2 | 0.53 |
| SIBX 40:60 DTC | 10.9 | 43.2 | 88.5 | 0.35 | 57.5 | 0.51 |
| SIBX 20:80 DTC | 11.0 | 40.9 | 90.3 | 0.32 | 59.3 | 0.52 |
| Pure DTC | 10.1 | 40.5 | 89.6 | 0.38 | 59.3 | 0.55 |

4.3.1 Water and Mass Recovery

Figure 20 shows the cumulative mass and water recoveries obtained with varying proportions of DTC mixed with SIBX. The water recovery with pure SIBX is significantly lower than that obtained with pure DTC and the mixtures of SIBX and DTC. This suggests that DTC had some froth stabilising effect on the system. The mixture of SIBX 90:10 DTC was the mixture with the lowest concentration of DTC in the range tested, yet it produced the highest water recovery (Figure 20). This indicates that only a small addition of DTC to SIBX may have significant effects on flotation performance. The increased water recoveries and consequent froth stability in the tests which contained DTC yielded higher mass recoveries over pure SIBX.

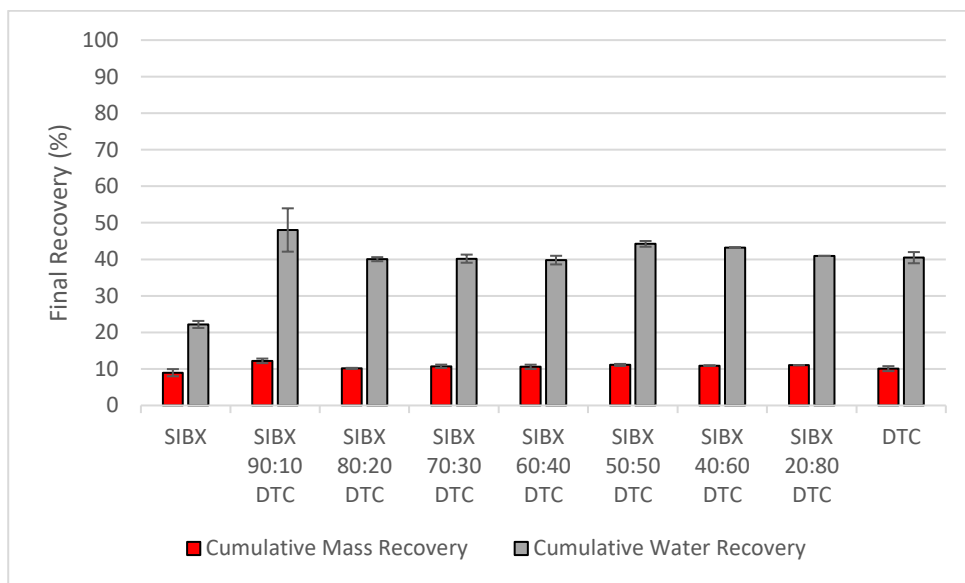


Figure 20: Cumulative mass and water recoveries obtained with mixtures of DTC with SIBX.

The mixture of SIBX 90:10 DTC also yielded the highest mass recovery due to the increased water recovery. The mass recoveries achieved for all mixtures of SIBX and DTC were higher than those achieved with the pure collectors. The mass recoveries for the SIBX 70:30 DTC and SIBX 60:40 DTC mixtures were higher than the mass recovery of pure DTC even though the water recoveries were the same. The increased mass recovery was independent of the concentrations of the constituents in the mixture. This suggests that mixtures of SIBX with DTC may increase the hydrophobicity of the minerals in the cell and may be an indication of synergism.

4.3.2 Copper Grade and Recovery

Figure 21 shows the cumulative copper grades versus recoveries obtained with mixtures of DTC with SIBX at various ratios.

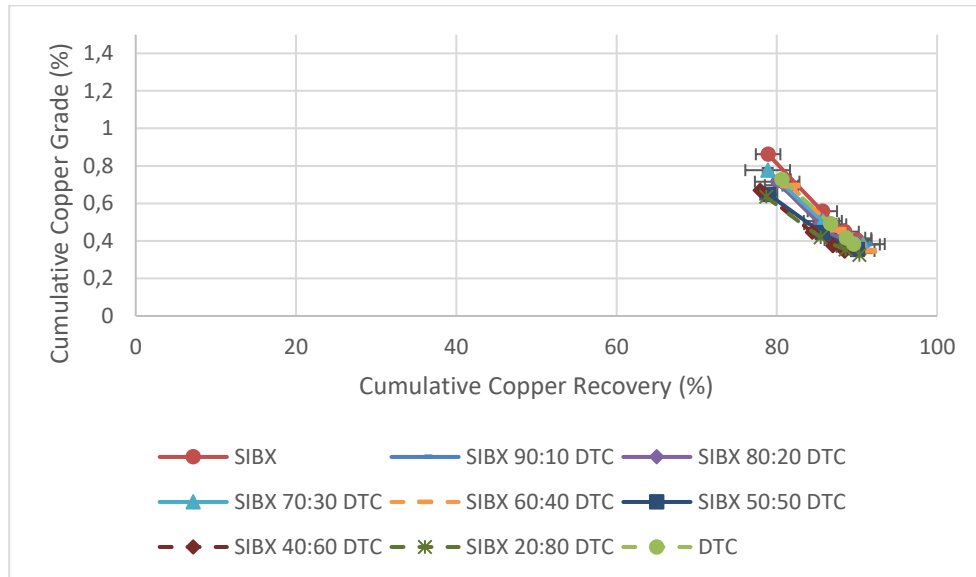


Figure 21: Percentage cumulative copper grade versus cumulative recovery for mixtures of DTC with SIBX.

The graph indicates that the copper recoveries and grades obtained with the mixture of SIBX and DTC were similar. A higher resolution of the data is presented in Figure 22.

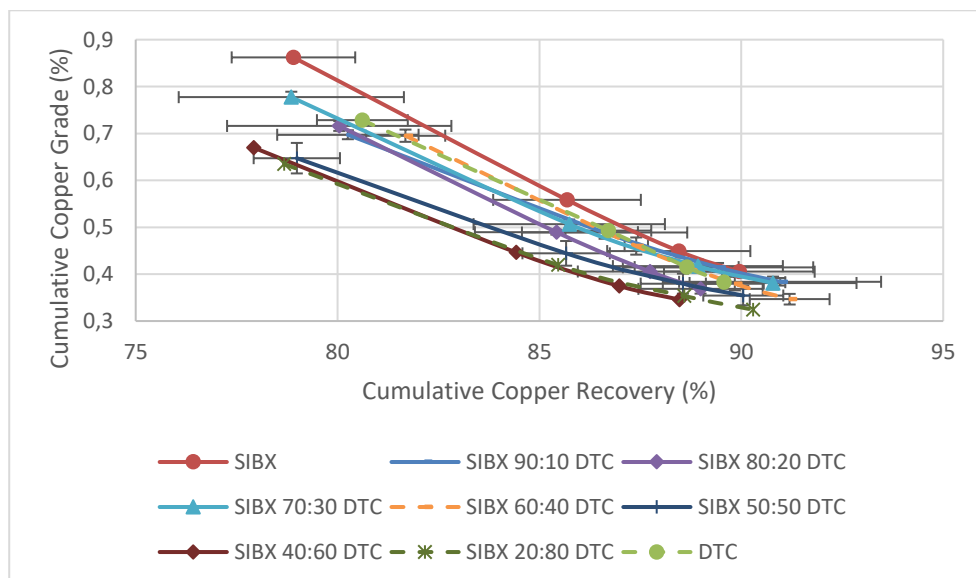


Figure 22: High resolution of grade-recovery curve in Figure 21

There was little variation in the final copper grades achieved in these tests. The SIBX 20:80 DTC mixture yielded the lowest cumulative grade (0.32%), however this test was not

conducted in duplicate and the results may therefore be unreliable. The cumulative grades for the other tests fell within a 0.06% range. SIBX produced the highest final grade (0.41%). This, and the lower water recoveries obtained relative to the mixtures and pure DTC, may suggest the higher grade was due to the lack of a stable froth. The froth with SIBX was sufficiently unstable to drain the entrained gangue and increase the copper grade.

The cumulative copper recovery for pure SIBX, DTC and their mixtures was within a 2% range of 90%. This similarity between the various reagent suites may be due to the fact that the flotation of copper was approaching its maximum. Chalcopyrite readily reacts with collectors as well as being naturally floatable. This suggests that recovery of copper should approach 100%. The feed grind of P₆₀₋₇₅ μm is considered coarse and many minerals included in the lattice of the host rock may not have been liberated (Behuidenhout, 2011). The consistency in feed sample size distribution and metal content suggests that the feed material for different tests were consistent and similar mineral liberations would have been achieved. The final copper recovery may indicate the level of liberation for chalcopyrite.

4.3.3 Nickel Grade and Recovery

Figure 23 shows the cumulative nickel grades versus recoveries obtained with mixtures of SIBX and DTC at various ratios.

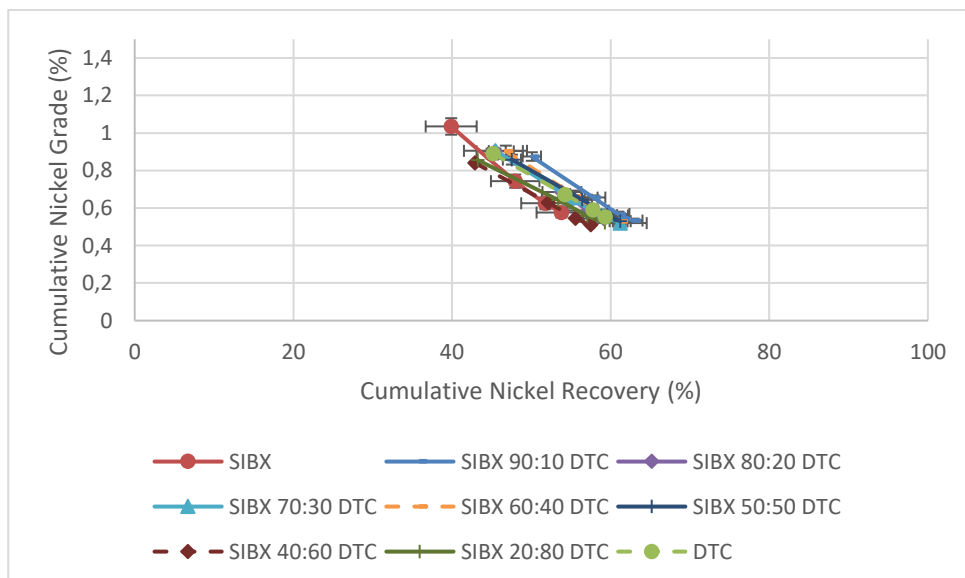


Figure 23: Percentage cumulative nickel grade versus cumulative recovery for mixtures of DTC with SIBX

Similar to copper, the graphs for nickel recoveries and grades with the mixture of SIBX and DTC were comparable. A higher resolution of the data is presented in Figure 24.

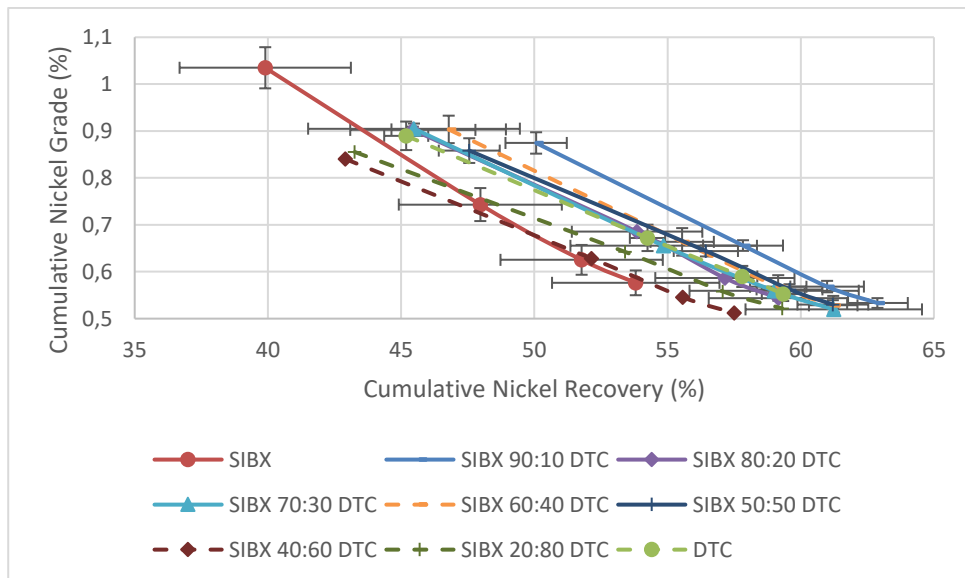


Figure 24: High resolution of grade-recovery curve in Figure 23

The cumulative nickel grades achieved were not significantly different between the various collector mixtures of SIBX and DTC tested. As with copper grade, the highest nickel grade was achieved with pure SIBX. This further emphasises that the less stable froth with SIBX increased the drainage which decreased entrainment.

A significant increase in nickel recovery was observed with pure DTC and the mixtures of SIBX and DTC over pure SIBX. This may have been due to an increase in non-sulphide entrainment to the concentrates as a result of the stabilised froth and increased water recovery, or because the metal-thiolate mechanisms between pentlandite and DTC was favoured in comparison to the dixanthogen formation on pentlandite (Nyambayo, 2014). The mixture of SIBX 90:10 DTC yielded the highest nickel recovery of 62.9%.

The trends in recoveries and grades observed for copper and nickel are summarised in Figure 25. The graph illustrates the effect that an increase in the concentration of DTC in the mixture has on recoveries and grade. On the graphs, 0% DTC represent pure SIBX. There are no occurrences of increased grade and recovery. The mixture of SIBX 90:10 DTC produced higher recoveries over the respective pure collectors for both copper and nickel, however the subsequent grades were reduced. The grades decreased with all mixtures of SIBX and DTC

over their pure constituents. This suggests that alterations in flotation performance was due to a recovery-grade trade off rather than synergism (Kawatra, 1995).

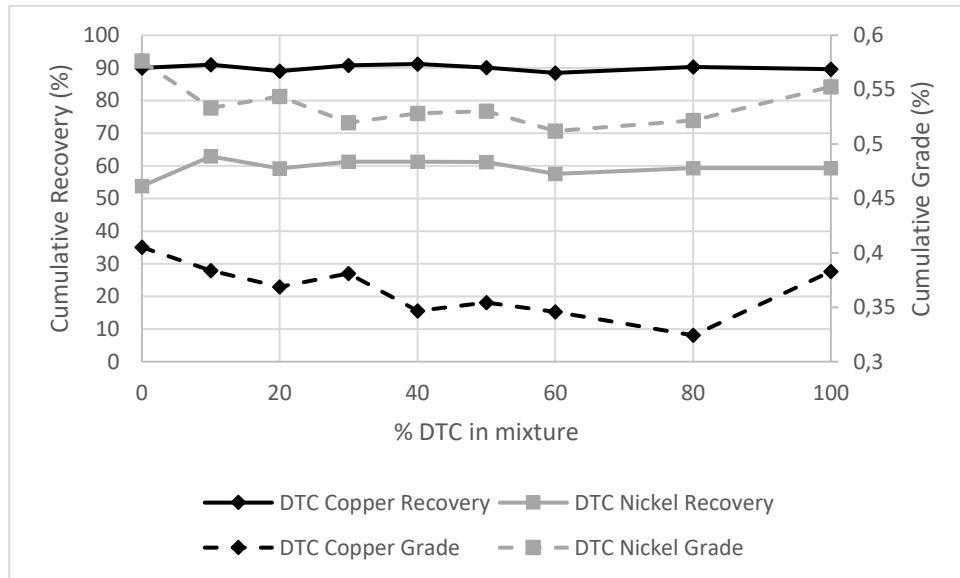


Figure 25: Comparison of final copper and nickel grade and recoveries for the mixtures of SIBX and DTC.

4.3.4 Froth Flotation Kinetics of Mixtures of SIBX and DTC

The different tests on the graph of copper and nickel recovery versus time were indistinguishable due to similar metal recoveries for all tests.

Table 14 shows the maximum copper and nickel recoveries as well as the first order rate constants obtained with the various mixtures of SIBX and DTC. The table shows that for both the copper and nickel recoveries, the actual recovery is not significantly lower than the infinite time recovery. This suggests that the residence time for both copper and nickel flotation was sufficient.

Table 14: The rate of flotation (k) and maximum recovery for copper (R_{max}) with mixtures of SIBX with DTC

| Collector | Max Copper Recovery (%) | | Max Nickel Recovery (%) | | Rate Constant, k (min^{-1}) | |
|----------------|-------------------------|---------------|-------------------------|---------------|--|--------|
| | Actual | R_{max} (%) | Actual | R_{max} (%) | Copper | Nickel |
| SIBX | 90.0 | 90.5 | 53.8 | 54.4 | 3.84 | 1.78 |
| SIBX 90:10 DTC | 91.0 | 91.4 | 62.9 | 63.4 | 4.03 | 2.30 |
| SIBX 80:20 DTC | 89.0 | 89.4 | 59.2 | 59.8 | 4.80 | 2.03 |
| SIBX 70:30 DTC | 90.8 | 91.1 | 61.2 | 61.8 | 3.65 | 1.86 |
| SIBX 60:40 DTC | 91.2 | 91.6 | 61.2 | 61.8 | 4.73 | 2.03 |
| SIBX 50:50 DTC | 90.0 | 90.5 | 61.2 | 62.1 | 3.84 | 2.11 |
| SIBX 40:60 DTC | 88.5 | 88.9 | 57.5 | 58.3 | 3.96 | 1.87 |
| SIBX 20:80 DTC | 90.3 | 90.7 | 59.3 | 60.1 | 3.69 | 1.76 |
| DTC | 89.6 | 95.9 | 59.3 | 60.4 | 4.63 | 1.91 |

The rate constants for copper were at least double ($3.65 - 4.8 \text{ min}^{-1}$) than the rate constants for nickel ($1.76 - 2.30 \text{ min}^{-1}$). This is attributed to the difference in flotation behaviour between chalcopyrite and pentlandite. The highest rate constant was achieved by two different collector mixtures for copper and nickel. SIBX 80:20 DTC produced the highest copper rate constant at (4.80 min^{-1}), while the highest rate constant for nickel was achieved by the SIBX 90:10 DTC mixture at (2.30 min^{-1}). This suggests that the reagent suites interacted differently with the copper and nickel minerals present and that different adsorption mechanisms may have been active.

4.4 Collector Mixtures of SIBX and DTP

This section describes the results of batch froth flotation tests conducted to investigate the response of SIBX mixtures with DTP at varying ratios in terms of mass and water recoveries, copper and nickel grades and recoveries and the rate of flotation on the platinum ore. The results are summarised in Table 15.

A similar naming convention as with the SIBX:DTC collector suites was employed for the SIBX:DTP collector suites, where DTC was replaced with DTP. The collectors were premixed and added to the flotation cell.

Table 15 summarises the final recoveries and grades obtained with tests of collector mixtures between SIBX and DTP. This will be used in this section for quantitative comparisons.

Table 15: Final grades and recoveries obtained for mixtures of SIBX with DTP at various ratios

| | Cumulative Concentrate Mass (%) | Cumulative Water Recovery (%) | Cumulative Copper Recovery (%) | Cumulative Copper Grade (%) | Cumulative Nickel Recovery (%) | Cumulative Nickel Grade (%) |
|----------------|---------------------------------|-------------------------------|--------------------------------|-----------------------------|--------------------------------|-----------------------------|
| SIBX | 8.98 | 22.2 | 90.0 | 0.41 | 53.8 | 0.58 |
| SIBX 90:10 DTP | 11.6 | 48.6 | 95.5 | 0.29 | 59.4 | 0.50 |
| SIBX 80:20 DTP | 11.8 | 53.8 | 97.1 | 0.26 | 58.4 | 0.48 |
| SIBX 70:30 DTP | 14.7 | 61.4 | 96.3 | 0.24 | 61.6 | 0.42 |
| SIBX 60:40 DTP | 15.3 | 63.9 | 97.0 | 0.22 | 61.2 | 0.42 |
| SIBX 50:50 DTP | 18.3 | 71.0 | 96.7 | 0.21 | 65.8 | 0.36 |
| DTP | 22.6 | 84.5 | 95.7 | 0.14 | 64.4 | 0.30 |

4.4.1 Water and Mass Recoveries

Figure 26 shows the cumulative mass and water recoveries for the various mixtures of SIBX and DTP as collector. DTP possesses strong froth stabilising properties. The collector mixtures that contained DTP yielded higher water recoveries than SIBX. The water recovery was found to increase proportionally as the concentration of DTP in the mixture was increased. The frothing properties of DTP resulted in 85% of the original amount of water in the flotation cell reporting to the concentrate with the use of pure DTP. A small addition of DTP to the flotation cell increased the water recovery significantly as the SIBX 90:10 DTP mixture yielded double the water recovery (48.6%) as pure SIBX (22.2%). To put this into perspective, frother was used in these tests at a dosage of 40 g/t. In the SIBX 90:10 DTP mixture, 10% of the 282 mmol/t total molar dosage would be DTP, which is equivalent to 12.7 g/t when corrected for active compound. This represents an extra 31% increase in froth stabilising compound that was added to the pulp.

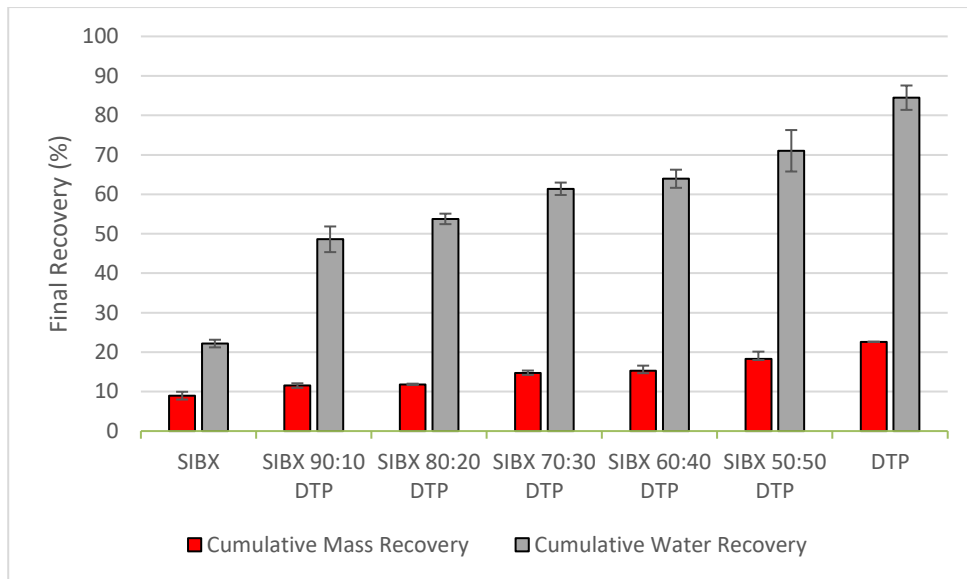


Figure 26: Cumulative mass and water recoveries obtained for mixtures of SIBX with DTC.

An increase in mass recovery proportional to the concentration of DTP in the mixture was observed. This is the same trend observed for water recovery which indicates that the increased mass recoveries were as a result of increased froth stability and entrainment. The total sulphide content of this ore was determined to be only 1.1% (Table 5). This suggests that the mass recoveries of above 11% observed for pure DTP and its mixtures with SIBX consisted predominantly of entrained gangue.

4.4.2 Copper Grade and Recovery

Figure 27 shows the cumulative copper grades versus recoveries obtained with mixtures of DTP with SIBX at various ratios.

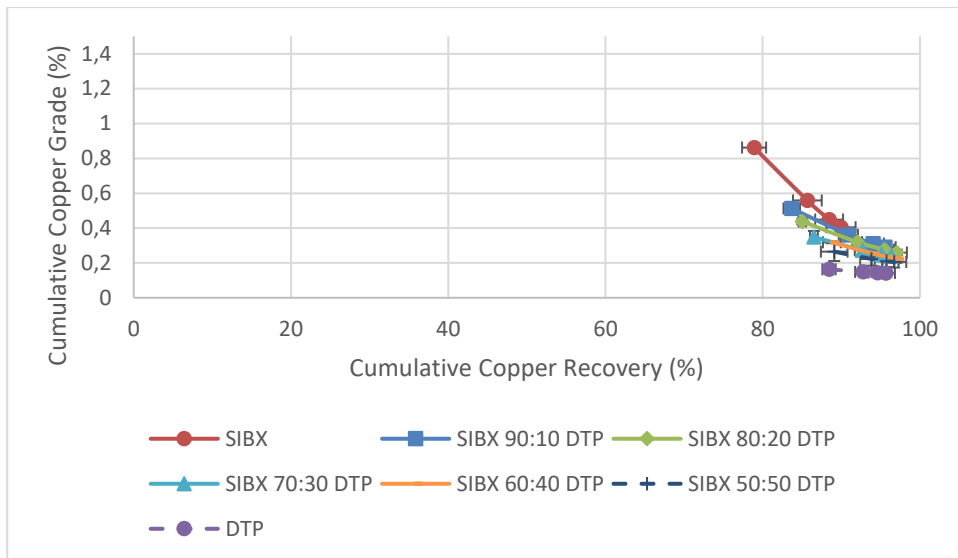


Figure 27: Percentage cumulative copper grade versus cumulative recovery for mixtures of DTP with SIBX.

From the graph it is evident that a trend in grade and recovery for the mixtures of SIBX and DTP does exist. These trends are illustrated in higher resolution (Figure 28).

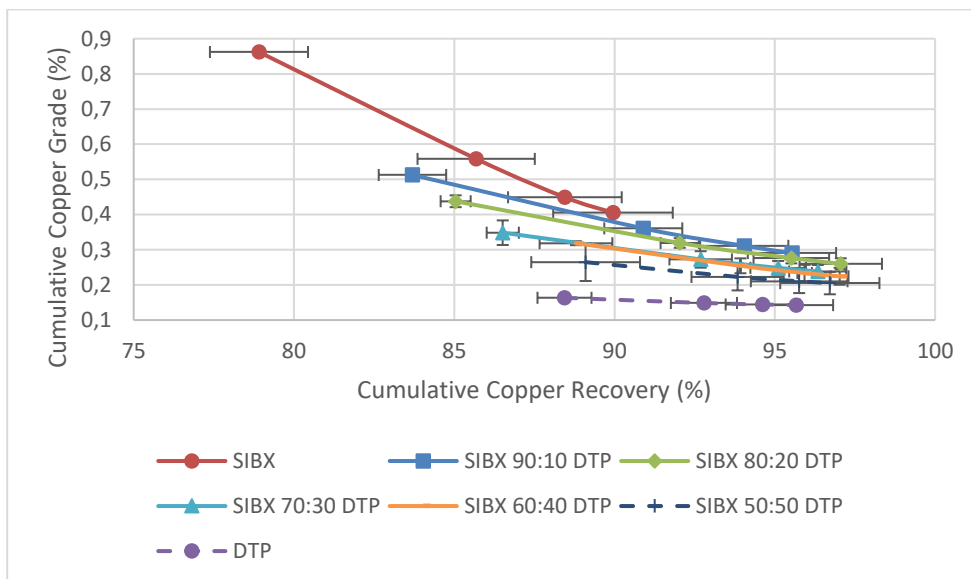


Figure 28: High resolution of grade-recovery curve in Figure 27.

There was a significantly increased cumulative copper recovery for the collector mixtures that contained DTP over pure SIBX (Figure 28). Pure DTP yielded a relatively high copper recovery (95.7%) at a very low grade (0.14%) as a result of the stabilised froth. The mixtures of SIBX and DTP however yielded similar copper recoveries to pure DTP (95-97%) but at significantly higher grade (0.2 – 0.3%). There was no association between the concentrations of DTP in the mixtures to the final copper recovery achieved as a result of the natural floatability of chalcopyrite.

The increased cumulative copper recoveries obtained with the mixtures of SIBX and DTP came at the expense of grade. This may suggest that collector-collector synergism between SIBX and DTP for copper recovery did not occur. The grade of copper decreased with an increase in the concentration of DTP in the mixtures. This may have been due to an increase in froth stability as the concentration of DTP in the mixture increased. At lower concentrations the froth allowed for some drainage of entrained gangue which resulted in the higher copper grades.

The naturally floatable chalcopyrite, was most probably recovered by true flotation, and would not be subjected to drainage from the froth phase (Wills and Napier-Munn, 2006). This explains the high copper recoveries obtained that were, independent of DTP concentration (Figure 28). The entrained gangue particles were subjected to drainage. An increase in the concentration of DTP in the mixture increased the froth stability, which decreased the drainage resulting in the lower grades. The higher mass recoveries, accompanied by an unaffected copper recovery obtained with increased DTP concentration corroborate this theory.

4.4.3 Nickel Grade and Recovery

Figure 28 shows the cumulative nickel grades versus recoveries obtained with mixtures of DTP with SIBX at various ratios.

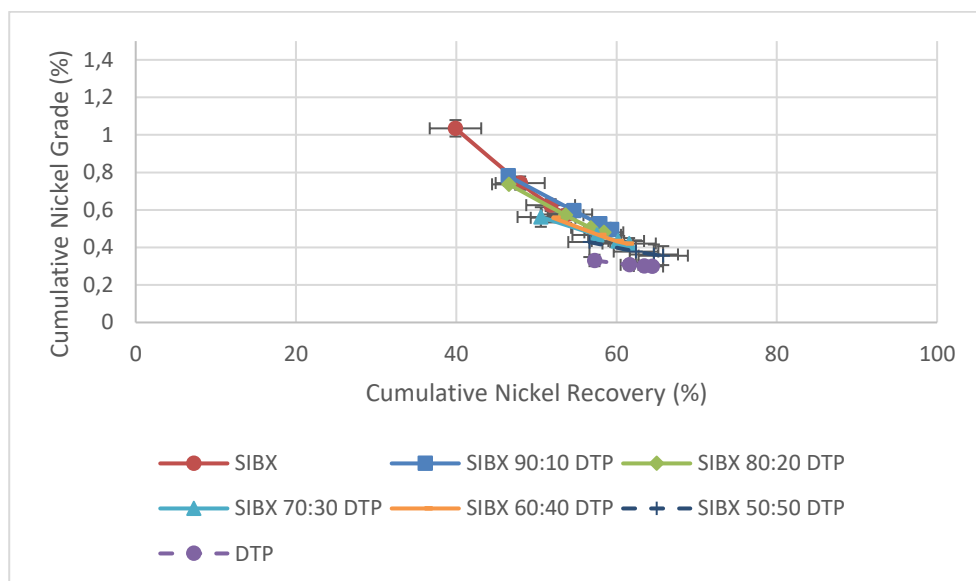


Figure 29: Percentage cumulative nickel grade versus cumulative recovery for mixtures of DTC with SIBX

Higher resolution of nickel recovery and grade is shown in Figure 30.

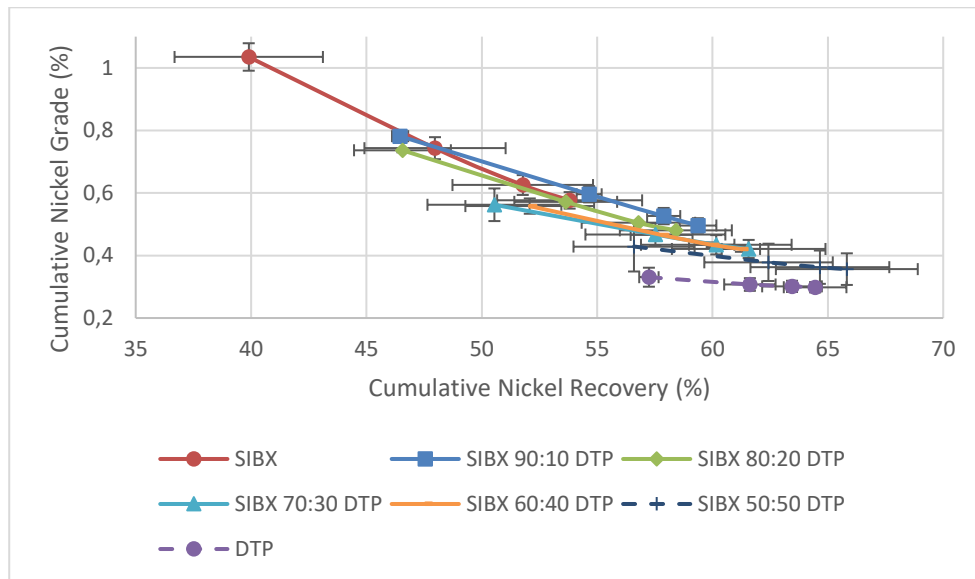


Figure 30: High resolution of grade-recovery curve in Figure 29

The trends for nickel recoveries and grades with the mixtures of SIBX and DTP were similar to those observed with the same collector suites on copper. There was however more variation in cumulative nickel recoveries for the different collector suites. The use of DTP in the collector suite improved the recovery of nickel over SIBX. These recoveries were independent of the concentration of DTP in the mixture. Similar cumulative nickel recoveries were reported on Merensky reef and Platreef ores (Behuidenhout, 2011; Wiese, 2006).

The final cumulative nickel grade decreased as the concentration of DTP in the mixture increased. The use of pure SIBX yielded the highest cumulative nickel grade (0.58%).

Figure 31 shows the trends for cumulative copper and nickel recoveries and grades as a function of the concentration of DTP in the mixture. Both copper and nickel recoveries increased as the concentration of DTP, and subsequent froth stability, increased. The copper and nickel grades decreased with an increase in DTP concentration. This indicates that there was a grade – recovery trade off which suggests that no synergism between SIBX and DTP collectors existed (Kawatra, 1995).

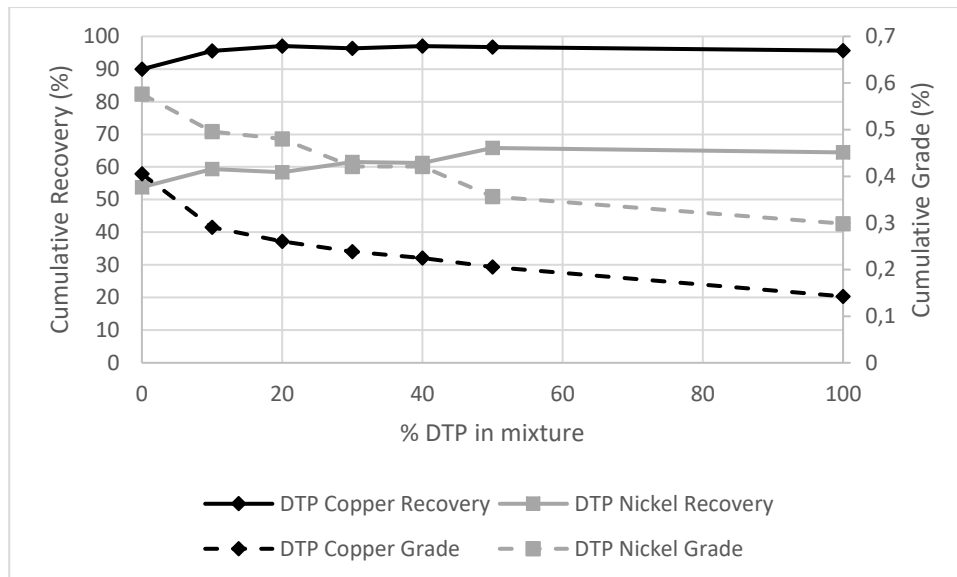


Figure 31: Comparison of final copper and nickel grade and recoveries for the mixtures of SIBX and DTP.

4.4.4 Froth Flotation Kinetics of Mixtures of SIBX and DTP

Table 16 shows copper and nickel recoveries as well as the first order rate constants obtained with mixtures of SIBX and DTP at various molar ratios. The infinite time recoveries for both copper and nickel were not significantly higher than those of the actual cumulative recoveries. This suggests that the residence time for both copper and nickel flotation was adequate.

Table 16: The rate of flotation (k) and maximum recovery for copper (R_{max}) with mixtures of SIBX with DTC

| Collector | Max Copper Recovery (%) | | Max Nickel Recovery (%) | | Rate Constant (min^{-1}) | |
|----------------|-------------------------|---------------|-------------------------|---------------|-------------------------------------|--------|
| | Actual | R_{max} (%) | Actual | R_{max} (%) | Copper | Nickel |
| SIBX | 90.0 | 90.5 | 53.8 | 54.4 | 3.84 | 1.78 |
| SIBX 90:10 DTP | 95.5 | 96.1 | 59.4 | 60.2 | 3.79 | 2.16 |
| SIBX 80:20 DTP | 97.1 | 97.5 | 58.4 | 58.9 | 3.82 | 2.34 |
| SIBX 70:30 DTP | 96.3 | 96.9 | 61.6 | 62.2 | 4.60 | 2.63 |
| SIBX 60:40 DTP | 97.0 | 97.4 | 61.2 | 61.7 | 5.73 | 3.33 |
| SIBX 50:50 DTP | 96.7 | 97.1 | 65.8 | 66.3 | 5.95 | 3.35 |
| DTP | 95.7 | 95.9 | 64.4 | 64.8 | 6.27 | 4.29 |

Chalcopyrite is a faster floating mineral as compared to pentlandite (Wills and Napier-Munn, 2006). This was observed as the rate constants for copper were higher than the corresponding rate constants for nickel. The rate constants for copper and nickel increase with an increase in DTP concentration. The rate constant for nickel obtained with pure DTP (4.29 min^{-1}) was higher than the rate constant for copper with pure SIBX (3.84 min^{-1}), as well as the mixtures SIBX

90:10 DTP (3.79 min⁻¹) and SIBX 80:20 DTP (3.82 min⁻¹). This substantiates the claim that entrainment was the dominant mechanism of recovery with pure DTP.

4.5 Effect of Depressant on Collector Mixtures

This section describes the results of batch froth flotation tests conducted where a depressant was added to the reagent suite to determine its role in the flotation of a platinum ore. The response on flotation performance was evaluated in terms of mass and water recoveries, copper and nickel grades and recoveries and the rates of flotation. A carboxymethyl cellulose (CMC) depressant, Norilose 8058 was used at a dosage of 100g/t. The collector and frother dosage were kept constant at 282 mmol/t and 40 g/t respectively. Standard solutions of depressant were prepared, added to the pulp and allowed to condition for two minutes before the collector was added. Tests with the depressant was conducted on pure collectors, mixtures of SIBX and DTC, as well as mixtures of SIBX and DTP.

The naming convention for this section of work was identical to that used with the collector mixtures. The addition of the abbreviation Dep indicated that the CMC depressant was present.

Platinum operations use depressants to inhibit the large amount of naturally floating gangue present (Wiese, 2006). The final grades and recoveries obtained for the pure collectors, with and without depressant, are summarised in Table 17 and was used to compare metallurgical performance.

Table 17: Final grades and recoveries obtained with pure collectors; with or without a depressant

| | Cumulative Concentrate Mass (%) | Cumulative Water Recovery (%) | Cumulative Copper Recovery (%) | Cumulative Copper Grade (%) | Cumulative Nickel Recovery (%) | Cumulative Nickel Grade (%) |
|--------------------|---------------------------------|-------------------------------|--------------------------------|-----------------------------|--------------------------------|-----------------------------|
| No Collector | 5.87 | 14.4 | 88.0 | 0.43 | 22.5 | 0.32 |
| No Collector + Dep | 5.35 | 13.1 | 82.1 | 0.46 | 19.4 | 0.33 |
| SIBX | 8.98 | 22.2 | 90.0 | 0.41 | 53.8 | 0.58 |
| SIBX + Dep | 8.82 | 20.7 | 82.3 | 0.46 | 51.2 | 0.66 |
| DTC | 10.1 | 40.5 | 89.6 | 0.38 | 59.3 | 0.55 |
| DTC + Dep | 8.32 | 30.3 | 80.2 | 0.45 | 56.0 | 0.60 |
| DTP | 22.6 | 84.5 | 95.7 | 0.14 | 64.4 | 0.30 |
| DTP + Dep | 11.1 | 36.8 | 87.1 | 0.28 | 56.5 | 0.45 |

The CMC depressant was added to tests of various molar ratio mixtures of SIBX and DTC. The final grades and recoveries are summarised in Table 18.

Table 18: Final grades and recoveries obtained with mixtures of SIBX with DTC; with depressant

| | Cumulative Concentrate Mass (%) | Cumulative Water Recovery (%) | Cumulative Copper Recovery (%) | Cumulative Copper Grade (%) | Cumulative Nickel Recovery (%) | Cumulative Nickel Grade (%) |
|----------------------|---------------------------------|-------------------------------|--------------------------------|-----------------------------|--------------------------------|-----------------------------|
| SIBX + Dep | 8.82 | 20.7 | 82.3 | 0.46 | 51.2 | 0.66 |
| SIBX 90:10 DTC + Dep | 10.5 | 38.5 | 88.8 | 0.40 | 58.5 | 0.55 |
| SIBX 70:30 DTC + Dep | 7.63 | 33.0 | 84.1 | 0.47 | 55.5 | 0.64 |
| SIBX 50:50 DTC + Dep | 7.32 | 34.6 | 87.3 | 0.43 | 56.3 | 0.61 |
| DTC + Dep | 8.32 | 30.3 | 80.2 | 0.45 | 56.0 | 0.60 |

Tests were conducted on mixtures of SIBX and DTP with added CMC depressant. The final grades and recoveries are presented in Table 19.

Table 19: Final grades and recoveries obtained with mixtures of SIBX with DTP; with depressant

| | Cumulative Concentrate Mass (%) | Cumulative Water Recovery (%) | Cumulative Copper Recovery (%) | Cumulative Copper Grade (%) | Cumulative Nickel Recovery (%) | Cumulative Nickel Grade (%) |
|----------------------|---------------------------------|-------------------------------|--------------------------------|-----------------------------|--------------------------------|-----------------------------|
| SIBX + Dep | 8.82 | 20.7 | 82.3 | 0.46 | 51.2 | 0.66 |
| SIBX 90:10 DTP + Dep | 10.7 | 44.5 | 92.2 | 0.41 | 52.1 | 0.58 |
| SIBX 70:30 DTP + Dep | 11.7 | 50.2 | 92.4 | 0.31 | 52.7 | 0.47 |
| SIBX 50:50 DTP + Dep | 13.4 | 50.4 | 87.6 | 0.30 | 58.7 | 0.45 |
| DTP + Dep | 11.1 | 36.8 | 87.1 | 0.28 | 56.5 | 0.45 |

4.5.1 Water and Mass Recovery

Figure 32 shows the cumulative mass and water recoveries obtained by the various pure collectors with and without depressant. The water recoveries obtained with the added depressant were lower than the tests without depressant. Talc, a major gangue mineral in the ore, is naturally floatable and has properties that stabilise froth (Bradshaw et al., 2004). The tests where no depressant was added may have allowed the talc to float and stabilise the froth.

Wiese (2006) reported that high dosages (>300 g/t) of CMC depressants may destabilise the froth. The water recovery for the DTP test with depressant was 56% lower than the test on DTP without a depressant. The tests without depressant yielded water recoveries 10% and 56% higher for DTC and DTP respectively over the test where depressant was added (Figure 32). The addition of a depressant to both no collector and SIBX had insignificant changes in water recoveries.

The mass recoveries for SIBX and no collector did not change with the addition of a depressant. DTC yielded slightly less mass recovery (-2%) with the added depressant, while the mass recovery for DTP halved when depressant was added (Figure 32).

Talc was present in small quantities (>4%) in the ore and could not solely be responsible for the significantly increased water and mass recoveries obtained in tests without a depressant over tests with depressant (Nyambayo, 2014). Wiese (2006) calculated the amount of natural floating gangue present in a similar Merensky reef ore and concluded that large dosages (300 g/t) are required to depress the gangue present. This is three times the dosage employed in these tests which may suggest that not all the talc would have been depressed at this lower dosage (100 g/t). Therefore more indirect mechanisms may have been involved in stabilising the froth. Also, if talc was the major factor for increased froth stability, then the no collector and SIBX tests should have produced similar results.

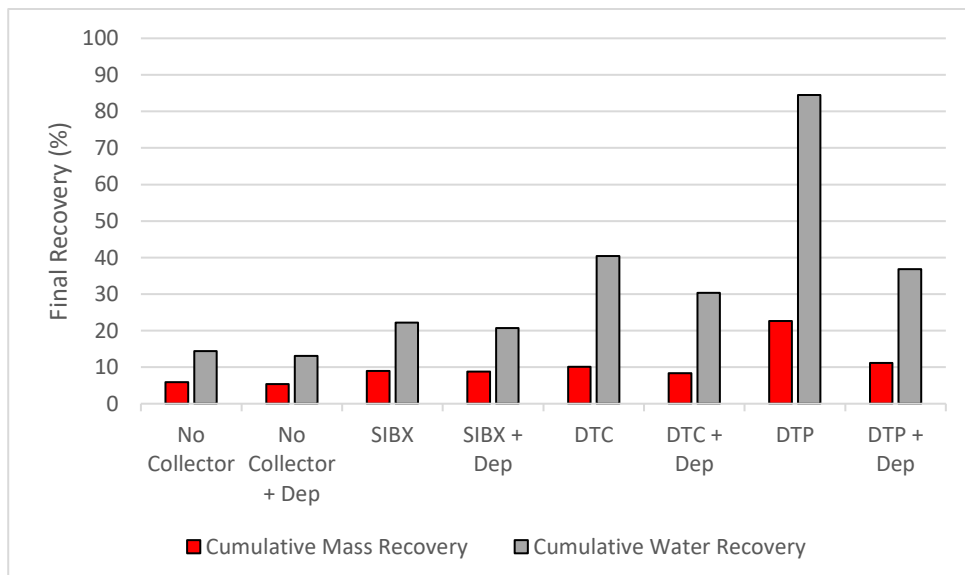


Figure 32: Cumulative mass and water recoveries obtained for pure collectors, with and without depressant

Figure 33 shows the cumulative mass and water recoveries obtained when mixtures of varying portions of SIBX and DTC were used with a depressant. Tests with depressant and mixtures of SIBX and DTC yielded higher water recoveries than the respective pure collectors with depressant. The water recoveries for tests that contained DTC were higher than that of SIBX. The SIBX 90:10 DTC + Dep mixture produced achieved the highest water recovery and consequent mass recovery.

The mass recoveries for the SIBX 70:30 DTC + Dep and SIBX 50:50 DTC + Dep mixtures were lower, while the water recoveries were higher over those of the pure collectors with depressant. This may suggest better drainage from the froth phase in each case.

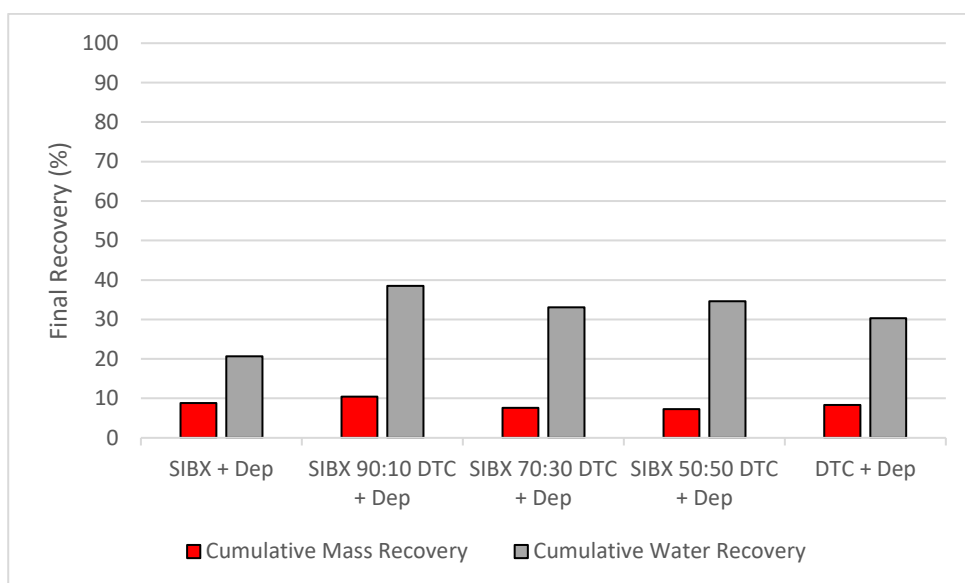


Figure 33: Cumulative mass and water recoveries obtained for mixtures of SIBX and DTC, with a depressant.

The water and mass recoveries for mixtures of SIBX and DTP in the presence of a depressant are presented in Figure 34. The mixtures yielded significantly higher water recoveries than the respective pure collectors which indicated that the froth stabilising effects of the mixtures containing DTP persisted with added depressant. Pure DTP with depressant, interestingly did not yield the highest water recovery. Instead the water recoveries were higher with the mixtures.

The mass recoveries were higher for the collector suites that contained DTP. The mass recovery increased with an increase in the concentration of DTP in the mixture. However pure DTP with depressant did not follow this trend. Instead it yielded the same mass recovery as the SIBX 90:10 DTP + Dep mixture.

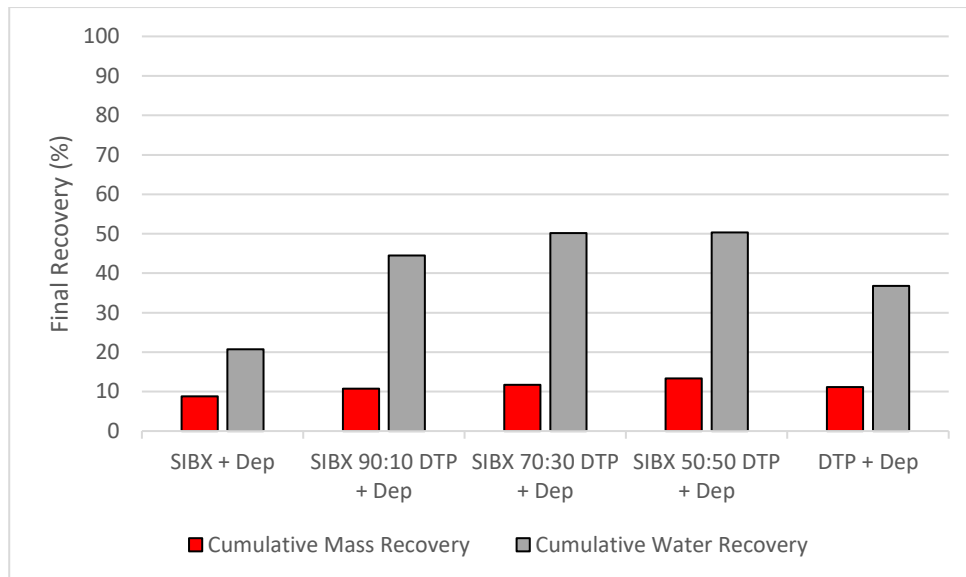


Figure 34: Cumulative mass and water recoveries obtained for mixtures of SIBX and DTP, with a depressant.

The lower than expected mass and water recoveries for DTP + Dep may have been due to the following:

- Increased froth stability formed larger bubbles in the froth phase, which decreased the carrying capacity of the bubbles in the froth.
- The addition of depressant increased the viscosity of the froth and prevented it from rising above the cell lip to the removed (Shortridge et al., 1999).

4.5.2 Copper Grade and Recovery

Figure 35 shows the cumulative copper grades versus recoveries of pure collector, with and without depressant.

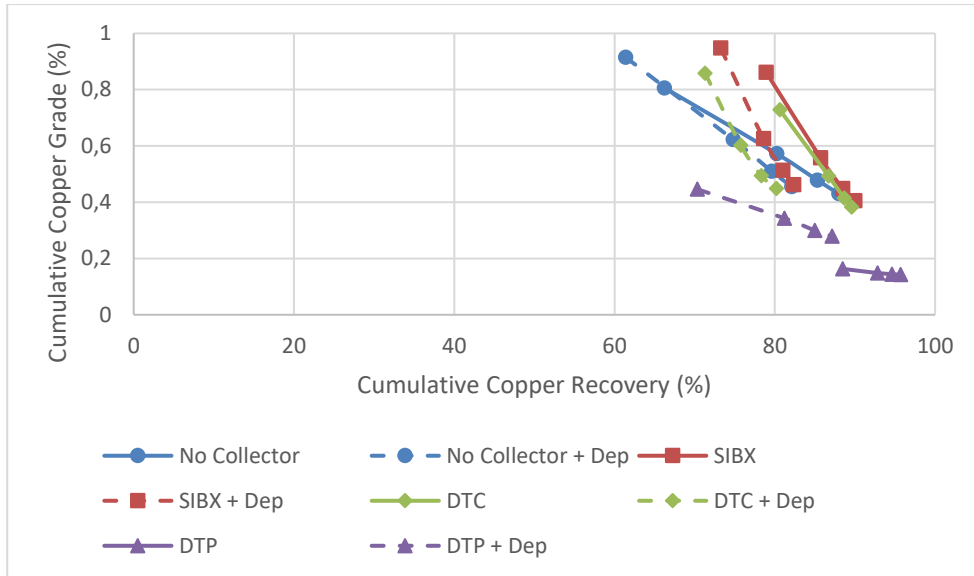


Figure 35: Percentage cumulative copper grade versus cumulative recovery for the pure collectors, with and without depressant.

The cumulative recoveries obtained for copper decreased significantly for all pure collectors when depressant was added. This may have been due to the decreased froth stability or more selective flotation of desired minerals (Figure 35). The addition of depressant to the pure collectors raised the grade of copper due to depression of natural floatable gangue. In the case of DTP, the increase was significant.

Figure 36 shows the grade versus recovery obtained for copper with the mixtures of SIBX and DTC, and added depressant. The cumulative copper recovery achieved for pure SIBX +Dep is higher than that of pure DTC + Dep while the mixtures of SIBX and DTC with depressant produced the greatest recoveries. There were no significant differences in the final copper grades obtained for all tests of SIBX, DTC and their mixtures with added depressant.

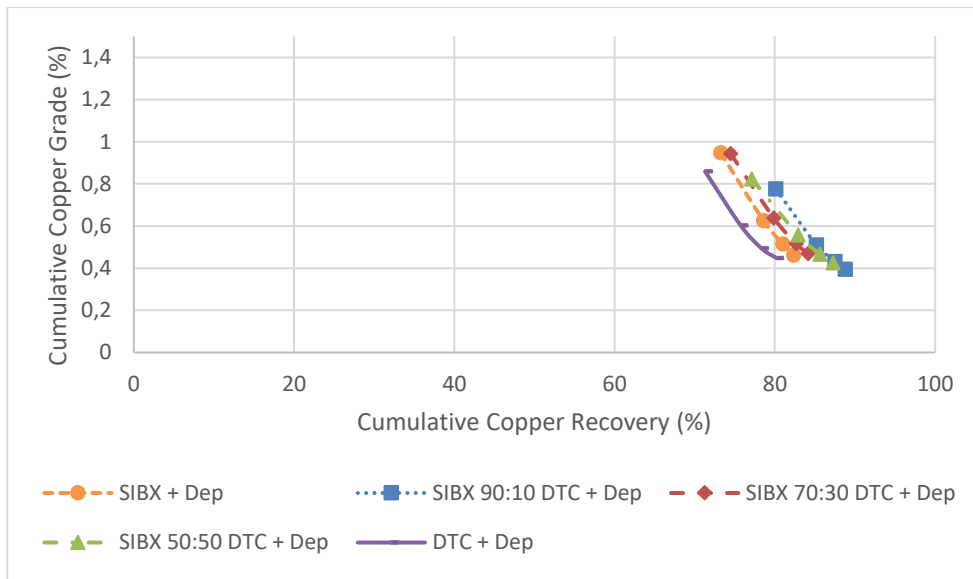


Figure 36: Percentage cumulative copper grade versus cumulative recovery for mixtures of SIBX and DTC, with a depressant.

The cumulative copper recoveries versus grades for the collector suites of SIBX and DTP with depressant is shown (Figure 37). The cumulative copper recovered for the collector suites that contained DTP were higher than that of pure SIBX. The use of the SIBX 90:10 DTP + Dep mixture improved the copper recovery over that of pure SIBX + Dep with only a slight decrease in grade (0.05%). The final copper grade was significantly lower for the reagents that contained more than 10 molar% DTP. The higher mass and water recoveries indicated that entrainment contributed to particle recovery which resulted in lower grades.

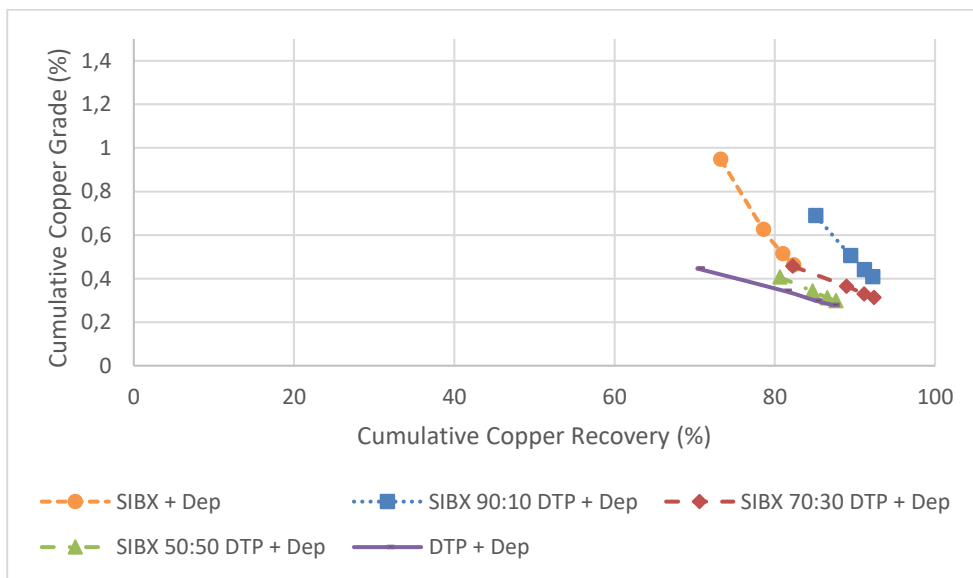


Figure 37: Percentage cumulative copper grade versus cumulative recovery for mixtures of SIBX and DTP, with a depressant

4.5.3 Nickel Grade and Recovery

Figure 38 shows the cumulative copper grades versus recoveries of pure collector, with and without depressant.

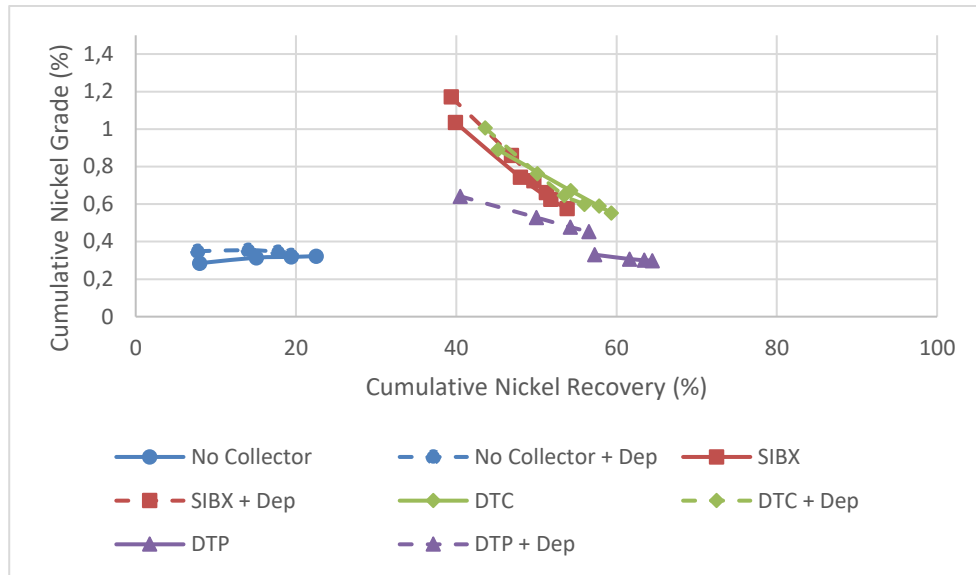


Figure 38: Percentage cumulative nickel grade versus cumulative recovery for the pure collectors, with and without depressant.

There was an overall decrease in nickel recovery when depressant was added to the various pure collectors (Figure 38). This may have been due to decreased froth stability when talc was depressed. The addition of depressant to pure DTP resulted in increased nickel grades (0.15%). The addition of depressant to the other pure thiol collectors had insignificant effect on the nickel grades.

Figure 39 shows the grade versus recovery obtained for nickel with the mixtures of SIBX and DTC, and added depressant. There was a general increase (4-7%) in nickel recovery with the addition of DTC to the collector mixture. This increase was independent of the concentration of DTC in the mixture. The increased recoveries resulted in decreased grades. The lowest copper grade (0.43%) was obtained by SIBX 90:10 DTC + Dep, which corresponded to the highest mass (10.5%) and water (38.5%) recoveries. This suggested that froth stability and subsequent entrainment greatly affect the final grade in the concentrates. It also suggests that a small amount of DTC in a mixture with SIBX may significantly increase flotation performance.

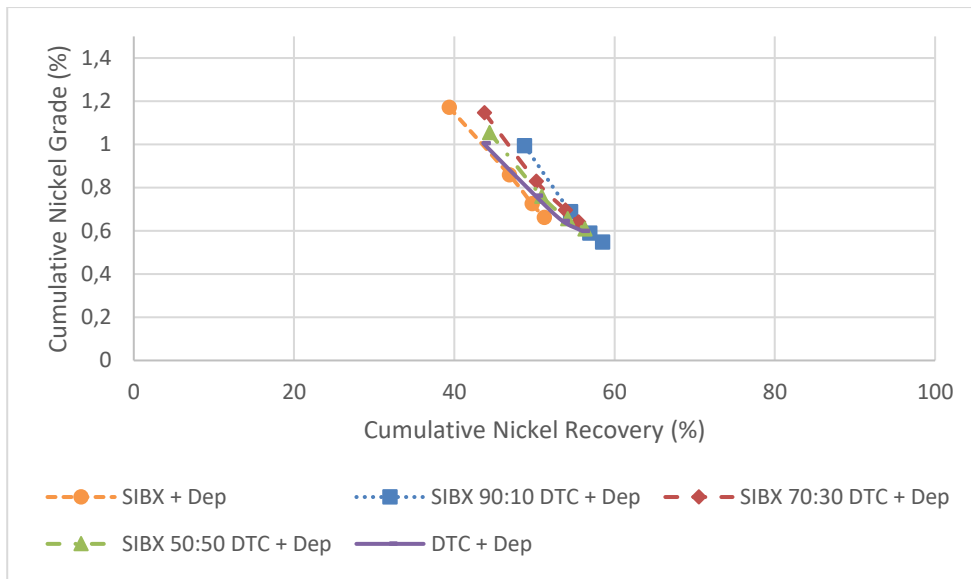


Figure 39: Percentage cumulative copper grade versus cumulative recovery for mixtures of SIBX and DTC, with a depressant.

The cumulative nickel recoveries versus grades for the mixtures of SIBX and DTP with depressant is shown in Figure 40. Pure DTP + Dep and the SIBX 50:50 DTP mixture produced significantly higher nickel recoveries (57-59%) relative to the other reagent suites (51-53%). The cumulative nickel recoveries for SIBX + Dep, SIBX 90:10 DTP + Dep and SIBX 70:30 DTP + Dep were analogous (52%).

The highest nickel grade was produced by SIBX + Dep (0.66%), followed by the SIBX 90:10 DTP + Dep mixture (0.58%). The remaining collector suites of SIBX 70:30 DTP + Dep, SIBX 50:50 DTP + Dep and DTP + Dep showed no difference in final nickel grade (0.45%).

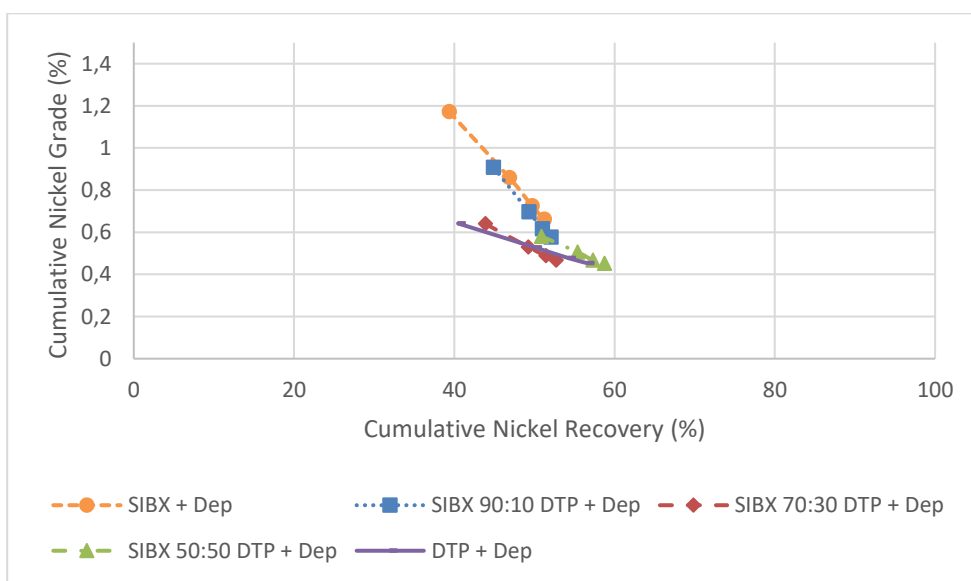


Figure 40: Percentage cumulative copper grade versus cumulative recovery for mixtures of SIBX and DTP, with a depressant.

The trends observed without depressant where metal, mass and water recoveries were dependant on the concentration of DTP in the mixture was different to the corresponding tests with added depressant. This illustrates how highly interactive froth flotation is, and that a change in one variable may affect the system differently under different conditions (Kawatra, 1995).

4.5.4 Froth Flotation Kinetic of Thiol Collector Mixtures with added Depressant

Table 20 shows the maximum copper and nickel recoveries as well as the first order rate constants obtained for the various pure collectors, with and without a depressant. The actual cumulative recoveries for copper and nickel were not much lower than the maximum recovery indicating that residence time was sufficient.

Table 20: The rate of flotation (k) and maximum recovery for copper (R_{max}) of pure collectors, with and without depressant.

| Collector | Max Copper Recovery (%) | | Max Nickel Recovery (%) | | Rate Constant, k (min^{-1}) | |
|--------------------|-------------------------|---------------|-------------------------|---------------|--|--------|
| | Actual | R_{max} (%) | Actual | R_{max} (%) | Copper | Nickel |
| No Collector | 88.0 | 89.5 | 22.5 | 25.5 | 1.85 | 0.37 |
| No Collector + Dep | 82.1 | 83.4 | 19.4 | 19.7 | 1.87 | 0.80 |
| SIBX | 90.0 | 90.5 | 53.8 | 54.4 | 3.84 | 1.78 |
| SIBX + Dep | 82.3 | 82.6 | 51.2 | 51.9 | 4.29 | 1.99 |
| DTC | 89.6 | 90.3 | 59.3 | 60.4 | 4.63 | 1.91 |
| DTC + Dep | 80.2 | 80.0 | 56.0 | 56.2 | 4.43 | 2.16 |
| DTP | 95.7 | 95.9 | 64.4 | 64.8 | 6.27 | 4.29 |
| DTP + Dep | 87.1 | 88.1 | 56.5 | 57.1 | 2.44 | 1.68 |

The faster floating copper yielded higher rate constants ($1.8 - 6.2 \text{ min}^{-1}$) than for nickel with all tests ($0.3 - 4.2 \text{ min}^{-1}$). With no collector and SIBX the rate constants for both copper and nickel increased with the addition of depressant. The copper and nickel rate constants for DTC and DTP however decreased with the addition of depressant. The rate constants for both copper and nickel recoveries for DTP with depressant were 39% that of the rate constants obtained without depressant. This may suggest that the addition of depressant indirectly effected froth flotation behaviour by altering the hydrophobic nature of particle surfaces. The different hydrophobic surfaces thus influenced the flotation kinetics.

Table 21 shows the maximum copper and nickel recoveries as well as the first order rate constants obtained for various mixtures of SIBX and DTC with depressant.

Table 21: The rate of flotation (k) and maximum recovery for copper (R_{max}) with mixtures of SIBX and DTC with a depressant

| Collector | Max Copper Recovery (%) | | Max Nickel Recovery (%) | | Rate Constant, k (min^{-1}) | |
|----------------------|-------------------------|---------------|-------------------------|---------------|--|--------|
| | Actual | R_{max} (%) | Actual | R_{max} (%) | Copper | Nickel |
| SIBX + Dep | 82.3 | 82.6 | 51.2 | 51.9 | 4.29 | 1.99 |
| SIBX 90:10 DTC + Dep | 88.8 | 89.1 | 58.5 | 58.8 | 4.86 | 2.86 |
| SIBX 70:30 DTC + Dep | 84.1 | 84.3 | 55.5 | 55.8 | 4.16 | 2.25 |
| SIBX 50:50 DTC + Dep | 87.3 | 87.5 | 56.3 | 56.4 | 4.12 | 2.29 |
| DTC + Dep | 80.2 | 80.0 | 56.0 | 56.2 | 4.43 | 2.16 |

The rate of copper and nickel flotation had no noticeable relationship with the concentration of DTC in the mixture. The highest rate for both copper and nickel recovery was obtained with the SIBX 90:10 DTC + Dep mixture, which was accompanied by the highest metal recoveries.

Table 22 shows the maximum copper and nickel recoveries as well as the first order rate constants obtained for various mixtures of SIBX and DTP with depressant.

Table 22 : The rate of flotation (k) and maximum recovery for copper (R_{max}) with mixtures of SIBX and DTP with a depressant

| Collector | Max Copper Recovery (%) | | Max Nickel Recovery (%) | | Rate Constant (min^{-1}) | |
|----------------------|-------------------------|---------------|-------------------------|---------------|-------------------------------------|--------|
| | Actual | R_{max} (%) | Actual | R_{max} (%) | Copper | Nickel |
| SIBX + Dep | 82.3 | 82.6 | 51.2 | 51.9 | 4.29 | 1.99 |
| SIBX 90:10 DTP + Dep | 92.2 | 92.5 | 52.1 | 52.4 | 6.14 | 3.43 |
| SIBX 70:30 DTP + Dep | 92.4 | 93.0 | 52.7 | 53.0 | 4.25 | 2.83 |
| SIBX 50:50 DTP + Dep | 87.6 | 87.8 | 58.7 | 58.8 | 5.96 | 3.60 |
| DTP + Dep | 87.1 | 88.1 | 56.5 | 57.1 | 2.44 | 1.68 |

The lowest rate of flotation for both copper (2.44 min^{-1}) and nickel (1.68 min^{-1}) was with DTP + Dep. The highest rate of flotation for copper was with the SIBX 90:10 DTP + Dep mixture (6.14 min^{-1}), and the highest rate of flotation for nickel was with the SIBX 50:50 DTP + Dep mixture (3.60 min^{-1}). The highest rates were produced by different mixtures for the respective metals, which suggests that thiol adsorption and froth stability were contributing factors. There exist an optimum contact angle that forms on particular mineral surfaces (Wills and Napier-Munn, 2006). This contact angle differs from each mineral and an optimum contact angle greatly affects hydrophobicity. It may be that the collector mixture of SIBX 90:10 DTP + Dep induced the optimum contact angle on the surface of chalcopyrite while the optimum contact angle for nickel flotation was induced by the SIBX 50:50 DTP + Dep mixture (Nyambayo, 2014).

4.6 Sulphur Grade versus Recovery

The Merensky reef is a sulphide dominant deposit. The platinum group elements (PGE) in the reef are closely associated with the sulphide minerals. Sulphide platinum group minerals (PGM) make up roughly 36% (Table 1) of the PGM distribution in Merensky reef ores. The response of the sulphur present in the ore is therefore important. To evaluate the effectiveness of collectors on this ore it is important to evaluate the recovery of the sulphur present.

The total sulphide mineral content of the ore used in this study was determined at 1.09% and the sulphur content was however determined at only 0.21% (Table 5). This difference was due to the lower molar mass of sulphur than the metals present in the sulphide minerals and because sulphur only accounts for a fraction of the content for each mineral (Jiwu et al, 1984).

Figure 41 shows the cumulative recoveries versus grades for sulphur with mixtures of SIBX and DTC. The results for no collector were added to describe the natural floatability of sulphur in the sulphur containing minerals of the ore. The no collector test recovered minimal sulphur (29%), which confirms the claim that most sulphide minerals are not naturally floatable and requires the addition of collectors (Bulatovic, 2010). The recovered sulphur was as a result of the recovery of the naturally floatable chalcopyrite. The high copper recoveries with no collector confirmed this. The low sulphur grade of the no collector test (0.7%) indicated that entrainment was a dominant mechanism in particle recovery.

Pure SIBX, pure DTC and the mixture of SIBX 90:10 DTC produced similar sulphur grades (1.2 – 1.4%) and recoveries (67 – 70%). The mixtures of SIBX 70:30 DTC and SIBX 50:50 DTC however showed improved sulphur recoveries over the respective pure collectors (Figure 41). The SIBX 70:30 DTC mixture also produced improved sulphur grades as compared to the pure collectors. This may indicate that there was collector-collector synergism, however the same improvement in recovery and grade was not observed for copper and nickel. This suggests that pyrhotite or pyrite, the sulphide minerals for which metal analyses (iron) was not conducted, was preferentially recovered for these tests.

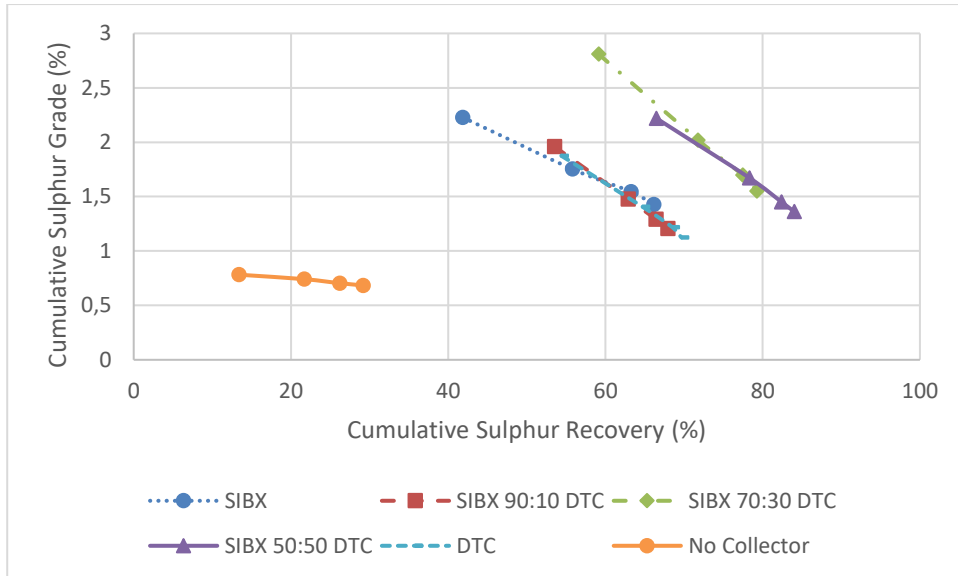


Figure 41: Percentage cumulative sulphur grade versus cumulative recovery for mixtures of SIBX and DTC

The cumulative sulphur recoveries and grades achieved by various mixtures of SIBX and DTP are shown (Figure 42). There appears to be a relationship between sulphur grade and recovery as a function of DTP concentration in the mixture. From pure SIBX to SIBX 90:10 DTP and SIBX 70:30 DTP, the grade appears to decrease slightly while the sulphur recovery increased significantly. From pure DTP to the mixtures of SIBX 50:50 DTP and SIBX 70:30 DTP there is a slight difference in sulphur recoveries however the grades increase significantly. There may have been collector-collector synergism and an optimum molar ratio between SIBX and DTP for sulphur recovery. Synergism between these collectors was however unlikely as large water and mass recoveries and low metal grades indicated that entrainment was dominant. This trend in sulphur recovery may have been coincidental.

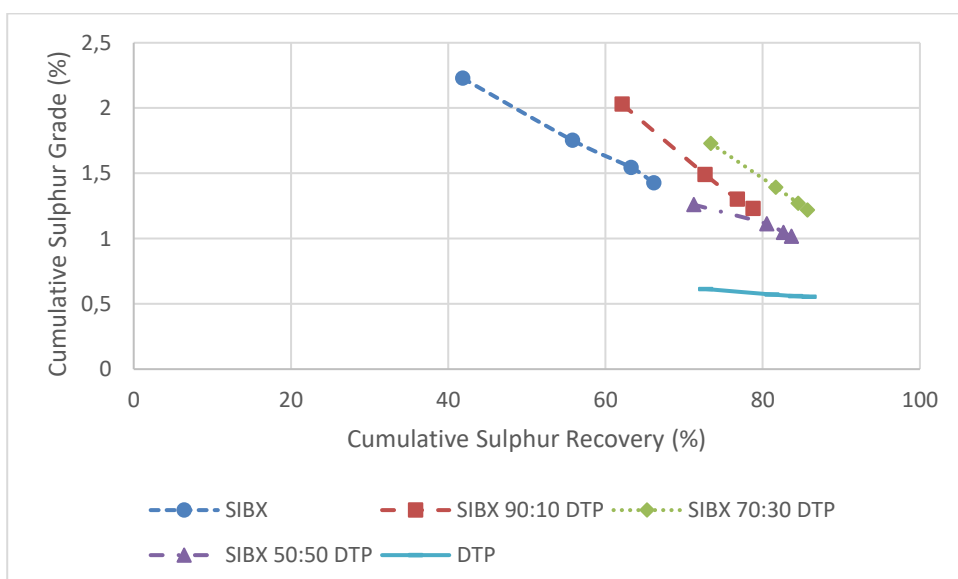


Figure 42: Percentage cumulative sulphur grade versus cumulative recovery for mixtures of SIBX and DTP

4.7 Particle Size Distribution

The feed was subjected to grinding to achieve a specific particle size distribution for which metals recovery is maximum. Particle size is an important variable as particles of different sizes behave differently in flotation systems. Reagents also interact differently to different particle sizes. The concentrate samples from selected tests were analysed for particle size distribution. This was done to establish how different collectors and their concentration in mixtures interacted with particles of different size.

Particles in flotation are classified as ultrafine, fine, medium, and coarse (Nyambayo, 2014). The size range for each classification is shown in Table 23.

Table 23: Classification of mineral particle size

| Description | Particle size range (μm) |
|-------------|---------------------------------------|
| Ultrafine | -10 |
| Fine | -25 +10 |
| Medium | -75 +25 |
| Coarse | +75 |

The particle size distribution (PSD) was determined by Malvern, and represents a volumetric PSD. The PSD was presented on a logarithmic scale to accommodate the large range of particle sizes and to increase resolution of the fine and ultrafine range. The original feed grind was 60% passing 75 μm , consequently a large proportion of particles would be classified as coarse.

Figure 43 shows the PSD of particles that were recovered in the different concentrates by the different pure collectors. The majority of the particles recovered in the first concentrate was medium to coarse. An increase in recovery of ultrafine and fine particles occurred in the second concentrate. For the final two concentrates the particle sizes that were recovered were evenly spread between ultrafine, fine, medium and coarse.

Finer particles have a larger tendency of being recovered by entrainment than coarser particles. DTP has been reported to enhance the recovery of fine particles due to the stabilised froth (Bezuidenhout, 2011). Compared to the PSD for SIBX and DTC in the first concentrate, DTP recovered more coarse particles and less ultrafine to fine particles. This depletion in coarse particle resulted in lower coarse particle recovery in later concentrates. The later concentrates recovered more ultrafine to fine particles with DTP compared to SIBX and DTC.

The PSD between DTC and SIBX for the first concentrate was essentially identical. However, in later concentrates, DTC recovered more coarse particles.

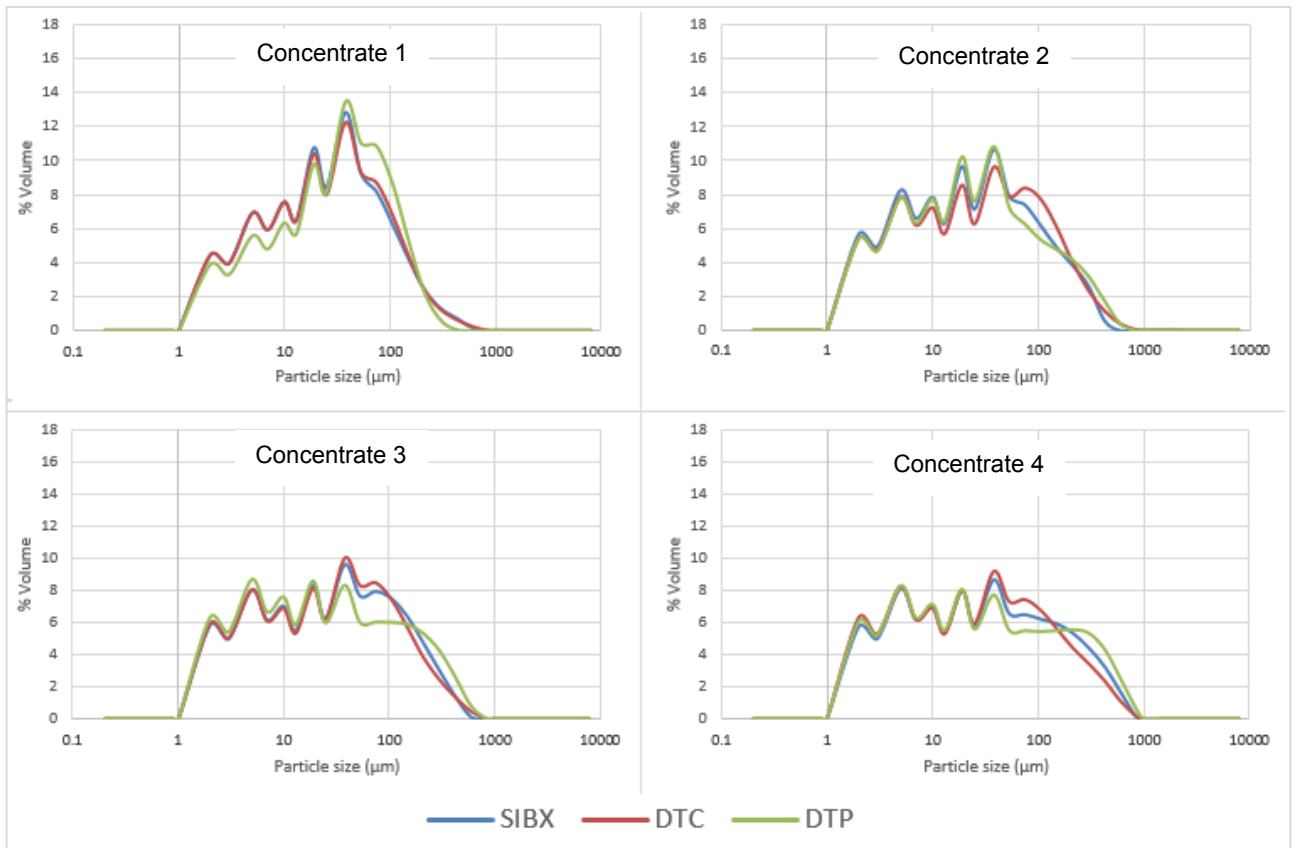


Figure 43: Particle size distribution by concentrate for pure collectors

Figure 44 shows the PSD for recovered particles in the four concentrates achieved with mixtures of SIBX and DTC.

The PSD for the first concentrates were essentially identical for all mixtures of SIBX and DTC. The size range contained predominately medium particles. In later concentrates more fine and ultrafine particles were recovered. Pure DTC and the SIBX 90:10 DTC mixture recovered more coarse particles in concentrates three and four as compared to the other mixtures.

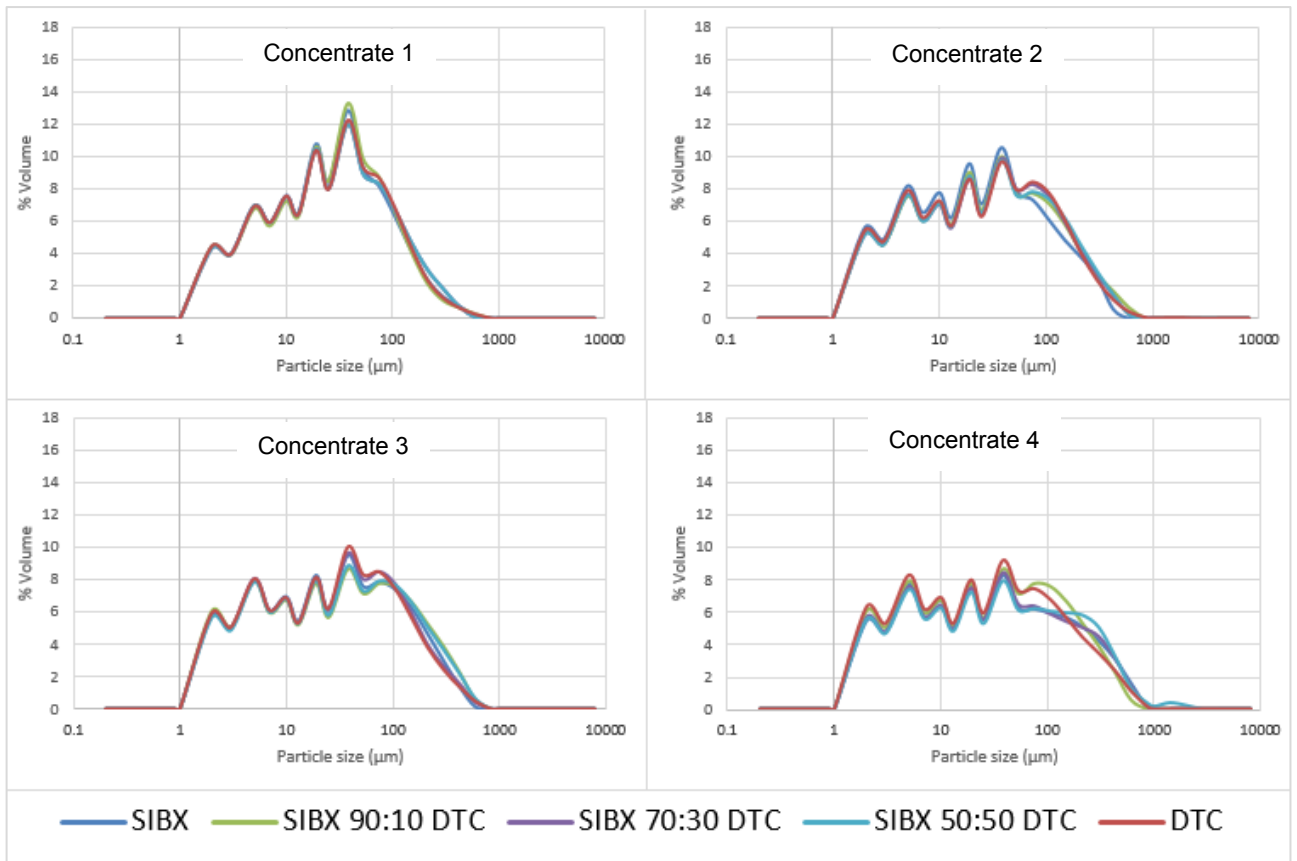


Figure 44: Particle size distribution by concentrate for mixtures of SIBX and DTC

Figure 45 shows the PSD in the four concentrates obtained with mixtures of SIBX and DTP. The general PSD in the first concentrates was classified as medium. There was a tendency for more coarse particles to be collected with an increase in DTP concentration. As the coarse particles became depleted from the second concentrate onwards, the recovery of finer particles was preferred.

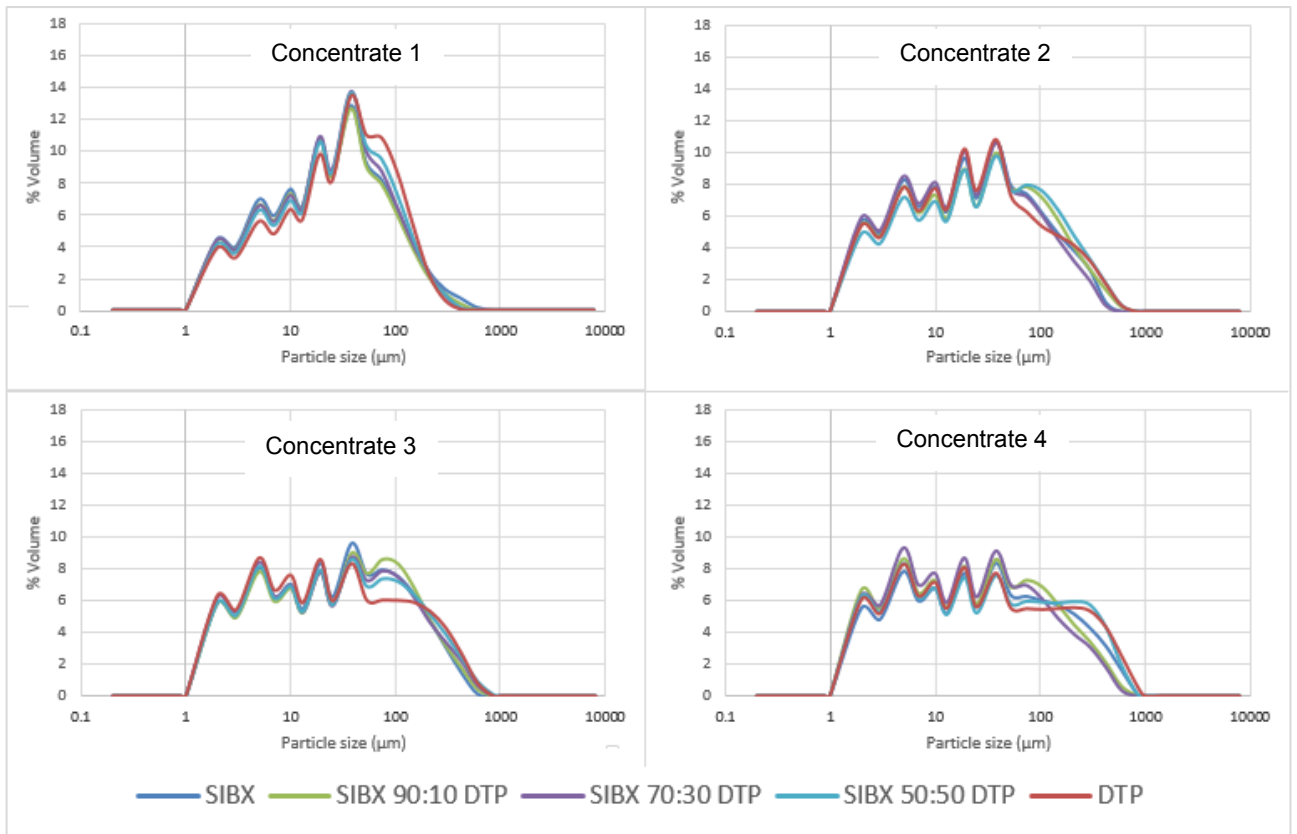


Figure 45: Particle size distribution by concentrate for mixtures of SIBX and DTP

The graphs all showed a peak at around 75μm for concentrate 1. These peaks all disappeared in later concentrates which validates the chosen feed grind.

CHAPTER 5

5.1 Conclusions

This research investigated the response of flotation performance when different thiol collectors were used in the flotation of a Merensky reef ore. These tests characterised the flotation behaviour of the different functional groups of the collectors. The results of these tests established a baseline of flotation performance for comparison. The thiol collectors used were: sodium isobutyl xanthate (SIBX), sodium diethyl dithiocarbamate (DTC) and sodium diethyl dithiophosphate (DTP). Further tests were conducted where DTC and DTP was each used in mixtures of different molar ratios with SIBX and the response on flotation performance was evaluated. The xanthate accounted for the major component in the mixtures. A number of tests were carried out in the presence of a carboxymethyl cellulose (CMC) to determine collector mixture responses to depressant. Total molar concentration of the collectors in the mixtures was 282mmol/t.

It was established that the copper in the ore, chalcopyrite, was readily floatable as it responded to no collector tests. The nickel, pentlandite, required the addition of collectors for successful flotation. The low recoveries obtained for nickel indicated that there are significant amounts of non-sulphide nickel present in the ore.

Each thiol collector exhibited unique metallurgical performances in the flotation of this ore. SIBX which is the industrially preferred thiol collector for platinum processing, yielded low water and mass recoveries which resulted in high copper and nickel grades. The same response was observed with the addition of a depressant. DTC reported similar trends for copper recovery as SIBX, however its use improved nickel recovery and flotation rate. DTC did however increase the stability of the froth.

The results of this study indicates that DTP exhibited strong froth stabilising properties. Water and mass recoveries were significantly higher than those of the other collectors. This resulted in improved metal recoveries at significantly lower grades. The addition of depressant to DTC and DTP decreased the froth stability and different flotation responses were observed.

The use of mixtures of DTC with SIBX increased water, mass and paymetal recoveries and the rate of flotation. The improvement were due to increased froth stability and no synergism was observed. The response of SIBX:DTC mixtures were similar to that of pure DTC and the concentration of DTC in the mixture yielded insignificant change on metallurgical performance.

This suggests that synergism may occur at lower concentrations of DTC. The addition of depressant to the mixtures yielded had insignificant change in flotation response.

The flotation rates, mass, water and paymetal recoveries as well as metal grade was a function of the concentration of DTP in its mixtures with SIBX. The froth stability increased proportionally to an increase in DTP concentration. This caused increased recoveries and decreased grades with increased DTP concentration. No synergistic interactions were observed between SIBX and DTP. Low concentration (10%) of DTP in the mixture improved recoveries significantly which suggests that even lower concentrations should be evaluated. The addition of a depressant decreased the froth stability, but entrainment was still dominant.

Synergism was observed for sulphur recovery with both SIBX:DTC and SIBX:DTP mixtures. Different trends observed with respective paymetal recoveries which suggests that the improved metallurgical performance for sulphur was due to the recovery of the iron sulphides, pyrrhotite and pyrite.

The particle size distribution of the concentrates recovered for the various collector mixtures suggest that the addition of DTP or DTC on mixtures with SIBX improves the recoveries of coarse particles. The added froth stability imparted by DTC and DTP may have decreased the drainage which resulted in the more abundant coarse particles being entrained.

There was a general lack of improvement in grades when depressant was added to the various collector suites. This suggests that the depressant dosage employed (100g/t) was not sufficient to depress the majority of the gangue present.

The dominance of froth stability in the recovery of mineral particles made the identification of mechanism responsible for imparting hydrophobicity on mineral surfaces impossible.

5.2 Recommendations

The recommendations for future work are:

- Analysis for platinum group elements (PGE) should be conducted. The association between PGE and base metal sulphides are well established. However, the PGEs may be fully liberated in the fine to ultrafine particle size range. The majority of these PGEs are not sulphide based (tellurides and arsenides) and may respond differently in

flotation systems. Technological improvements have increased the sensitivity for analysis of these trace elements and may provide a better fundamental understanding of the flotation of platinum group minerals with mixtures of thiol collectors.

- Mineralogical analysis of the concentrates, feeds and tailings should be carried out to establish which minerals are affected, and in what way, by flotation.
- Microflotation tests should be conducted on the various pure collectors and their mixtures to better understand the frothing properties of each functional group and how the frothing properties are transferred into the mixtures. This will also provide a better understanding of the froth and pulp phase effects.
- Collector adsorption tests should be conducted to evaluate how, if at all, collectors interact with the minerals.
- The test conditions should be repeated with DTC and DTP collectors of higher purity.
- Tests should be conducted at lower molar concentrations of DTC and DTP respectively.
- The dosages for the mixtures were based on a local maximum achieved with pure SIBX. More dosage tests should be conducted to determine the optimum dosage, and the dosages for the collector mixtures should be altered.
- Pulp zeta potential measurement should be conducted on the same scope of work to provide insight into the chemistry and transfer of electrons that occurs in the pulp.
- The scope of the work should be repeated at higher depressant dosages.

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APPENDIX

Appendix A: Collector Mixtures Preparation

Collector Dosage:

$$SIBX_{50g/t} = \frac{50g}{1 \text{ tonne Ore}} \div \text{Molar mass} \times \text{purity}$$

$$SIBX_{50g/t} = \frac{50g}{1 \text{ tonne Ore}} \times \frac{\text{mol}}{172g} \times 0.97$$

$$SIBX_{\frac{50g}{t}} = 0.282 \frac{\text{mol}}{t} = 282 \frac{\text{mmol}}{\text{ton}} = 0.282 \frac{\text{mmol}}{\text{kg}}$$

Equivalent Mass Dosage:

$$\text{Equivalent Collector Dosage} = 282 \times 10^{-6} \frac{\text{mol}}{\text{kg}} \times \text{Molar mass} \times \text{purity}$$

Preparing Standard Solution

$$\text{Collector}_{\text{mass}} = \left(\frac{\text{volume}_{\text{flask}}}{\text{volume}_{\text{pipette}}} \right) \times \text{Equivalent Collector Dosage}$$

Mass Equivalent for Mixtures of Collectors

Collector mixture of SIBX 70:30 DTC will be used as an example.

$$SIBX \text{ 70:30 DTC} = SIBX_{50g/t} \times \text{Ratio of SIBX} \times Mr_{SIBX} + SIBX_{50g/t} \times \text{Ratio of DTC} \times Mr_{DTC} \div \text{purity}$$

$$SIBX \text{ 70:30 DTC} = 282 \times 10^{-6} \frac{\text{mol}}{\text{kg}} \times 0.7 \times \frac{172g}{\text{mol}} + 282 \times 10^{-6} \frac{\text{mol}}{\text{kg}} \times 0.3 \times \frac{171g}{\text{mol}} \div 0.45$$

$$SIBX \text{ 70:30 DTC} = 0.03395g \text{ SIBX} + 0.0322g \text{ DTC}$$

Appendix B: Analysis of Flotation Data

All results were presented as a percentage of the original amount to allow for comparison.

Copper Analysis

% given by XRF analysis

Cu Mass = % x Mass of Concentrate

Cu Grade = (Cumulative mass of Cu) / (Cumulative mass of Concentrate) x 100

% Cu Recovery = (Cumulative mass of Cu) / (Mass of Cu in feed) x 100

Nickel Analysis

% given by XRF analysis

Ni Mass = % x Mass of Concentrate

Ni Grade = (Cumulative mass of Ni) / (Cumulative mass of Concentrate) x 100

% Ni Recovery = (Cumulative mass of Ni) / (Mass of Ni in feed) x 100

Sulphur Analysis

% given by LECO analysis

S Mass = % x Mass of Concentrate

S Grade = (Cumulative mass of S) / (Cumulative mass of Concentrate) x 100

% Cu Recovery = (Cumulative mass of S) / (Mass of S in feed) x 100

Water Recovery Analysis

Mass of water recovered = mass of concentrate dish with concentrate – mass of dry concentrate – mass of concentrate dish – mass of water used to rinse lip of cell into dish

% Water recovery = Cumulative mass of water recovered / Mass of water originally in the cell x100