The Role of Collectors in the Flotation of Partially Oxidised Copper Ores

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NOMENCLATURE

$A^{-}_{(aq)}$	an oxidised anion
Eh	electrochemical potential
E^{o}	standard reduction potential
IR	infrared spectroscopy
$MA_{(s)}$	oxidised species on the sulphide mineral surface
MS	sulphide mineral
$MX_{(s)}$	metal xanthate
MX_2	metal dixanthate
R	recovery at infinite time (%)
r	recovery at time, t (%)
$W_{S/A}$	work of adhesion between air bubble and mineral surface (N/m)
k	Klimpel rate constant (min^{-1})

LIST OF ABBREVIATIONS

$[Cu(DTC)]^{+}$	cupric ion attached to a single dithiocarbamate anion
$Cu(DTC)_2$	cupric diethyl dithiocarbamate
$Cu(DTP)_2$	cupric diethyl dithiophosphate
iC4-X	sodium isobutyl xanthate
C2-X	sodium ethyl xanthate
Cu(DTC)	cuprous dithiocarbamate
DCDTP	dicresyl dithiophosphate
di-C2-DTC	diethyl dithiocarbamate
di-C2-DTP	diethyl dithiophosphate
di-C4-DTC	dibutyl dithiocarbamate
di-iC4-DTP	di-isobutyl dithiophosphate
DTC^{-}	diethyl dithiocarbamate anion
DTP^{-}	diethyl dithiophosphate anion
$(DTC)_2$	thiouram disulphide
$(DTP)_2$	dithiophosphatogen
isoC3 DTP	isopropyl dithiophosphate
mono-n-C4-DTC	mono butyl dithiocarbamate
OCC	Okiep Copper Company
PMC	Palaborwa Mining Company
PNBX	potassium n-butyl xanthate
SMBT	sodium mercaptobenzothiazole
UV	ultraviolet spectroscopy
X^{-}	ethyl xanthate anion
X_2	dixanthogen

GREEK LETTERS

$\gamma_{S/A}$	surface tension between solid and vapour (N/m)
$\gamma_{S/W}$	surface tension between solid and liquid (N/m)
$\gamma_{W/A}$	surface tension between vapour and liquid (N/m)
θ	contact angle between bubble mineral surface (°)

SYNOPSIS

The effects of xanthates, dithiophosphates, dithiocarbamates and mixtures of these collectors on the froth flotation performance of partially oxidised and oxidised copper sulphide ores were investigated in this study. More specifically, the role of the functional groups of the collectors, their dosages and the effect of collector mixtures and their dosages were investigated. Batch flotation tests were used to assess the performance in terms of mass-water recovery, sulphur grade-recovery, copper grade-recovery and acid soluble copper grade-recovery relationships and the Klimpel rate constant for copper recovery.

Flotation characteristics of bornite rich Carolusberg copper sulphide ore from Okiep Copper Company (1.8% copper) and bornite and chalcopyrite rich ore from Palaborwa Mining Company (0.58% copper) were compared.

In the flotation of the Okiep ore, it was observed that di-ethyl-dithiocarbamate was a weak collector of copper sulphide minerals even at the maximum tested concentration, 4.6×10^{-5} mol/L. This was well below the optimal range of concentration for maximum copper recovery with this collector: 5 to 8.3×10^{-4} mol/L (Mangalam and Khangoankar, 1985 and Bhaskar Raju and Khangoankar, 1984). Consequently, the cupric dithiolate necessary for sufficient hydrophobicity of the mineral surface and good flotation performance may not have formed (Finkelstein and Poling, 1977). The di-ethyl-dithiocarbamate therefore was not able to collect particles as large as those collected by di-ethyl-dithiophosphate.

The use of di-ethyl-dithiophosphate generally contributed to more watery froths than those obtained with the other collectors. This was accompanied by a loss of grade attributed to increased unselective recovery by entrainment.

Lower recoveries were obtained with the Palaborwa ore than those obtained with Okiep ore. This was attributed to products of oxidation on the mineral surfaces that impaired thiol collector adsorption to result in the relatively low recoveries. The consequently low hydrophobicity of the particles in the pulp phase resulted in low recovery by true flotation but still a significant recovery by entrainment. These factors accounted for the generally lower copper recoveries and grades obtained with the Palaborwa ore despite having had a similar spectrum of copper sulphide minerals as the Okiep ore. However, no mineralogical analysis or surface investigation was done to confirm this

The total copper and acid soluble copper recoveries obtained with the xanthate were higher than those obtained with the dithiophosphate or the dithiocarbamate in the flotation of the Palaborwa ore. This was attributed to a greater readiness to form dithiolate on the oxidised sulphide mineral surface.

Generally, higher dosages led to higher recoveries and rates until some maximum value was reached in the case of each collector. When collector dosages in excess of this maximum were used, copper recovery and rates of copper recovery declined. This followed established relationships between collector dosage and copper recovery (Somasundaran, 1975) and collector dosage and rate of copper recovery (Smar et al, 1994) and was attributed to a reduction in overall hydrophobicity of the minerals at the higher collector dosages due to the adsorption of a second layer of collector on the mineral surface which may have had an opposite orientation of the first layer.

Significantly superior copper recoveries were obtained with the 90% ethyl xanthate:10% di-ethyl-dithiophosphate and 90% ethyl xanthate:10% di-ethyl-dithiocarbamate collector mixtures compared to that obtained with ethyl xanthate at a collector dosage of 0.139 mol/ton ore in the flotation of the Okiep ore. This was accompanied by significantly greater water and mass recoveries with the mixtures and a consequent loss of copper grade. A significantly superior copper grade was obtained with the 90% ethyl xanthate:10% di-ethyl-dithiocarbamate collector mixture at a dosage of 0.0695 mol/ton ore compared to that obtained with ethyl xanthate at the same equivalent dosage. This may have been due to the increased hydrophobicity that reduced froth stability that led to better drained froths with a consequent increase in copper grade.

The use of the 90% ethyl xanthate:10% di-ethyl-dithiocarbamate collector mixture with the Palaborwa ore also produced a higher grade compared to that obtained with ethyl xanthate. However, there were no significant differences in the performances obtained with isobutyl xanthate and the 90% isobutyl xanthate:10% di-ethyl-dithiocarbamate collector mixture.

1. INTRODUCTION

1.1. Scope of Thesis

Flotation is a complex physico-chemiclal beneficiation process that separates valuable minerals from unwanted gangue minerals based on their relative surface properties. This separation takes place in both pulp and froth phases and the success is governed by many sub-processes as well as the effect of various reagents that are added to enable the separation. Most commonly, collectors react with mineral surfaces thus rendering them hydrophobic, frothers promote bubble formation in the pulp phase and the stability of the froth phase, depressants render the surfaces of unwanted minerals hydrophilic and activators promote the flotation of desired minerals.

It has been shown that in the practice of flotation, mixtures of two collectors are often more effective than either of them used separately even in equivalent total molar concentration. Here the combined effect of the collectors exceeds the sum of the weighted individual effects. This is an example of synergism in flotation (Bradshaw et al, 1998). Synergism is known to occur in collector:collector, collector:frother and frother:frother interactions and may improve recovery and selectivity in differential flotation. The interactions between reagents that result in synergism are complex and depend upon their chemical nature and the extent and nature of the adsorption reactions on the mineral surfaces. This study seeks to explore factors that affect the effectiveness of collectors and collector mixtures when used in the froth flotation of partially oxidised copper sulphide ores.

This chapter provides the theoretical background for the discussion of the experimental results. After briefly discussing its origin and historical development, the principles of froth flotation including physical, chemical and operational parameters are considered. Included are the flotation of sulphide ores with particular focus on copper sulphide and oxidised copper sulphide ores.

The next chapter describes the experimental details (Chapter 2). Subsequently the results obtained with an Okiep Copper Company ore which was bornite rich (1.8% copper) and a Palaborwa Mining Company ore which was bornite and chalcopyrite rich (0.6% copper) are reported (Chapter 3) and discussed (Chapter 4). The thesis ends with conclusions (Chapter 5) and recommendations for future work (Chapter 6).

Figure 1.1. locates the work of the thesis in the field of flotation and provides a schematic representation of its scope.

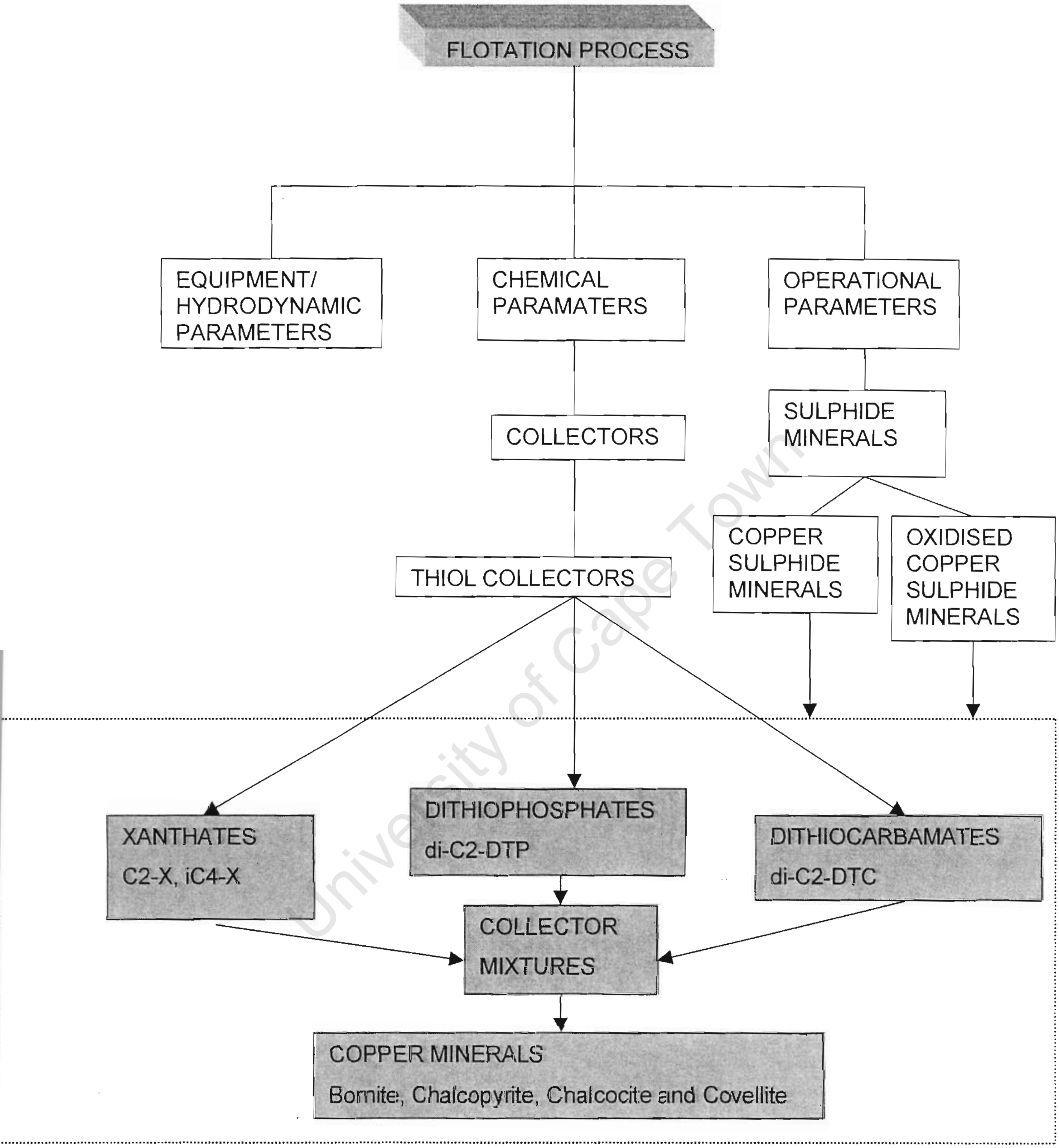


Figure 1.1. A schematic representation of the scope and boundaries of the thesis

1.2. Principles of Flotation

In froth flotation, differences in the physico-chemical surface properties of the various minerals are exploited (Wills, 1988). In a froth flotation cell, the desired minerals and gangue material are suspended in the water of the pulp phase by an agitator (Figure 1.2). Normally air is fed into the agitator where it is broken into bubbles that rise through the pulp phase to the froth phase. The air bubbles are able to displace water from the surfaces of hydrophobic minerals and carry sufficiently small particles to the froth phase.

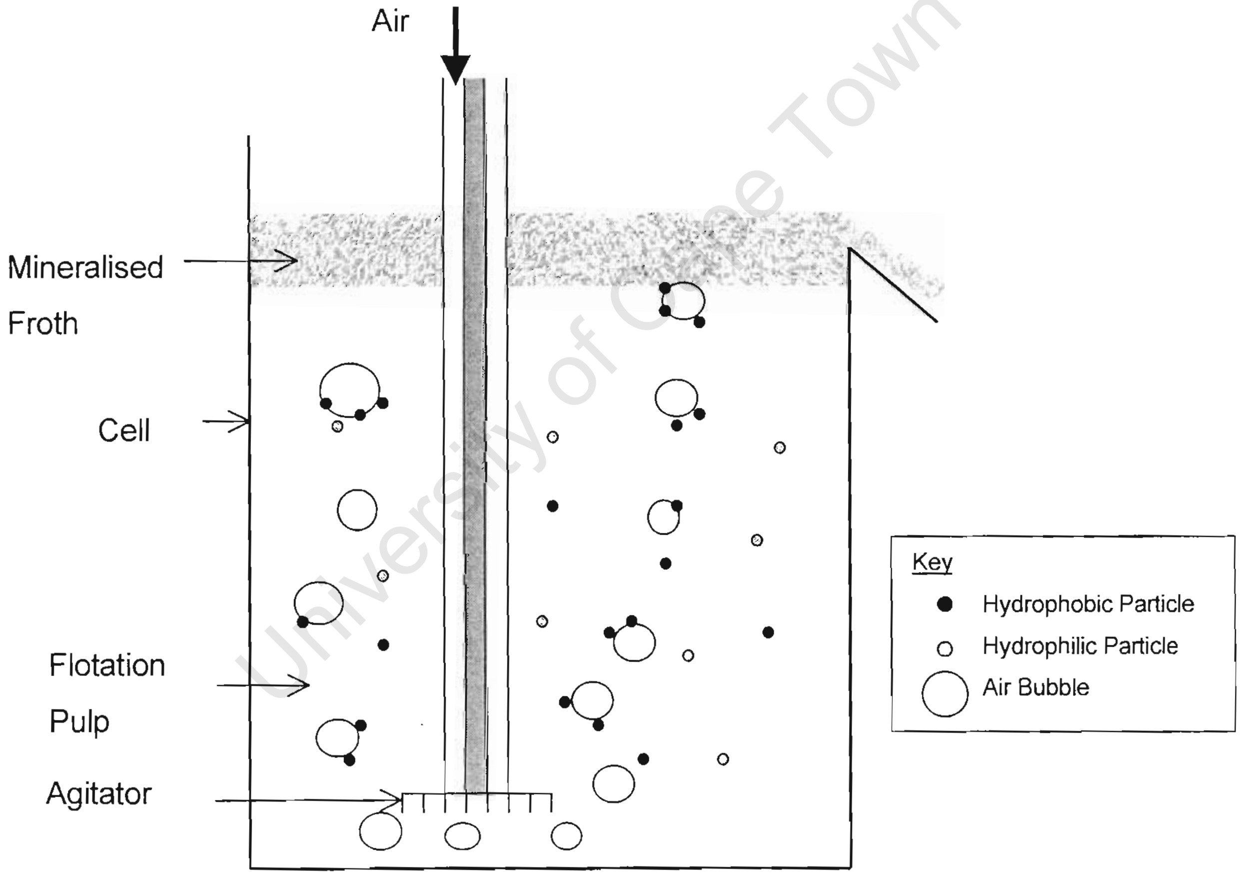


Figure 1.2. Schematic representation of the froth flotation process

The modern froth flotation process has been in development for more than 135 years and a few early innovations deserve mention.

The Bessel brothers of Dresden patented the first true flotation process in 1877 (Sutherland and Wark, 1955). They concentrated a graphite ore by pulverising it and mixing it with 1 to 10 % of paraffin oil. After water was added, the mixture was boiled. The gangue remained in the water phase and the graphite, with the assistance of the oil, floated to the surface where it was collected. In 1896, they improved the process by introducing a gas phase that drove the oil-graphite aggregates to the surface. Froment, working in Italy in 1902, extended the Bessel process to sulphide minerals. The mass of oil used was 1 to 1.5 % and the reaction of limestone and acid produced the required gas phase. Sulman, Picard and Ballot (1906) and Chapman (1906) developed this technique by aerating the pulp by means of violent agitation. Thus, was the modern flotation process born.

Lowry and Greenway (1912) used sodium dichromate as a depressant for the lead mineral and produced zinc blende as a concentrate. Bradford (1913) depressed the zinc blende while floating the lead mineral. He also discovered that the floatability of zinc blende was immensely improved by the addition of copper sulphate; one of the first uses of copper sulphate as an activator.

Perkins (1921) reported that soluble organic compounds containing trivalent nitrogen or bivalent sulphur atoms could be substituted for oils as collectors. Also, these compounds were more selective. The next milestone in froth flotation occurred in 1925 when the use of xanthates was patented by Keller and Lewis. The manufacture of xanthates has always been simple and cheap and their usage, by 1955, was rivalled only by the “aerofloat” (dithiophosphate) compounds patented in 1926 by Whitworth.

Froth flotation made it economically viable to extract metals from low grade complex ore bodies and copper ores. Today, it is used to concentrate most sulphide minerals. Also included are gold ores; nonmetallic ores such as calcium phosphate, limestone, fluorite, magnesite and dolomite; minerals such as zircon, ilmenite, rutile, barytes, kyanite, chromite, cassiterite, beryl, spodumene, nephelite, quartz, mica, magnetite and alunite as well as oxidised or oxide ores.

1.2.1. Flotation Fundamentals

Fuerstenau (1995) summed up the status of flotation research and reported that the initial and subsequent development of the flotation process took place through a great deal of empirical and intuitive work on complex ores. The result is that there are inconsistencies in our understanding of the fundamental principles involved.

The froth flotation process involves the interaction of three phases: solid, liquid and gas. The solid phase is the ore, ground into an acceptably fine particle size. The liquid is most commonly water while the gas is air. Furthermore, successful flotation separations depend on the interrelation among the various physical, chemical and mechanical factors involved (Figure 1.3) (Fuerstenau, 1995).

Some of the physical phenomena of importance are the bubble/particle interactions (also referred to as flotation micro kinetics) and particle/particle interactions (which are affected by slime coatings, flocculation, dispersion). Mechanical factors lie in the domain of flotation engineering. Areas of interest here include flotation cell design that controls bubble generation and mineral-particle dispersion. These factors determine the macroscopic kinetics of flotation. In practice, flotation engineers may manipulate system variables such as air flow rate, impeller speed and bubble size to optimise flotation processes.

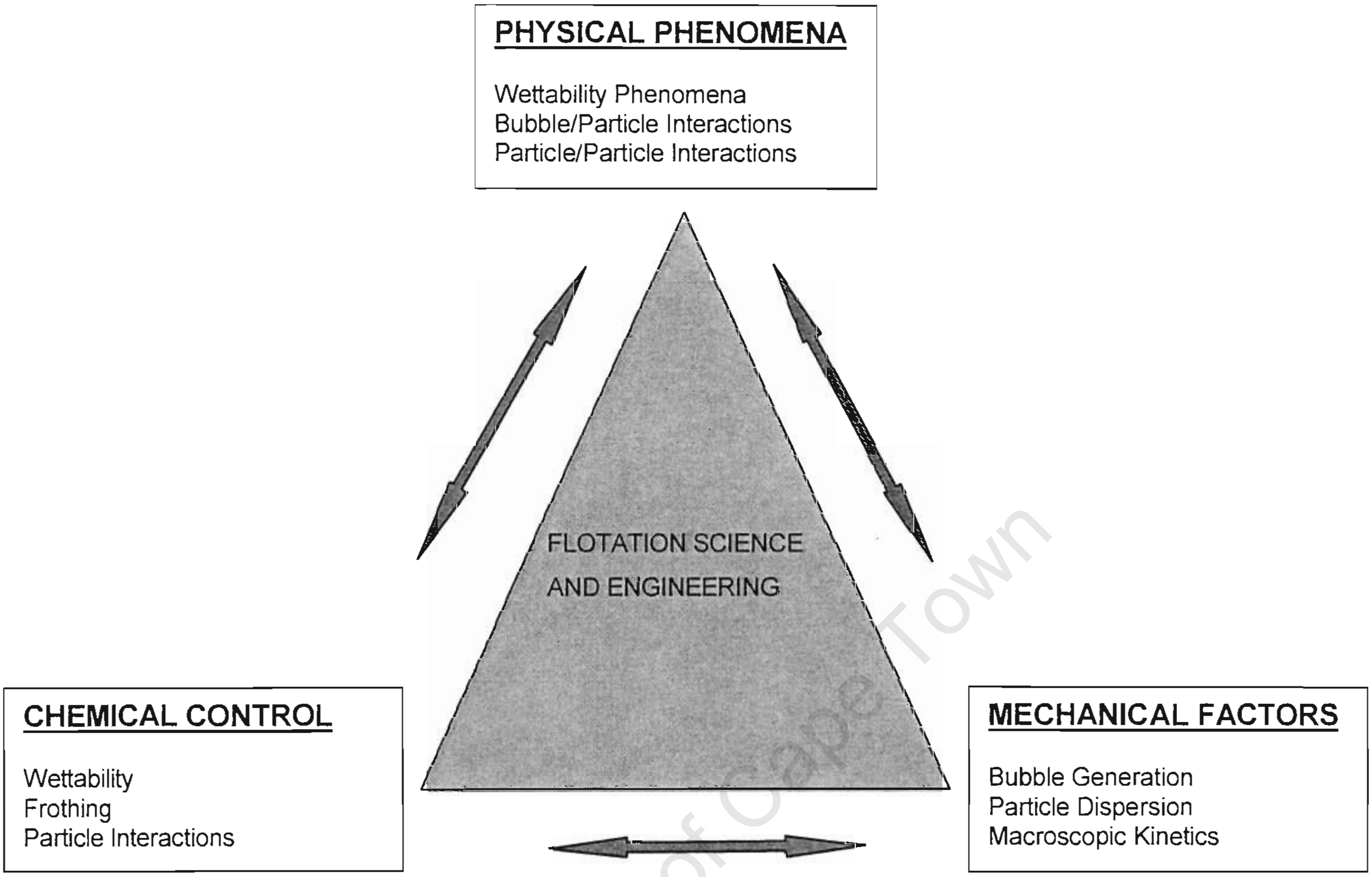


Figure 1.3. A schematic representation of the three elements of flotation science and engineering (Fuerstenau, 1995)

It is, however, chemical control that "is the key to flotation processing, in that the concentration of minerals by flotation is achieved by modifying the interaction between water molecules and mineral surfaces. The success of this process rests in the judicious use of a variety of chemical reagents. These, upon their adsorption at the solid/liquid, solid/gas and liquid/gas interfaces modify the physical-chemical characteristics of the system and create the differences in hydrophobicity between valuable and gangue minerals in the pulp and froth zones" (Fuerstenau, 1995). Flotation reagents control factors such as wettability, particle dispersion/aggregation, bubble stability and electrochemical factors including Eh (Fuerstenau, 1995).

Solid particles report to the concentrate by two mechanisms. Those recovered by true flotation are attached to rising air bubbles while those recovered by entrainment are carried in the water associated with these bubbles. The former depends on hydrophobicity of the particle, while the latter is non-selective and related to water recovery. Both hydrophobic and hydrophilic fine particles are recovered by entrainment. The extent of entrainment increases with decreasing particle size. The rate of recovery of non-hydrophobic gangue minerals such as quartz is approximately proportional to the rate of water flow in the froth (Subrahmanyam and Forssberg, 1988 & Kelly and Spottiswood, 1982). There is therefore a relationship between the amount of water in the froth and the concentrate grade. Water recovery in turn is affected by the type of frother, its concentration and the particle size of the ore (Subrahmanyam and Forssberg, 1988).

In their work on chalcopyrite ores, Johnson, McKee and Lynch (1974) identified two important mechanisms for the recovery of nonsulphide gangue. For the fine size fractions, they reported entrainment of free gangue in the recovered water, while for coarse size fractions there was natural flotation of composite particles of chalcopyrite and gangue. They reported an approximately linear relationship between the rates of recovery of non-sulphide gangue material and water recovery. In addition, for the chalcopyrite ores examined, a reduction in the pulp density of the gangue reduced the contribution of the entrainment mechanism. This implied that the concentrate grades could be improved by reducing the water recovery rates or the pulp density of the feed. They reported that the recovery of chalcopyrite was not "greatly" affected by the reduced water recovery rates. Batch flotation tests showed that the initial rate of siliceous gangue recovery was more sensitive to an increase in water recovery than the initial rate of chalcopyrite recovery.

1.2.2. Mathematical Description of Flotation

1.2.2.1. Klimpel Model

The Klimpel model is used to calculate the Klimpel rate constant. k (Klimpel, 1984). It represents a two parameter model that relates flotation rate and recovery (equation 1.1). k may be calculated by fitting flotation recovery versus time experimental data to equation 1.1.

$$r = R\{1-(1/kt)[1-\exp(-kt)]\} \tag{1.1}$$

where r = recovery at time, t (%)
R = recovery at infinite time (%)
k = rate constant (min^{-1})

Measured Klimpel rate constants may be used in the optimization of the performance of industrial flotation circuits (Klimpel, 1984). Knowledge of the consistent patterns of response, of both flotation rate and equilibrium recovery, to changing settings of flotation circuits is required for process optimisation. The effect of the chemical components (e.g. frothers and collectors) on the rate of recovery may be quantified by measuring k.

The key limitation to this model is that it should be used to compare systems where the recovery is similar at infinite time. Improved models have been developed (Harris, 2003), however the use of the Klimpel model is still widespread.

1.2.3. Influential Parameters in Flotation

1.2.3.1. Operational Components

Large-scale ore processing involves the interaction between the mineralogical characteristics of the ore, the chemistry that controls the system and the process variables (Fuerstenau, 1995). These relationships are represented in Figure 1.4.

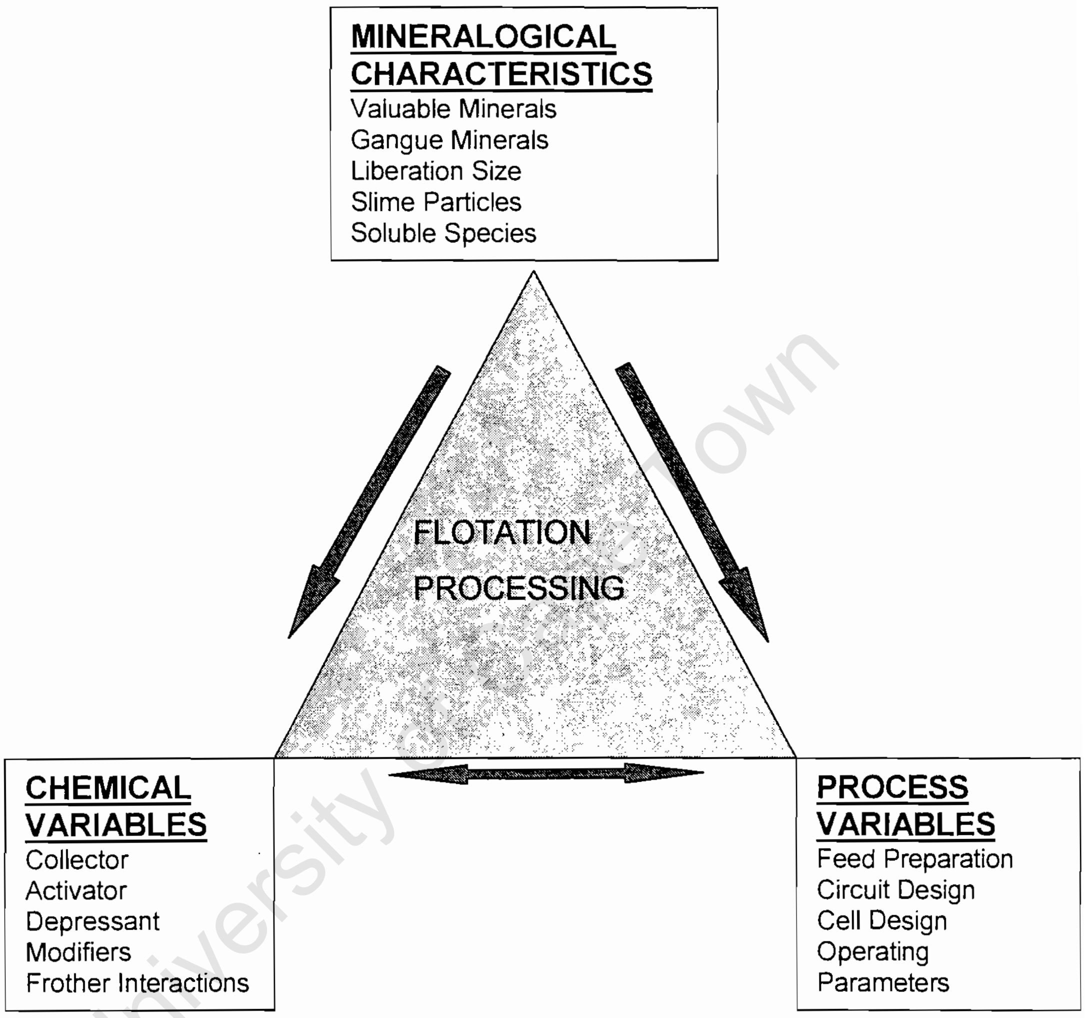


Figure 1.4. Interaction between mineralogical, chemical and process variables in flotation processing (Fuerstenau, 1995)

1.2.3.1.1. Mineral Type

Mineralogical characteristics determine the chemical and process variables (Fuerstenau, 1995). This is represented by unidirectional arrows in Figure 1.4. The nature of the ore determines which minerals have to be separated from each other and the grain size and texture of the mineral determines the size to which particles have be reduced to effect liberation. The gangue minerals may determine the process flow-sheet e.g. the flow-sheets for an apatite-quartz ore greatly differs from that of an apatite-calcite ore.

The flotation of an ore of given mineralogy is regulated by the control of the pulp chemistry by means of collectors, depressants and modifiers, which in turn determines the surface chemistry of the particles and bubbles.

1.2.3.2. Chemical Components

1.2.3.2.1. Collectors

Collectors are heteropolar compounds that contain an active inorganic group coupled with a hydrocarbon chain. The classical mechanism of collector action is for the inorganic group to adsorb onto the mineral surface while the non-ionic chain, that does not form hydrogen bonds with water, is hydrophobic and thereby renders the mineral surface hydrophobic. However there are various methods of collector-mineral interaction (Yoon and Basilio, 1993) which are discussed in more detail later (Section 1.4).

Collectors are classified as anionic or cationic. The major class of cationic collectors used in the flotation of sulphides under alkaline conditions is the amines (Fuerstenau, 1982a). There are two major classes of anionic collectors; oxyhydryl and sulphydryl or thiol collectors (Fuerstenau, 1982a).

The oxyhydryl class of collectors includes the carboxylates (fatty acids), sulphonates, alkyl sulphates, hydroxamates and certain chelating agents. Impure oleic acid and tall oil are the fatty acids most often used commercially in the flotation of non-sulphide minerals such as apatite, calcite and hematite.

Commonly used classes of sulphydryl collectors, listed in order of commercial importance are xanthates, thiophosphates, thiocarbamates, thionocarbamates, mercaptans, thioureas and mercaptobenzothiazoles. They are used in the flotation of sulphide minerals and the xanthates, thiophosphates and thiocarbamates are dealt with in more detail in Section 1.4.

1.2.3.2.2. Frothers

Typically, frothers are non-ionic heteropolar, surface-active organic reagents (Wills, 1988). They may also be referred to as surfactants and concentrate at the air-water interface. The water dipoles hydrate the polar groups and do not react with the non-polar hydrophobic groups of the frother so that the non-polar part of the molecule is forced into the air phase. The nett effect is that the surface tension is reduced and the air-bubbles and froth are stabilised. Surface tension is a measure of the surface activity of frothers and in general increased surface activity results in decreased surface tension and froth stability.

In flotation, frothers are added to:

1. Aid bubble dispersion,
2. Stabilise the bubble formation,
3. Create a reasonably stable froth that allows selective drainage of the froth of entrained gangue
4. Improve the flotation kinetics (Bradshaw et al, 1998).

Ideally the frother acts in the liquid phase and does not influence the state of the mineral surface. Practically, however, interactions exist between the frother, mineral, collector and other reagents (Bradshaw et al, 1998).

It has been suggested that co-adsorption of collector and frother on the mineral surface could lead to increased mineral hydrophobicity and synergistic enhancement of flotation performance. This can lead to increased rate and copper recovery. This synergy has been shown to exist in the flotation of chalcocite with di-C2-DTP as collector and Dow 200 as frother (Dai et al, 2001). Some collectors show surface activity and may increase the frothability of frothers. An example of such a collector is di-iC4-DTP (Dai et al, 2001).

1.2.3.2.3. Depressants and Dispersants

The flotation of certain minerals can be reduced by adding reagents to render their surfaces hydrophilic. Such duty is achieved by a class of modifiers called depressants (Wills, 1988). Inorganic depressants such as cyanide may be used to depress the pyrite in the differential flotation of copper-iron ores, whereas polymeric depressants are widely used in the depression of talcous minerals particularly in the platinum industry in South Africa (Shortridge, 2002).

1.2.3.2.4. Activators

Usually, activators are soluble salts and their ions, in solution, chemically react with the mineral surface (Wills, 1988). This reaction renders the mineral surface more amenable to collector adsorption or reaction e.g. copper sulphate is used as an activator of sphalerite in the differential flotation of lead-zinc ores with xanthate as a collector. As copper is more electronegative than zinc, it displaces the zinc atom in sphalerite (ZnS) thus depositing copper sulphide on the sphalerite surface. This reacts readily with xanthate to form insoluble copper xanthate that renders the sphalerite surface hydrophobic. Copper sulphate is also used to activate galena, chalcocite and pyrite.

1.2.3.2.5. pH and Eh modifiers

Lime, sodium carbonate and to a lesser degree sodium hydroxide or ammonia are used to control the pulp alkalinity (Wills, 1988). When a decrease in pH is required, sulphuric or sulphurous acids are used. The addition of lime with xanthate collectors may act as a strong depressant of pyrite and arsenopyrite.

The pulp pH affects collector ionisation, surface chemistry and collector selectivity (Wills, 1988). Alkaline pulps promote collector stability and reduce corrosion of plant equipment.

Hydroxyl and hydrogen ions, from pH modifiers, alter the electrical double layer and zeta potential of the mineral surface. It follows then that the hydration of the particle and hence its floatability is also affected by solution pH.

A sufficiently high pH will depress most iron sulphide minerals with xanthate as a collector. Furthermore, there exists a pH above which a particular mineral, with a particular collector concentration, will float and below which it will not. This is called the critical pH and it depends on the nature of the collector, the mineral surface, the collector concentration and temperature (Sutherland and Wark, 1955). The critical pH is used in the differential flotation of complex ores e.g. when using 50 mg/L of sodium aeroflot at pH 8, chalcopyrite may be floated from galena and pyrite. The critical pH of pyrite at 650 mg xanthate/L is approximately 6 (Taggart et. al., 1929).

1.2.3.3. Effect of the Froth Phase

The nature of the froth strongly influences the outcome of the flotation process. Closely-knit froths with small bubbles promote high recoveries as they support heavy mineral loads, while loosely-textured froths with large bubbles tend to release particles and thereby produce concentrates of higher grade (Booth & Freyberger, 1976 and Subrahmanyam and Forssberg, 1988).

Froth depth and mobility has also been shown to affect recovery rate and grade. Generally, highly mobile and relatively deep froth beds have been shown to result from high frother concentrations and poorly mobile, thin froth beds result from low frother concentrations (Smar et al, 1994).

The presence of solids in the froth greatly alters the characteristics of the froth. How the froth is affected depends on the degree of hydrophobicity and size of the particles. Moderately hydrophobic particles stabilise the froth, while hydrophilic particles exerted no influence on its stability (Harris, 1982). The presence of fine particles has been observed to produce overstable froths. Examples of unstable or flat froths in the presence of highly hydrophobic solids have, however, been recorded. Harris reviewed the work of Livshitz and Dudenkov (1960, 1965) and Dudenkov (1967). They proposed that fine hydrophobic precipitates, formed by the reaction between the collector and metal ions in solution destabilised froths. Examination of these particles showed they were in the size range 0.2 to 0.5 μm. They suggested that these very small hydrophobic particles (with contact angles greater than 90^o) ruptured thin films between bubbles and accelerated the coalescence of bubbles in the pulp and froth phases and promoted froth break-down (Dippenaar, 1978).

Froth destabilisation can result in better drainage with the consequence of improved selectivity and grades. Alternatively, the presence of hydrophilic or slightly hydrophobic minerals could stabilise the froth zone and thereby increase recovery by entrainment and decrease the concentrate grades (Dippenaar, 1978).

The stabilisation of a froth film requires a number of particles and stabilisation of a film with particles of low hydrophobicity occurs only when a close packed monolayer of particles is formed in the froth films. Here the size of the solid particles match the film thickness. The particles are both attached to and situated between two air interfaces and cannot be forced out of the film (Dippenaar, 1978).

Froth stability was completely destroyed when small amounts of galena particles (<37μm) treated with butyl xanthate were added to a frother solution (Dippenaar, 1978). Similarly sized quartz particles treated with dichloromethylsilane (DDMS) did the same. When the galena was treated with ethyl xanthate, no effect on the froth stability was observed even at higher solid additions. This suggested that larger particles than proposed by Dudenkov could break froths. Dudenkov indicated that contact angles greater than 90° were required for froth destabilisation and that lesser contact angles led to froth stabilisation. Dippenaar reported that a contact angle of 74° was sufficient to break the froth. Further work on 250 μm diameter glass beads by Harris (1982) and Dippenaar (1978) showed that large particles with a sufficiently large contact angle destabilise froths.

The presence of certain minerals such as talc may enhance froth stability (Robinson, 2002).

1.3. Measurement of Hydrophobicity and Flotability

1.3.1. Surface Hydrophobicity

As this study focuses on the role of the collector and modification of the hydrophobicity or wettability of copper sulphide minerals, some clarity on defining and quantifying hydrophobicity is required. The hydrophobicity of a mineral surface refers to its aptitude to repel water and thereby promote its attachment to air bubbles. The classical method of quantifying hydrophobicity of a mineral surface is by measuring its contact angle with an air bubble in water. Another method is the measurement of the flotability of the mineral particle.

1.3.1.1. Contact Angle (θ)

Tensile forces separate a mineral particle and air bubble in water and create an angle between the mineral surface and the bubble surface (Figure 1.5). This angle is the contact angle, θ.

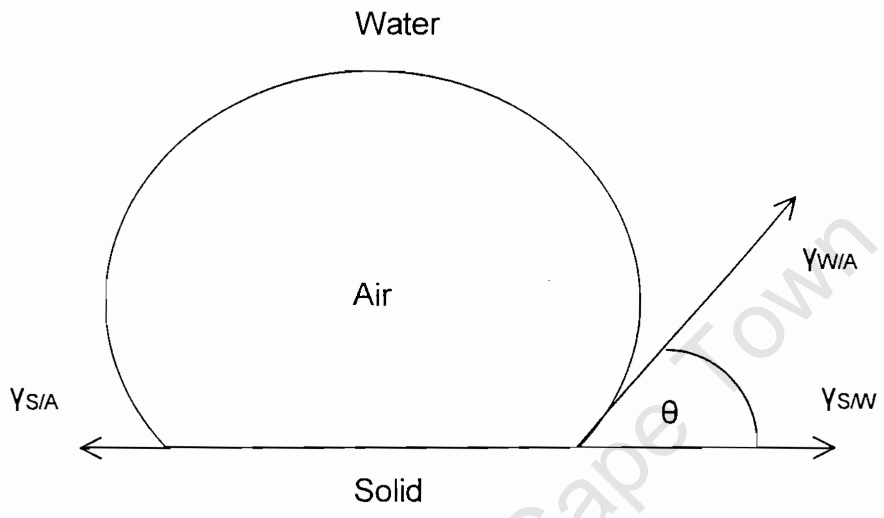


Figure 1.5 Contact angle between air bubble and particle surface in water (Wills, 1988)

At equilibrium, the relationship between the surface tension between the surface and the air, the surface and the water and the air and the water is as follows:

$$\gamma_{S/A} = \gamma_{S/W} + \gamma_{W/A}\cos\theta \qquad (1.2)$$

The work of adhesion, $W_{s/A}$, is the force required to separate the particle from the bubble and is easily shown to be:

$$W_{S/A} = \gamma_{W/A}\,(1 - \cos\theta) \qquad (1.3)$$

From this equation, an increased contact angle clearly results in greater adhesion between the particle and the bubble. It may then be concluded that the higher the contact angle of the mineral, the greater its hydrophobicity and by implication its floatability.

1.3.1.1.1. Limitations of Hydrophobicity Measurements

Crozier (1991), however, cautions that certain conclusions drawn from published contact angle research and Hallimond tube flotation work apply only to oily collectors and not to sulphydryl collectors and the flotation of sulphide minerals. In addition, these conclusions obscure the data that support nascent bubble flotation theory. On the subject of the use and applicability of contact angles he quotes Laskowski (1974) and Leja (1982, p.7):

> Laskowski: These authors [Klassen and Mokrousov (1963)] point out that flotation is typically a non-equilibrium process. The phenomena that occur on the surface of particles and bubbles in agitated, aerated mineral pulps, when these particles strike bubbles, are dynamic non-equilibrium processes which cannot be analysed based on contact angle values obtained at equilibrium
>
> Leja: In the opinion of the author, the contact angle is an indicator, but is not a measure of the hydrophilic character [of an ore].

Furthermore, the contact angle is measured on a polished section of mineral. This may not represent the characteristics of a particle of the same mineral in a flotation pulp.

Considering the above, contact angle measurements do not exclusively characterise the hydrophobicity of a mineral surface.

1.3.1.2. Floatability

"A mineral particle is classified as floatable when it can successfully attach to an air bubble and be removed with it from the flotation slurry." (Laskowski, 1974)

For a particle to be floatable, the dewetting of the particle surface has to be thermodynamically favourable and the following criteria have to be satisfied:

1. The particle and the bubble have to collide.
2. The film separating the particle and the bubble must be thin, rupture and recede during the collision.
3. The adhesion of the particle to the bubble must be of sufficient strength to withstand the shearing forces in the flotation cell.

Thus, the measurement of flotability as a kinetic property is more useful than the thermodynamic property of contact angle and hydrophobicity.

The order of decreasing floatability with the thionocarbamate collectors is as follows (Ackerman et al, 1984):

chalcocite ≥ chalcopyrite > bornite > covellite ≥ pyrite

Approximately the same order has been established for the other thiol collectors, except that bornite and covellite are floated more easily with the thionocarbamates. All of the copper sulphides are floated easily with these collectors, both in acidic and alkaline solutions.

1.4. Mineral - Collector Interactions

1.4.1. Characteristics of Copper Oxide Minerals

Sulphide and oxide minerals are referred to as acid insoluble and acid soluble respectively. This is an approximate representation as it is known that about 1.5% of chalcocite and 2% of bornite is acid soluble copper, while native copper and a fraction of cuprite respond as acid insoluble copper (Siame et al, 2002).

The copper oxides, unlike the sulphides, are inherently hydrophilic in nature as they form hydrogen bonds (Chabuka and Witika, 2001). Furthermore, as they are not conductors or semi-conductors, they do not tend to react with thiol collectors. It is for this reason that the surfaces of oxides require sulphidisation to form a pseudo-sulphide surface that reacts with thiol collectors. This reaction renders them hydrophobic and suitable for separation by flotation.

Bhaskar Raju and Forsling (1991) reported that given the same time or the same equilibrium concentration of the dithiocarbamate collector, significantly greater collector adsorption densities were obtained with the copper sulphide mineral, covellite (CuS), compared to those obtained with the copper oxide minerals cuprite (Cu_2O) and tenorite (CuO). This implied that the copper sulphide minerals were more easily rendered hydrophobic by the dithiocarbamate collector than the copper oxide minerals.

1.4.2. Characteristics of Copper Sulphide Minerals

1.4.2.1. Sulphide Minerals and their Oxidation in Solution

Sulphide minerals can be broadly categorised as either having natural or induced floatability. Floatability can be induced by collectors or sulphur formation at the mineral surface. The flotability of sulphide minerals, except those that are inherently hydrophobic, is dependent on slight oxidation of the mineral surface (Guy and Trahar, 1985). The initial oxidation of simple sulphides in acid solution is of the type (Guy and Trahar, 1985):

$$M_zS = z\,M^{n+} + S + zne \qquad (1.4)$$

In alkaline or neutral solutions the initial oxidation reaction is (Guy and Trahar, 1985):

$$M_zS + znH_2O = zM(OH)_n + S + znH^+ + zne \qquad (1.5)$$

Further oxidation may lead to the formation of oxy-sulphur species by (Guy and Trahar, 1985):

$$x\,M_zS + (zxn + y)H_2O = z\,x\,M(OH)_n + S_xO_y^{2-} + (2y + zxn)\,H^+ + (2y + zxn\text{-}2)e \qquad (1.6)$$

The nature of the reaction products on the mineral surface determined the flotation behaviour. The insoluble, hydrophobic sulphur or sulphur-like entity that remained near the mineral-solution boundary (reaction (1.5)) led to self-induced flotability. This phenomenon did not occur when the oxy-sulphur species were formed (reaction (1.6)) as they were partly soluble and may have been removed from the mineral surface in an agitated system (Guy and Trahar, 1985). (It was uncertain whether the metal hydroxides formed in reactions (1.5) and (1.6) remained at the mineral-solution interface or not.) In summary, oxidised copper minerals may become naturally floatable or not depending on the degree of oxidation of the mineral surface.

The floatability of oxidised chalcopyrite was high in the absence of collectors, while bornite and covellite were significantly less floatable and chalcocite and pyrite were only slightly floatable (Guy and Trahar, 1985). This ranking in floatability may be attributed the formation of sulphur on the chalcopyrite surface, the formation of $S_2O_3^{2-}$ in addition to sulphur on covellite, the absence of sulphur on bornite and chalcocite and the formation of SO_4^- on pyrite (Table 1.1). It may be deduced that the copper sulphide oxidation products contribute to floatability.

Table 1.1 Anodic oxidation products of sulphide Minerals in alkaline solutions (Woods, 1984)

Minerals		Products			
Name	Chemical Formula	Oxide	Sulphide	Major Sulphur	Minor Sulphur
Pyrite	FeS_2	$Fe(OH)_3$	-	SO_4^-	S
Bornite	Cu_5FeS_4	$Fe(OH)_3$	Cu_5S_4	-	-
Chalcopyrite	$CuFeS_2$	$Fe(OH)_3$	CuS	S	-
Chalcocite	Cu_2S	$Cu(OH)_2$	$Cu_{2-x}S$	-	-
Covellite	CuS	$Cu(OH)_2$	-	S	$S_2O_3^{2-}$

With the exception of chalcopyrite, the ease of collection of a particular sulphide mineral follows the opposite trend to the ease of oxidation (Guy and Trahar, 1985).

The effect of oxidation on the natural floatability of copper sulphide minerals will now be examined. in more detail.

1.4.2.1.1. Chalcopyrite

The self-induced flotation of chalcopyrite is a well-established phenomenon (Guy and Trahar, 1985). It floats efficiently in the absence of a collector in an oxidising environment and does not float under reducing conditions. This implies that the hydrophobic entity is generated by superficial oxidation and that floatability may be induced by the formation of a surface that is sulphur-rich or metal deficient or both. This is represented by reaction (1.4). Alternatively, at the pH values of most flotation testing where the surface solubility product of the metal hydroxide has been exceeded the mechanism is represented by reaction (1.5). The flotability of chalcopyrite also depends upon the grinding environment and on the nature of the frother (Heyes and Trahar (1977)).

The oxidation reactions and their products on the surface of chalcopyrite have been identified (Buckley et al, 1985). In an alkaline solution the oxidation reaction was:

$$CuFeS_2 + 3H_2O \rightarrow CuS + S + Fe(OH)_3 + 3H^+ + 3e^- \qquad (1.7)$$

There is evidence to suggest that when the temperature is above 295K, sulphur does not form and that a copper sulphide of stoichiometry close to CuS_2 forms via reaction (1.8) (Buckley et al (1985). Guy and Trahar (1985) and Walker et al (1989) support this view.

$$CuFeS_2 + 3H_2O \rightarrow CuS_2 + Fe(OH)_3 + 3H^+ + 3e \qquad (1.8)$$

The oxidation process may be seen as the removal of iron atoms from the chalcopyrite lattice leaving a chalcocite-type product with the same sulphur lattice as chalcopyrite.

Gardner and Woods (1979a) suggest that the oxidation products of chalcopyrite via reaction (1.7) might be further oxidised as follows:

$$CuS + 2H_2O \rightarrow Cu(OH)_2 + S + 2H^+ + 2e^- \qquad (1.9)$$

1.4.2.1.2. Chalcocite

Evidence suggests that copper transfers from the surface to the solution during the oxidation of chalcocite (Guy and Trahar, 1985). It is not significantly self-floatable. Chalcocite does not initially oxidise by reactions (1.4) or (1.5). The first complete overall reaction is either

$$Cu_2S \rightarrow Cu^{2+} + CuS + 2e \qquad (E^\circ = +0.530\ V) \qquad (1.10)$$

or its alkaline equivalent. Sulphur is not formed in either reaction. This would explain chalcocite's virtual absence of self induced flotation. The oxidation of the formed covellite to sulphur ($CuS \rightarrow Cu^{2+} + S + 2e$) is slow and may require the absence of chalcocite as Cu_2S, CuS and S are not simultaneously stable.

1.4.2.1.3. Bornite

An oxidised bornite surface contained a copper sulphide, rather than a copper iron sulphide with a lower Fe/Cu ratio and the iron species was an iron hydroxy-oxide i.e. the oxidation reaction in an alkaline solution was (Buckley et al, 1985):

$$Cu_5FeS_4 + 3H_2O \rightarrow Cu_5S_4 + Fe(OH)_3 + 3H^+ + 3e^- \qquad (1.11)$$

When the copper sulphide was further oxidised, a sulphide of lower Cu/S ratio resulted with the release of either Cu^{2+} ions or the deposition of $Cu(OH)_2$, depending on the pH of the solution. Copper (II) was identified on surfaces exposed to air for prolonged periods Buckley et al (1985).

1.4.2.1.4. Covellite

The oxidation products of covellite in alkaline solutions are $Cu(OH)_2$, S and $S_2O_3^-$ as listed in Table 1.1 (Woods, 1984).

1.4.3. Role of Collectors

1.4.3.1. Sulphydryl Collectors

Xanthates are the most frequently employed sulphydryl collectors and still account for over 80% of collector usage (Fuerstenau, 1995). Others are thiophosphates, thiocarbamates, thionocarbamates, mercaptans, thioureas and mercaptobenzothiazoles (Fuerstenau, 1995).

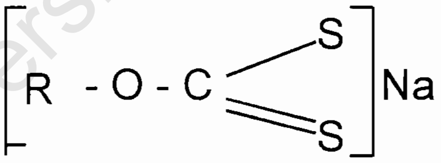
Nagaraj (1988) identified the following order of collector strength with sulphide minerals: dithiocarbamate > xanthate > dithiophosphate

Generally, the effects of increasing the length of the nonpolar part of the collector molecule is that it increases the hydrophobicity of the mineral surface and enhances flotation recovery at the expense of selectivity (Ackerman et al, 1984) i.e. selectivity arises from particle-to-bubble attachment and this in turn depends on the alkyl chain (Coetzer and Davidtz, 1989). The lower selectivity has been ascribed to increased adsorption at the solid-liquid interface due to Van der Waals' bonding among the adsorbed species to form two-dimensional aggregates (Somasundaran, 1975 and Fuerstenau, 1982b).

1.4.3.1.1. Xanthates

The manufacture of xanthates is relatively simple and cheap (Sutherland and Wark, 1955). Their range of application include substantially all sulphide minerals and metallic elements. These include copper gold, silver and platinum bearing minerals and oxidised minerals of lead, copper and cobalt.

The chemical structure of sodium xanthate is shown below. R is the alkyl group e.g. ethyl, amyl or isobutyl groups. The sodium ion may be replaced by a potassium ion.



The xanthates are weak acids with low ionisation constants (Table 1.2). The molecular species of xanthic acid predominates in solution at pH 3, while the ionic species is predominant at pH 8 (Fuerstenau, 1982a).

Table 1.2 Ionisation constants of C_2 to C_5 xanthates (Fuerstenau, 1982a)

Xanthic Acid	Ionisation Constant
C_2	1.00×10^{-5}
C_3	7.94×10^{-6}
C_4	1.00×10^{-5}
C_5	1.00×10^{-5}

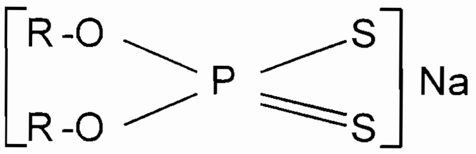
The alkali metal and the alkaline earth metal xanthates are soluble in water, whereas heavy metal xanthate salts have only a limited solubility. In addition, the solubility products of metal xanthates decrease with increased chain length (Fuerstenau, 1982a).

1.4.3.1.2. Dithiophosphates

The dialkyl dithiophosphates are more resistant to hydrolysis and oxidation than the corresponding xanthates (Sutherland and Wark, 1955). The metal-dithiophosphate salts are more soluble than those of the corresponding metal xanthates (Fuerstenau, 1982a). They are commonly used as co-collectors with xanthates.

Dithiophosphate collectors have been used in the flotation of pyrite, molybdenite, copper sulphide minerals, copper-activated sphalerite and galena (Finkelstein and Goold, 1972).

The chemical structure of dithiophosphate collectors may be represented by:



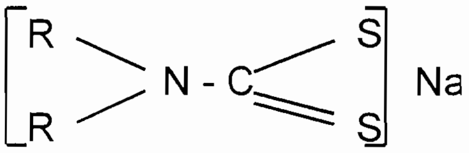
Under the conditions of their study, Grano et al (1997) list a number of advantages of the dithiophosphates over xanthates. Those relevant to this work are:

- Dithiophosphates have high standard reduction potentials (relative to SHE) for their dimerisation: +0.255 V for diethyl dithiophosphate, relative to –0.060 V for ethyl xanthate.
- The dimer of dithiophosphate is highly insoluble compared to diethyl dixanthogen.

1.4.3.1.3. Dithiocarbamates

The dithiocarbamates are used in the flotation of copper sulphide minerals, copper activated sphalerite and galena (Finkelstein and Goold, 1972). They are sometimes chosen for their combined frothing and collecting properties (Jiwu et al, 1984).

The chemical structure of dithiocarbamate collectors is as follows:



One of the conclusions drawn by Coetzer and Davidtz (1989) was that longer aliphatic chains in the N-position of the dithiocarbamates increased recoveries but decreased selectivity in the selective and bulk flotation of a copper-lead-zinc-iron ore. They used the example of an ethyl N-mono-substituted dithiocarbamate and noted that the "critical hydrophobicity" in the case of galena was not reached with this collector, which promoted detachment.

Bhaskar Raju and Forsling (1991) reported that the dithiocarbamates are particularly selective and exhibit several advantages as collectors for copper minerals. Recent investigations on the beneficiation of mixtures of copper oxides, carbonates, sulphides and arsenopyrite have revealed that dithiocarbamates are more promising than xanthates in this regard. It has been shown that a mixture of copper minerals can be effectively beneficiated without prior sulphidisation by using dithiocarbamates as collectors.

The advantages of the dithiocarbamates are due to the formation of a strong coordinate bond between metal and collector because of

1. enhanced electron-donating ability to metal Lewis acid sites due to the mesomeric electron-releasing tendency of the R_2N group and
2. the possibility of forming an additional dative π bond.

The formation of this strong bond makes it less likely that the dithiocarbamate would be oxidised to its dimer (Bhaskar Raju and Forsling, 1991 and Bradshaw, 1997).

Furthermore, di-C2-DTC has two alkyl groups as opposed to the single one on the xanthate molecule, thus rendering it more hydrophobic (Bhaskar Raju and Forsling, 1991 and Bradshaw, 1997).

1.4.4. Reaction Mechanisms of Collectors and Sulphide Minerals

Thiol collectors adsorb on sulphide minerals via a mixed potential mechanism, involving anodic oxidation of collectors and cathodic reduction of oxygen (Yoon and Basilio, 1993). The mechanism represents four classes of reactions that depend on the minerals involved, their pretreatment and the collector used. These are chemisorption, metathetical substitution catalytic oxidation and metal-thiol formation. Each will now be briefly described.

1.4.4.1. Chemisorption

Chemisorption or underpotential deposition, involves the formation of a monolayer of the thiol reaction product at potentials below the thermodynamic potential for the formation of the metal thiol compound i.e. metal ions are not removed from their lattice sites. The chemisorbed layer of collector may induce flotation (Woods, 1994). The anodic reaction is:

$$X^- \rightarrow X_{(ads)} + e^- \qquad (1.12)$$

Subsequently, metal ions may be removed from their lattice sites by surface chemical reactions and multilayers may form. If these reactions occur in the bulk solution, a hydrophobic surface will only be established if there is bulk precipitation on the mineral surface (Bradshaw et al, 1998).

The chemisorption of xanthate onto copper, chalcocite and galena has been confirmed by numerous authors (Yoon and Basilio, 1993).

1.4.4.2. Metathetical Substitution

In 1930, Taggart proposed metathetical substitution as a theory for xanthate adsorption on the mineral surface. In metathetical substitution, the oxidation product on a mineral surface is substituted by a thiol collector. This may be expressed by the following chemical reaction in which $MA_{(s)}$ represents the oxidised species on the sulphide mineral surface and A^- the oxidised anion of this species (Fuerstenau, 1995):

$$MA_{(s)} + X^-_{(aq)} \rightleftharpoons MX_{(s)} + A^-_{(aq)} \qquad (1.13)$$

This mechanism occurs only on heavily oxidised sulphide minerals (Yoon and Basilio, 1993).

1.4.4.3. Catalytic Oxidation

In catalytic oxidation, 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. This mechanism applies to the adsorption of xanthates onto pyrite and chalcopyrite to form dixanthogen (Yoon and Basilio, 1993). The oxidation product (X_2) is uncharged and physisorbed on the surface:

$$2X^- \rightarrow X_2 + 2e^- \qquad (1.14)$$

In physisorption, the bonds between the dithiolate and the mineral surface are amorphous and the Gibbs free energy of adsorption is relatively low (Bradshaw et al, 1998).

1.4.4.4. Metal - Thiol Formation (Electro-chemical Chemical (EC) Mechanism)

Here, the mineral participates in the adsorption process to form a metal thiol compound on the surface. The metal thiol formation, controlled by the electrochemical potential (E_h), involves the following electrochemical reaction (E):

$$MS \rightarrow M^{2+} + S^{o} + 2e^{-} \qquad (1.15)$$

This is followed by a chemical reaction with a thiol collector (C). This step is controlled by the stability constant of the metal-thiol compound (pK)

$$M^{2+} + 2X^{-} \rightarrow MX_2 \qquad (1.16)$$

The overall reaction is (EC):

$$MS + 2X^{-} \rightarrow MX_2 + S^{o} + 2e^{-} \qquad (1.17)$$

1.4.4.5. Comparison of Specific Collector-Mineral Interactions

The concentration required to give a certain potential of xanthate-dixanthogen couples is reduced by approximately 20% for each CH_2 group added to the xanthate homologous series (Majima and Takada, 1968). This implies that dixanthogen forms more readily with the longer-chained xanthates.

A significant difference was observed between the behaviour of the minerals that formed the metal xanthate and those that formed dixanthogen. Those that formed dixanthogen reacted at a rate that decreased regularly with time. Those that formed the metal xanthate reacted much more rapidly during an initial period (less than a minute) after which the rate fell to about the same level as that observed for the dixanthogen formation (Allison et al (1972)). The identities of the reaction products were not affected by the pH of the solution or the chain length of the xanthate used.

In general, dimers or dithiolates on the mineral surface gave increased floatability although they were not essential for the collecting action of thiol collectors (Finkelstein and Poling, 1977).

Woods (1984), commenting on Allison et al (1972) and Finkelstein and Goold (1972), stated that useful information may be gained from the comparison of the rest potential of the mineral with the reversible potential of the dithiolate formation reaction. Woods, however cautioned that care should be exercised in identifying surface reactions by this method as the procedure had two limitations. Firstly, as the calculated equilibrium potentials were derived from the thermodynamic properties of bulk phases, identification was only valid when multilayers were formed. Secondly, many of the reactions involving sulphides are irreversible. This implies that a process may occur because it has the greatest rate rather than being the most thermodynamically favourable.

The oxidation of xanthate, dithiophosphate and dithiocarbamate yield the dimers: dixanthogen, dithiophosphatogen and thiouram disulphide respectively (Fuerstenau, 1990). From the standard cell potentials for the oxidation reactions below the diethyl dithiophosphate (DTP^-) is more difficult to oxidise than ethyl xanthate (X^-) or diethyl dithiocarbamate (DTC^-) (Fuerstenau, 1990). Dithiolate formation on the mineral surface occurs when the rest potential of the mineral in the solution of the collector is greater than the reduction potentials of the dithiolate (Allison et al, 1972 and Finkelstein and Goold, 1972).

$X_2(l) + 2e^- \leftrightarrow 2X^-$ $E^\circ = -0.06$ V (1.18)

$(DTP)_2(l) + 2e^- \leftrightarrow 2DTP^-$ $E^\circ = 0.25$ V (1.19)

$(DTC)_2(l) + 2e^- \leftrightarrow 2DTC^-$ $E^\circ = -0.068$ V (1.20)

Valli and Persson (1994) noted that significantly smaller amounts of copper were observed in the aqueous phase after treating chalcopyrite with aqueous potassium ethylxanthate in comparison with covellite. This was attributed to the partial oxidation of covellite to thiosulphate ions that form stable complexes with copper (I). In addition, the solubility of copper (I) alkylxanthate increases as the concentration of free copper (I) ions becomes very low. In the case of chalcopyrite, the oxidation product of sulphur is sulphate ions. These do not stabilise copper (I) and the concentration of free copper (I) ions is not reduced as it is in the presence of thiosulphate. The copper (I) alkylxanthate solubility then remains low due to the presence of free copper (I) ions.

1.4.4.5.1. Adsorption of Thiol Collectors onto Chalcopyrite ($CuFeS_2$)

Xanthates

According to Abramov (1966), flotation of chalcopyrite is reduced significantly when dixanthogen does not form. However, good flotation could be achieved with chemisorbed xanthate corresponding to four to five monolayers of collector coatings.

Allison et al (1972) determined the products of the reaction between chalcopyrite and aqueous methyl, ethyl, propyl and butyl xanthates to be dixanthogen in each case.

Chalcopyrite was slightly depressed in oxygen-saturated solutions as oxygen promoted the formation of cupric and ferric hydroxides that prevented the adsorption of dixanthogen on the mineral surface (Klymowsky and Salman, 1970 & Guy and Trahar, 1985). The presence of metal hydroxides is implied by reactions (1.5) and (1.6). Guy and Trahar (1985) reported that lead and copper hydroxides were effective at suppressing the flotation of chalcopyrite. Chalcopyrite suppression by ferrous hydroxide was variable and depended upon the degree of its conversion to ferric oxide. Small amounts of copper ions (as low as 10 ppm) were seen to have pronounced detrimental effects on chalcopyrite flotation.

Yoon and Basilio (1993) reported that xanthate formed dixanthogen on chalcopyrite at potentials near the reversible potential for the xanthate/dixanthogen couple. At higher potentials, however, chalcopyrite oxidised and copper ions were released. These reacted to form the metal xanthate and this in turn co-existed with the dixanthogen. There is no evidence to suggest that underpotential deposition of xanthate took place on chalcopyrite (Yoon and Basilio, 1993). Xanthate adsorption may therefore be ascribed to the catalytic oxidation mechanism.

Suoninen and Laajalehto (1993) used X-ray photoelectron spectroscopy (XPS) measurements to further elucidate the surface chemistry of potassium ethyl xanthate and chalcopyrite. They reported that after reaction no ionic xanthate species could be detected on the chalcopyrite surface and that the dithiolate was probably present.

Valli and Persson (1994) also used XPS and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy to show that copper was present as copper (I) on the surfaces of chalcopyrite. They showed that the only alkylxanthate species resulting from the reaction of chalcopyrite and an aqueous potassium alkylxanthate solution was solid cuprous alkylxanthate i.e. dialkyl dixanthogen and iron alkylxanthate did not form. This disagreed with Allison et al (1972), Klymowsky and Salman (1970), Guy and Trahar (1985), Yoon and Basilio (1993), Suoninen and Laajalehto (1993) and Woods (1994). Woods (1994) reported that there was unequivocal evidence for the formation of dixanthogen on chalcopyrite and that this may take place after the chemisorption of xanthate. In the chalcopyrite xanthate/system, cuprous xanthate was additionally formed at high potentials. It may therefore be that Valli and Persson conducted their work at high potentials or other conditions that did not promote the formation of dixanthogen.

Dithiophosphates

Finkelstein and Goold (1972) reported the presence of $Cu(DTP)_2$ on chalcopyrite after reaction with potassium diethyl dithiophosphate.

Grano et al (1997) reported that the rate of adsorption of dicresyl dithiophosphate (DCDTP) onto chalcopyrite was pH dependent and that above pH 6, the adsorption of DCDTP onto chalcopyrite occurred to a lesser extent. The maximum flotation recovery of chalcopyrite was, however, largely independent of pH. It was noted that this was also observed with di-C2-DTP as collector and that the maximum flotation rate with this collector occurred at pH 5.

For chalcopyrite, a hydrated iron oxyhydroxide was the main oxidation product observed under alkaline conditions and normal oxidising potentials. As the predominant iron oxyhydroxide phases were expected to weakly interact with dithiophosphate collectors under alkaline conditions, there would be a decrease in the amount of DCDTP adsorbed. It is therefore improbable that chalcopyrite oxidation accounted for multilayer DCDTP adsorption under these conditions.

The oxidised chalcopyrite surface was more than likely a heterogeneous one consisting of unoxidised chalcopyrite, iron-deficient chalcopyrite ($CuFe_{1-x}S_2$) and iron oxyhydroxide. As the surface was not heterogeneous, the DCDTP adsorption rate showed multicomponent behaviour with respect to its adsorption rate (Grano et al (1997)).

Dithiocarbamates

Finkelstein and Goold (1972) observed the presence of $Cu(DTC)_2$ on chalcopyrite after reaction with sodium diethyl dithiocarbamate.

UV, visible and IR spectroscopy indicated the presence of copper-di-C2-DTC complex as a surface product during the electroflotation of chalcopyrite fines (Bhaskar Raju and Khangaonkar, 1984). The maximum copper recoveries occurred at a collector concentration in the region of 5×10^{-4} mol/L at all current densities tested.

In a zeta-potential and adsorption study of the chalopyrite-di-C2-DTC system Mangalam and Khangoankar (1985), observed that a zeta potential of zero occurred at a concentration of 0.83×10^{-3} mol/L of di-C2-DTC and a pH of 9. The authors point out that this concentration also corresponded to the optimum adsorption density of the collector. They also observed that Van der Waals and electrostatic forces did not play a significant role in the adsorption of di-C2-DTC on chalcopyrite and that the adsorption was due to chemisorption with an equilibrium constant of $(2.38 \pm 0.03) \times 10^{8}$.

In summary, although there are views to the contrary (Valli and Persson, 1994), it is widely accepted that the hydrophobic species responsible for the flotation of chalcopyrite, when xanthate is used as a collector, is dixanthogen. The hydrophobic species responsible for the flotation of chalcopyrite was $Cu(DTP)_2$, when potassium diethyl dithiophosphate was the collector and $Cu(DTC)_2$ or Cu(DTC) in the case of sodium diethyl dithiocarbamate.

1.4.4.5.2. Adsorption of Thiol Collectors onto Chalcocite (Cu_2S)

Xanthates

Allison et al (1972) determined the products of the reaction between chalcocite and aqueous propyl and butyl xanthates to be cuprous xanthate in each case. Kowal and Pomianowski (1973) support a two step chemisorption of a monolayer of xanthate on chalcocite as they too observed cuprous xanthate on the mineral surface. Heyes and Trahar (1979) observed that chemisorbed xanthate was responsible for the flotation of chalcocite.

Xanthate could adsorb on chalcocite by anodic oxidation in the presence of oxygen and by ion exchange with previously formed oxidised species (Barzyk et al (1981) & Richardson et al (1984)). Barzyk et al (1981) observed that to achieve the same flotation recovery, greater xanthate coverage was required with the most heavily oxidised mineral compared to the coverage required for the least oxidised mineral. Richardson et al (1984) observed there were at least four and probably five distinct reactions in the Cu_2S, O_2, H_2O and ethyl xanthate system:

1. Ethyl xanthate was oxidised to ethylperxanthate.
2. Ethyl xanthate reacted with Cu(II) produced from the anodic dissolution of Cu_2S.
3. An "inferred" reaction where ethyl xanthate was converted to a non-reducible xanthate derivative.
4. Ethyl xanthate reacted by the electrochemical reaction:

$$Cu_xS + \lambda X^- = Cu_{x-\lambda} + \lambda CuX + \lambda e^- \qquad (1.21)$$

5. Ethyl xanthate (X^-) reacted by:

$$Cu(OH)_2 + X^- + e^- = CuX + 2OH^- \quad \text{or} \qquad (1.22)$$

$$Cu(OH)_2 + 2X^- = CuX_2 + 2OH^- \qquad (1.23)$$

With enough time available, it was assumed that the cupric xanthate decomposed to cuprous xanthate and dixanthogen.

Richardson et al (1984) reported a good correlation between xanthate uptake, anodic oxidation and flotation recovery. They reported that 20 to 40% of the adsorbed xanthate was involved in a reaction producing a non-reducible species. Also, the mechanism of interaction of the xanthate and chalcocite depended upon the conditions experienced prior to the addition of the collector.

Guy and Trahar (1985) examined the flotation of chalcocite with collectors. They inferred that only a small amount of the soluble oxy-sulphur species was formed during oxidation (reaction (1.6)). Cuprous ethyl xanthate was assumed to be the hydrophobic entity. Combining the oxidation of chalcocite with the cupric ion xanthate reaction:

$Cu_2S \rightarrow Cu^{2+} + CuS + 2e^-$ (1.24)

$Cu^{2+} + X^- + e \rightarrow CuX$ (1.25)

$Cu_2S + X^- \rightarrow CuS + CuX + e$ ($E^o = -0.234$ V) (1.26)

The absence of a pH effect on the lower flotation edge, suggests a reaction of the last type.

Fuerstenau (1990) reported that xanthate adsorption on chalcocite was a two stage process. The first stage involved xanthate adsorption followed by the formation of an unleachable xanthate species on the chalcocite surface. After the formation of the unleachable chemisorbed layer, multilayers of cuprous xanthate formed and adsorbed on the surface. At relatively high xanthate dosages (0.006 mol/l) approximately 25% of the xanthate added was unleachable, while the remaining 75% remained on the chalcocite surface as cuprous xanthate. Approximately half of the ions exchanged upon xanthate adsorption were hydroxyl and the balance was principally carbonate and some sulphate.

The electrochemical mechanism may represent the metal xanthate formation on chalcocite and copper. As the chalcocite was readily oxidised, the electrochemical mechanism explains its flotation in the presence of short chain xanthates. (Yoon and Basilio, 1993).

Electrochemical studies of particulate chalcocite-xanthate interaction have shown that there is a formation of bulk cuprous xanthate via reaction 1.27 (Woods, 1994).

$Cu_2S + xC_2H_5OCS_2^- \rightarrow xCu(C_2H_5OCS_2) + Cu_{2-x} + xe^-$ (1.27)

Dithiophosphates and Dithiocarbamates

Finkelstein and Goold (1972) reported the presence of $Cu(DTP)_2$ or Cu(DTC) on chalcocite after reaction with potassium diethyl dithiophosphate or sodium diethyl dithiocarbamate respectively.

Chander and Fuerstenau (1974) examined the chalcocite/diethyldithiophosphate system and reported a good correlation between the development of a finite contact angle, efficient flotation and chemisorption of dithiophosphate on the mineral surface and copper dithiophosphate formation. They acknowledged that the collector could also be adsorbed by ion exchange with oxidised chalcocite.

There is evidence to suggest that an initial chemisorbed layer of diethyl dithiophosphate deposits on chalcocite (Woods, 1994).

Similar adsorption behaviour has been noted in the xanthate-chalcocite system and the dithiophosphate-chalcocite system. The chemisorption of dithiophosphate and the formation of cuprous and cupric diethyl dithiophosphate on the chalcocite surface has been recorded (Fuerstenau, 1990).

In summary, in general the hydrophobic species responsible for the flotation of chalcocite was the metal thiolate, when xanthate was used as a collector. The mechanism of interaction of the xanthate and chalcocite, however, depended upon the degree of oxidation of the chalcocite surface. The hydrophobic species responsible for the flotation of chalcocite was $Cu(DTP)_2$, when potassium diethyl dithiophosphate was the collector and Cu(DTC) in the case of sodium diethyl dithiocarbamate.

1.4.4.5.3. Adsorption of Thiol Collectors onto Bornite (Cu_5FeS_4)

Xanthates

Allison et al (1972) determined the products of the reaction between bornite and aqueous propyl and butyl xanthates to be cuprous xanthate in each case.

Dithiophosphates

Finkelstein and Goold (1972) reported $Cu(DTP)_2$ on the surface of bornite after reaction with potassium diethyl dithiophosphate and $Cu(DTC)_2$ after reaction with sodium diethyl dithiocarbamate.

1.4.4.5.4. Adsorption of Thiol Collectors onto Covellite (CuS)

Xanthates

Allison et al. (1972) determined the products of the reaction between covellite and aqueous methyl, ethyl, propyl and butyl xanthates. They observed only dixanthogen in the cases methyl and ethyl xanthates and a mixture of dixanthogen and cuprous xanthate in the cases of propyl and butyl xanthates. They explained the formation of dixanthogen by a mechanism that involved the reduction of the cupric ion (chemical reaction 1.28).

$$CuS + 2X^- \rightarrow CuX + X_2 + 2e^- \qquad (1.28)$$

Copper (I) was present on the surface of covellite and solid cuprous alkylxanthate was assumed to be responsible for its hydrophobicity (Valli and Persson, 1994).

Dithiophosphates

Finkelstein and Goold (1972) reported the presence of $Cu(DTP)_2$ on covellite after reaction with potassium diethyl dithiophosphate and $Cu(DTC)_2$ on covellite after reaction with sodium diethyl dithiocarbamate as collector.

Dithiocarbamates

Bhaskar Raju and Forsling (1991) studied the adsorption mechanism of diethylthiocarbamate on covellite. They reported that:

1. The attachment of di-C2-DTC on the mineral took place via a chemisorption mechanism whereby cations were dislodged from the mineral surface. The di-C2-DTC acted either directly or through copper hydroxyl complexes precipitated at the surface.
2. Two types of surface species, $[Cu(DTC)]^+$ or $Cu(DTC)_2$, were possible on covellite, depending on the dithiocarbamate concentration. Initially, at low concentrations of di-C2-DTC, $[Cu(DTC)]^+$ was formed. This was converted to $Cu(DTC)_2$, as the concentration of the di-C2-DTC was increased.
3. A kinetic study revealed that the overall process of adsorption was controlled by the rate of diffusion.

In summary, dixanthogen is considered responsible for the hydrophobicity of covellite in the cases methyl and ethyl xanthates and a mixture of dixanthogen and cuprous xanthate in the cases of propyl and butyl xanthates. The hydrophobic species responsible for the flotation of covellite was $Cu(DTP)_2$, when potassium diethyl dithiophosphate was the collector and $Cu(DTC)_2$ in the case of sodium diethyl dithiocarbamate.

Table 1.3 contains a summary of the reports of different species formed on copper sulphide minerals after the addition of thiol collectors,

Table 1.3 Species responsible for the surface hydrophobicity of minerals

	Collector					
	C2-X		**di-C2-DTP**		**di-C2-DTC**	
Mineral	**Species Responsible for Hydrophobicity**	**Reference**	**Species Responsible for Hydrophobicity**	**Reference**	**Species Responsible for Hydrophobicity**	**Reference**
bornite Cu_5FeS_4	CuX	1, 5	$Cu(DTP)_2$	3	$Cu(DTC)_2$	3
chalcopyrite $CuFeS_2$	X_2	1, 7, 8, 9, 10	$Cu(DTP)_2$	3	Cu(DTC) $Cu(DTC)_2$	11, 12 3
chalcocite Cu_2S	CuX*, $Cu(X)_2$	2, 5, 6, 8, 9, 10	$Cu(DTP)_2$, Cu(DTP)*	3 2,5	Cu(DTC)	3
covellite CuS	X_2, CuX	1, 4, 8	$Cu(DTP)_2$	3	$Cu(DTC)_2$	3

References for Table 1.3

*Depends upon the degree of oxidation of the chalcocite surface ($Cu(X)_2$ or Cu(DTP) is formed on the oxidised mineral.)

1. Allison et al (1972)
2. Chander and Fuerstenau (1974).
3. Finkelstein and Goold (1972)
4. Fuerstenau (1982c)
5. Fuerstenau (1990)
6. Guy and Trahar (1985)
7. Suoninen and Laajalehto (1993)
8. Valli and Persson (1994).
9. Woods (1994)
10. Yoon and Basilio (1993)
11. Mangalam and Khangoankar (1985),
12. Bhaskar Raju and Khangaonkar (1984)

1.4.4.6. The Effect of Collector Concentration

Flotation recovery strongly depends on the concentration of the collector (Somasundaran, 1975). An excess of collector has been shown to reduce the flotation recovery of minerals. Two of the mechanisms that have been proposed are adsorption of a second layer of collector on the mineral surface with the opposite orientation of the first layer and adsorption as micelles. The second is less likely as only a small fraction of the surface needs to be hydrophobic for flotation to occur.

Taggart (1951) reported a decrease in hydrophobicity of minerals at high collector dosages. He used contact angle measurements and floatability as measures of hydrophobicity.

Smar et al (1994) reported that the rate and recovery of flotation increased as the collector concentration increased until some maximum in concentration was reached. When the collector concentration was increased beyond the value corresponding to this maximum, the rate decreased more than the recovery.

A relatively high collector dosage, might be necessary for economical recovery of coarse particles of sulphide minerals. This high dosage might decrease the rate of flotation of the average-sized particle and usually negatively affects selectivity in separations by froth flotation. (Smar et al, 1994).

1.5 Mixtures of Collectors and Sulphide Minerals

It has been shown that the use of collector mixtures can have benefits over the use of pure collectors (Bradshaw et al, 1998, Bradshaw, 1997, Bradshaw and O'Connor, 1994, Bradshaw and O'Connor, 1996, Bradshaw, Harris and O'Connor, 1998, Helbig, Bradshaw, Harris, O'Connor and Baldauf, 2000, Rao, and Forrsberg, 1997). These benefits include lower dosage requirements, improved selectivity, rates and recovery and an increase in the recovery of coarse particles. They have been reported for anionic, cationic and non-ionic collectors. Often there was an optimum ratio of constituent collectors. The dithiophosphates are widely used in mixtures and form a class of collectors called promoters (Bradshaw et al, 1998).

1.5.1. Mechanisms of Synergistic Interactions

It is commonly known in the practice of flotation that collector mixtures are often more effective than would be expected from their individual known characteristics. Here the combined effect of the collectors exceeds the sum of the weighted individual effects. This is an example of synergism in flotation (Bradshaw et al, 1998). Synergism is known to occur in collector:collector, collector:frother and frother:frother interactions. It may improve recovery and selectivity in differential flotation. The interactions between reagents that result in synergism are complex and depend upon their chemical nature and their chemisorptive or physisorptive properties.

Various mechanisms have been proposed to explain the benefits of collector mixtures including that there is a greater extent of adsorption when collector mixtures are used (Bradshaw et al, 1998). This might improve the hydrophobicity of the surface by providing a more evenly distributed surface species or provide a surface collector layer more suitable for frother-collector interactions. The change in hydrophobicity might be observed as changes in contact angle, bubble loading and recovery (Bradshaw et al, 1998).

1.5.1.1. Synergistic Interactions between Collectors in Sulphide Mineral Flotation

Bradshaw and O'Connor (1994) used mixtures of dithiocarbamates in the flotation of pyrite. They reported that mixtures were superior collectors to the pure components as they yielded higher recoveries, grades, mass pulls and greater recovery of coarse particles. The best results were obtained with a collector mixture consisting of 90:10 mole% ratio of di-n-propyl dithiocarbamate and cyclo-hexyl dithiocarbamate. The improved recovery may have been due to the selective adsorption of the different collectors on particular sites or changes in the orientation of the alkyl chains resulting in superior surface coverage. Increased dosages in both mixtures and pure collectors resulted in increased recoveries and grades and masked the synergistic effect of the mixtures.

Binary mixtures of the dithiocarbamates and PNBX, SMBT or iso-C3-DTP were also tested (Bradshaw and O'Connor, 1994). The dithiocarbamates and their mixtures were weaker collectors than any one of the other thiol collectors at the same equivalent collector dosage.

The effect of dosage on recoveries and grades was examined with pure di-n-propyl dithiocarbamate and cyclo-hexyl dithiocarbamate and their mixtures (Bradshaw and O'Connor, 1994). Recoveries and grades increased when the dosage of the pure reagents was increased. They were almost unchanged when the dosage of the 90:10 mixtures was increased. Equimolar mixtures at dosages of 50, 60 and 80 mmoles/ton were compared. The recovery increased marginally when the dosage was increased, but this came at the expense of a decreased grade; indicating a greater, less selective mass pull. It was therefore beneficial to use the collector mixtures at the lower dosage as this reduced reagent consumption with no significant loss in recovery. The poorer grade at high dosages (80 mmoles /ton) was attributed to the greater likelihood that collector molecules would adsorb at all sites irrespective of surface heterogeneity; rendering even the coarse particles sufficiently hydrophobic. This enhanced floatability but lowered selectivity. In addition, it had been shown by Wakamatsu and Numata (1980), that for a mixture of xanthate and dithiophosphate there was enhanced co-adsorption of collectors at low collector concentrations. At higher dosages, there was competitive adsorption of the stronger collector. The consequence of this was that the collector mixture behaved as the stronger collector.

The method of collector addition was examined (Bradshaw and O'Connor, 1994). It was observed that premixing or simultaneous addition made no difference to flotation performance. The addition of the weaker collector before the addition of the stronger one, however, led to a slightly enhanced performance. This was explained by the preferential adsorption of the weaker collector on strong sites and the subsequent adsorption of the stronger collector on the weaker sites.

Helbig et al (2000), using microflotation experiments, concluded that under the conditions of their study di-n- and di-iC4-DTC were the most effective pure collectors and that di-C4-DTP was the least effective for the collection of pyrite. The mono-n-C4-DTC showed a higher strength of adsorption compared to iC4-X. Similar flotation results were however obtained with these collectors. When pure collectors adsorbed onto pyrite at dosages below that corresponding to monolayer coverage only the metal thiolate formed.

The authors record significant synergistic effects with mono-n-C4-DTC/iC4-X and iC4-X/di-C4-DTP mixtures. This work was done at a collector concentration of 9×10^{-6} mol/L with the mono-n-C4-DTC/iC4-X mixtures and synergism occurred most markedly when the mono-n-C4-DTC percentage was in the 40 to 80% range. The concentration of the iC4-X/di-C4-DTP mixtures was 2×10^{-5} mol/L and synergism occurred most markedly when the iC4-X percentage was in the 40 to 80% range.

Synergistic effects were not observed with di-C4-DTC/iC4-X mixtures at a collector concentration of 8.7×10^{-7} mol/L. Dixanthogen was shown not to have formed at the lower concentration (Helbig et al, 2000).

The above conclusions are in agreement with the hypothesis of Bradshaw and O'Connor (1996). They postulated that synergism was due to the formation of mixed multilayers, consisting of dithiolates and metal thiolates, at the mineral surface. The formation of these multilayers would occur at the higher concentration of collector mixtures as it is here that dixanthogen forms in the presence xanthate and oxygen.

The froth structure and final concentrate grade may be influenced by a combination of collectors that result in both physisorbed and chemisorbed surface products. It has been noted that enhanced performance results from the use of a strong collector with no frothing properties in combination with a weaker collector with frothing properties. The stronger collector increased the recovery of coarse particles, while the weaker one improved the recovery of the finer particles. This is not a true synergy as the combined effects equal the sum of the individual effects (Bradshaw et al, 1998).

The synergistic interactions that have been reported and that are relevant to this study are presented in Table 1.4.

Table 1.4. Summary of synergistic effects observed in flotation (Bradshaw et al, 1998)

Interactions	Reagents (mole ratios tested)	Minerals	Techniques	Benefit of Mixture
Collector:Collector Thiol-Thiol	Dithiocarbamates:xanthates, dithiophosphates	Copper sulphides		Best results were obtained with dithiocarbamates and other collectors
	Dithiophosphates, xanthates, mercaptobenzothiazole, di-iso butyl DTP:iC4-X (30:70; 50:50; 70:30	Various sulphides	Batch flotation	Improved recoveries due to combined properties Optimum ratio 70:30
	Isobutyl xanthate:cyano diethyl dithiocarbamate (12:44)	Chalcopyrite Pyrite	Batch flotation	Increased recovery and grade with 12:44 mixture
	Dithio-, monothio-phosphates (75:25; 50:50; 25:75)	Mixed copper sulphides	Batch flotation	Optimum recovery at 75:25 due to combination of properties
	Xanthate:dicresyl dithiophosphate	Copper sulphides	Batch flotation	Enhanced kinetics at lower dosages
Collector:Frother	Xanthate:alcohols	Chalcocite	Frothability	Enhanced frothability
	Ethyl xanthate:α-terpinol	Chalcocite	Adsorption, Film thickness, Batch flotation	Increased xanthate adsorption with terpinol addition
	Ethyl xanthate:diacetone	Copper ores	Frothability	Only froths in 3 phase

The flotation of pyrite with collector mixtures has been explored (Bradshaw et al, 1998), but not much is mentioned in the literature reviewed on the use of collector mixtures in the flotation of partially oxidised copper sulphide ores. The potential of collector mixtures in this area is therefore unproven and this study seeks to address this shortcoming and investigate other factors affecting collector behaviour.

1.6. Research Objectives

The overall objective of this study was to investigate factors that affect the effectiveness of the collectors and collector mixtures on the flotation of partially oxidised and oxidised copper ores. The effectiveness was evaluated by assessing the flotation performance in terms of the mass, water, sulphur, copper and acid soluble copper recoveries; sulphur, copper and acid soluble copper grades; and the Klimpel rate constants.

The specific research objectives were to evaluate the effect of:

1. The collector structure by evaluating the role of the following selected functional groups: xanthates, dithiophosphates and dithiocarbamates.

2. Dosage of collectors, including establishing whether the trend of collector effectiveness changes with changing dosage.

3. The use of collector mixtures, including their effectiveness at reduced dosages as compared to that obtained with the pure component collectors.

4. The role of ore type by comparing the behaviour obtained with the partially oxidised bornite rich Carolusberg copper sulphide ore from Okiep and an oxidised bornite and chalcopyrite rich ore with covellite from Palaborwa.

2. EXPERIMENTAL DETAILS

Batch flotation tests were done in order to establish the effects of different functional groups of collectors, dosage of collectors and collector mixtures on flotation performance. In addition, the role of ore type was assessed. The collector classes of xanthates dithiophosphates and dithiocarbamates were selected and the reagents C2-X, iC4-X, di-C2-DTP and di-C2-DTC were tested at selected dosages. The collector mixtures 90 mol%C2-X:10 mol%di-C2-DTC, 90 mol%C2-X:10mol%di-C2-DTP and 90 mol%iC4-X:10 mol%di-C2-DTC were also tested at selected dosages.

The collector dosages used were 0.0348, 0.0695, 0.139 or 0.209 mol/ton ore; molar equivalent values to 5, 10, 20 and 30 (g C2-X)/(ton ore) respectively.

The flotation performance of the Okiep Copper Company (OCC) ore was assessed in terms of the cumulative mass, water, sulphur and copper recoveries; cumulative copper and sulphur grades; and the Klimpel rate constants for copper recovery. The cumulative acid soluble copper recoveries and grades were used to assess the performance of the Palaborwa Mining Company (PMC) ore.

Copper recoveries were calculated based on the copper in the concentrates and the residual copper in the tailings. The sulphur recoveries were calculated on the same basis.

The error bars in the figures presented in Chapter 3 represent one standard deviation above and below the respective mean values obtained in tests that were repeated. The results of the analysis of variance (ANOVA) of repeated test runs are presented in Appendix D.

2.1. Apparatus

2.1.1. The Flotation Cell

The flotation cell used was a modified Leeds laboratory cell with a 3L capacity (Figure 2.1). The impeller was fitted with a speed controller and the air flow rate was adjustable. The pulp level was controlled with a constant head device to have a froth height of 1.0 cm. The froth was removed manually as described in Section 2.3.2.

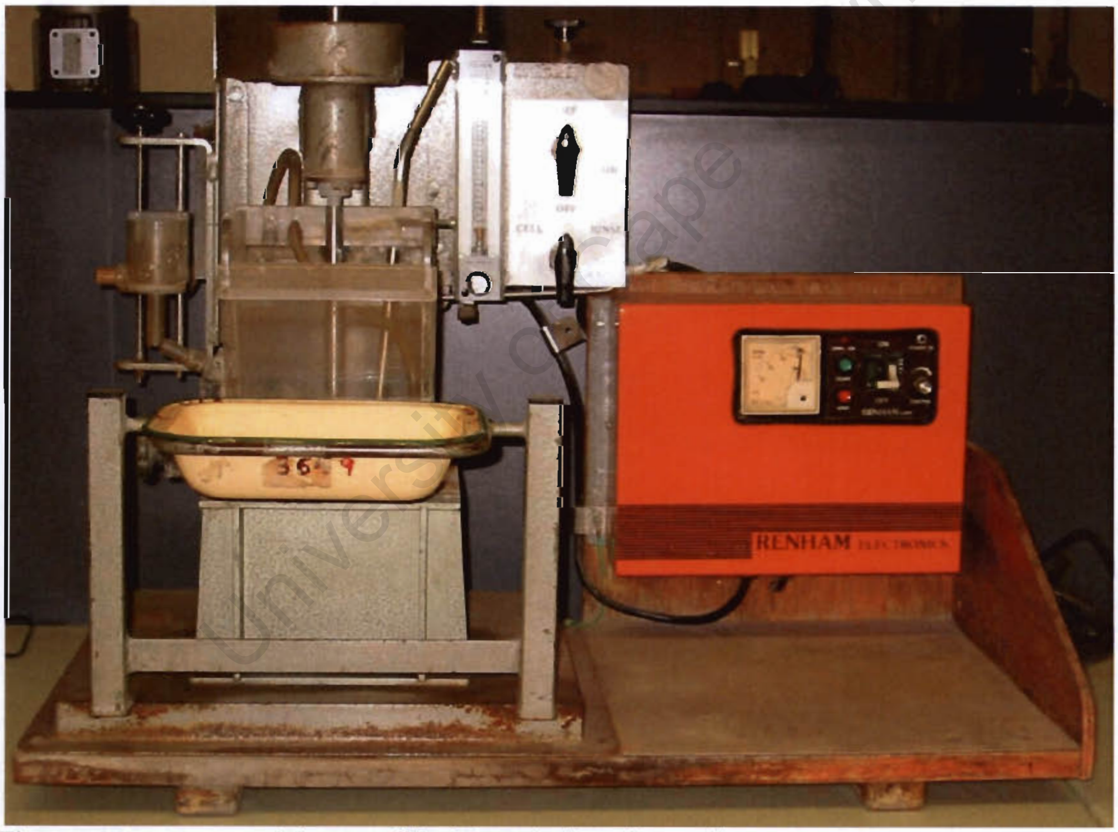


Figure 2.1. The modified Leeds flotation cell

2.1.2. The Rod Mill

Each ore was milled prior to flotation in a Sala stainless steel rod mill. The diameter and length of the mill was 300 mm and the diameter of each of the rods was 25 mm. The mill charge was 25 rods.

2.2 The Ores

The OCC and PMC ore samples were carefully split into smaller representative samples of approximately 1 kg in mass.

Process Mineralogy and Services at Mintek, Johannesburg, prepared the feed ore mineralogies for both the OCC and PMC ores. The gangue mineralogy was determined by X-ray diffraction analysis. Optical and scanning electron microscopy was used to identify the subordinate phases in polished sections of the samples.

2.2.1 Okiep Copper Company Ore

The ore tested came from near the town of Okiep, Namaqualand. It was from an unusual late Proterozoic deposit that involved ortho-pyroxene-plagioclase "noritoid" intrusions into granulite-facies gneisses, carrying disseminations and injected masses of chalcopyrite (1.65% Cu average grade) with accessory cobaltian pyrite and pentlandite (Guilbert and Park, 1999).

The average copper grade of the samples tested was 1.8%. The mineralogy showed that the main copper sulphide was bornite. Other copper sulphides noted were chalcocite, chalcopyrite, digenite and possibly enargite (Table 2.1). Pyrite was the main sulphide gangue mineral. The chief silicate gangue phases were pyroxene, quartz and K-feldspar. Mica was a minor constituent. The micas are complex aluminium silicates.

Table 2.1 Mineralogy of the Okiep Copper Company Ore

Copper Sulphides		Other Sulphides		Chief Silicate Gangue		Trace Minerals	
bornite	Cu_5FeS_4	pyrite	FeS_2	pyroxene	Fe-Mg	talc	$Mg_3Si_4O_{10}(OH)_2$
chalcocite	Cu_2S			quartz	SiO_2	hematite	Fe_2O_3
chalcopyrite	$CuFeS_2$			K-feldspar	$KAlSi_3O_8$	ilmenite	$FeTiO_3$
digenite	Cu_9S_5			biotite	$K(Mg, Fe)_3AlSi_3O_{10}(OH, F)_2$	magnetite	Fe_3O_4
enargite	Cu_3AsS_4			phlogopite	$KMg_3AlSi_3O_{10}(OH, F)_2$		

Table 2.2 Mineralogy of the Palaborwa Mining Company Ore

Copper Sulphides		Accessory Phases (Excluding cubanite and copper sulphide)		Carbonate Gangue Phase		Minor Constituent and Trace Mineral	
Bornite	Cu_5FeS_3	Pyrite	FeS_2	Calcite	$CaCO_3$	Biotite	$K(Mg, Fe)_3AlSi_3O_{10}(OH, F)_2$
Chalcopyrite	$CuFeS_2$	Galena	PbS	Dolomite	$CaMg(CO_3)_2$	Phlogopite	$KMg_3AlSi_3O_{10}(OH, F)_2$
Copper sulphide	CuS	Ilmenite	$FeTiO_3$	Ankerite	$Ca(Mg, Fe)(CO_3)_2$		
Cubanite	$CuFe_2S_3$	Baddeleyite	ZrO_2			Apatite	$Ca_5(F, Cl)(PO_3)_3$
						Magnetite	Fe_3O_3
						Serpentine	$Mg_3Si_2O_5(OH)_3$

Biotite and phlogopite were the examples of mica present. There were traces of talc, magnetite, hematite and ilmenite.

2.2.2. Palaborwa Mining Company Ore

The second ore used was from a deposit near Palaborwa, in the North East Province. This is a large composite alkalic carbonatite pipe, known as the Palaborwa complex (Guilbert and Park, 1999). It is approximately 7 km long by 3 km wide and vertically invades granitic basement rocks. The deposit is estimated to contain 700 million tons of ore averaging 0.68% copper. Chalcopyrite is the principle sulphide with bornite and chalcocite with minor amounts of other copper minerals.

Copper, apatite, and vermiculite are mined from the northern two of three pipes. Co-products are magnetite, uranium, cobalt and zirconium-hafnium. Also, there are trace amounts of nickel, gold, silver and platinum metals (Guilbert and Park, 1999).

Copper minerals appear in transgressive carbonatite, banded carbonatite and phoskorite. All carbonatites contain calcite, dolomite or siderite. Chalcopyrite, with minor cubanite, is the dominant copper mineral near the centre of the pipe, especially in the transgressive carbonatite, which has 1% copper. Bornite, at grades averaging 0.5% copper, is the dominant copper mineral in the lower grade banded carbonatite. Phoskorite contains predominantly bornite of the copper minerals (averaging 0.2 to 0.3% copper) and economic amounts of apatite. Magnetite, with 2 to 4% brookite, baddeleyite and vallerite, are present in transgressive carbonatite and banded carbonatite. Vallerite poses recovery problems, as recovery by flotation is less than 20%. In addition, it interferes with the flotation of other sulphides so causing copper losses. (Evans, 1992).

The average copper grade of the samples tested was 0.58%, while the average feed grade of the acid soluble copper minerals was 0.06%. (Approximately 10% of the copper present in the ore was in the form of acid-soluble copper i.e. 10% was in the form of copper oxide minerals.) The mineralogy of the PMC ore showed bornite and chalcopyrite were the main sulphides. The accessory phases contained copper sulphide, pyrite, galena, cubanite, ilmenite. and baddeleyite. Carbonate (calcite and dolomite/ankerite) was the main gangue phase. Mica (biotite/phlogopite) is a minor constituent. Trace components were serpentine, magnetite and apatite. The chemical formulae of the above minerals are given in Table 2.2. No copper oxides were reported in the mineralogy of the ore (Table 2.2). This was not surprising as mineralogy can only give qualitative results for such low feed grades.

2.3 Experimental Procedures

Procedures were adapted for laboratory conditions.

2.3.1. Milling Procedure

Each of the 1 kg samples was wet milled at 60% solids in a laboratory-scale Sala rod mill. The OCC ore was milled for nine minutes while the PMC ore was milled for five minutes. At these times, approximately 60% of the ore was milled to -75μm in each case. The milling curves for each ore are included in Appendix A. Also included are sieve analyses of the mill product after nine minutes in the case of the OCC ore and five minutes in the case of the PMC ore.

2.3.2. Flotation Procedure

1. A 3L laboratory batch flotation cell was charged with wet milled ore.
2. The impeller speed was adjusted to 1200 rpm.
3. Water was allowed to enter the cell until a froth height of 1 cm could be maintained.
4. A 50 ml feed sample was taken from the cell for copper assay.The pulp pH was adjusted to 10.2 with a calcium hydroxide slurry. The pH was maintained here for 1 minute.
5. Collector was added and allowed to condition for 1 minute.
6. 6010 frother was added and after 45 seconds air was allowed to enter the batch flotation cell at 6L/sec.
7. Scraping at 10-second intervals started 15 seconds after air was introduced to the flotation cell.
8. Cumulative samples were taken after 1, 2, 7, 12 and 20 minutes.
9. The tailings from the cell was pressure filtered.
10. The feed sample and floated samples were filtered in a Buchner funnel. These and the tails were oven dried overnight. They were then weighed and analysed for sulphur and copper.

2.3.3. Analyses

The sulphur analyses were done using a Leco by standard method (Appendix C).

The acid digestion method used for the copper analysis and the acid digestion method used for the analysis of acid-soluble copper are detailed in Appendix C.

2.4 Research Programme

Okiep Copper Company Ore

1. To investigate the role of the different functional groups of collectors and to test the effect of collector dosage, the performances of sodium ethyl xanthate, sodium diethyl-dithiophosphate and sodium diethyl-dithiocarbamate were tested and compared at dosages of 0.0348, 0.0695 and 0.139 moles collector/ton ore. The relevant test runs were 2 to 7 and 9 to 14.

2. To compare the effect of mixtures of collectors to that of the pure major component of the mixtures, the performances of 90 mol% sodium ethyl xanthate - 10 mol% sodium diethyl-dithiophosphate and 90 mol% sodium ethyl xanthate - 10 mol% sodium diethyl-dithiocarbamate mixtures were tested and compared to that of sodium ethyl xanthate at collector dosages of 0.0695 and 0.139 mol/ton ore. The relevant test runs were 3 to 7 and 20 to 27.

Palaborwa Mining Company Ore

1. To investigate the role of the different functional groups of collectors and to test the effect of collector dosage, the performances of sodium ethyl xanthate, sodium diethyl-dithiophosphate sodium diethyl-dithiocarbamate were tested and compared at dosages of 0.0695 and 0.139 moles collector/ton ore. The relevant test runs were 29 to 32 and 35 to 38.

2. To compare the effect of mixtures of collectors to that of the pure major component of the mixtures, the performances of 90 mol% sodium ethyl xanthate - 10 mol% sodium diethyl-dithiophosphate and 90 mol% sodium ethyl xanthate - 10 mol% sodium diethyl-dithiocarbamate mixtures were

compared to that of sodium ethyl xanthate at 0.139 mol/ton. Also, the performance of 90 mol% sodium isobutyl xanthate - 10 mol% sodium diethyldithiocarbamate mixture was tested and compared to that of sodium isobutyl xanthate at 0.139 mol/ton ore. The relevant test runs here were 30 to 31 and 39 to 46.

3. RESULTS

In this chapter, the results pertaining to the Okiep Copper Company (OCC) ore will be followed by those for the Palaborwa Mining Company ore (PMC). For each ore, the milling curves and the reproducibility study will be considered. These will be followed by the examination of the effects of the dosage of the collectors, functional groups of the collectors and mixtures of collectors and a consideration of the ore mineralogy.

3.1. Okiep Copper Company Ore

3.1.1. Milling Relationship obtained with the Okiep Copper Company Ore

From the milling curve, a time of 9 minutes gave 62.3% of particles below 75μ in size. The milling curve and sieve analysis of the OCC ore, milled for 9 minutes, are presented in Appendix A.

3.1.2. Reproducibility Study on the Okiep Copper Company Ore

The xanthate, C2-X, was used in the reproducibility study. The mass-water recovery, cumulative copper grade-recovery and cumulative sulphur grade-recovery relationships obtained with the OCC ore at an equivalent collector dosage of 0.139 mol/C2-X/ton ore for test runs 5, 6 and 7 are presented in Figures 3.1, 3.2 and 3.3 respectively.

The mass recovery vs water recovery relationships are in close agreement with one another (Figure 3.1) with acceptable standard deviations from the mean of less than 3% (Table 3.1).

Figure 3.2 shows a greater spread in the initial cumulative copper grades and recoveries than in the final ones. The standard deviation for the cumulative copper recovery in the first concentrate was 3.23% while for the last cumulative concentrate it was 1.28% (Table 3.1). The spread in recovery was reflected in the cumulative copper grade. The standard deviation for the cumulative copper grade in the first concentrate was 1.53% and for the last cumulative concentrate it was 0.61% (Table 3.1).

A greater spread in results was obtained with the cumulative sulphur recoveries than for the cumulative sulphur grades (Figure 3.3). The standard deviations for the cumulative sulphur recoveries in the first and last concentrates were 3.92 and 3.60% respectively, while for the cumulative sulphur grades they were 0.58 and 0.15% respectively (Table 3.1).

Table 3.2 is the summary table of the results obtained with the OCC ore, while Appendix B contains the experimental results.

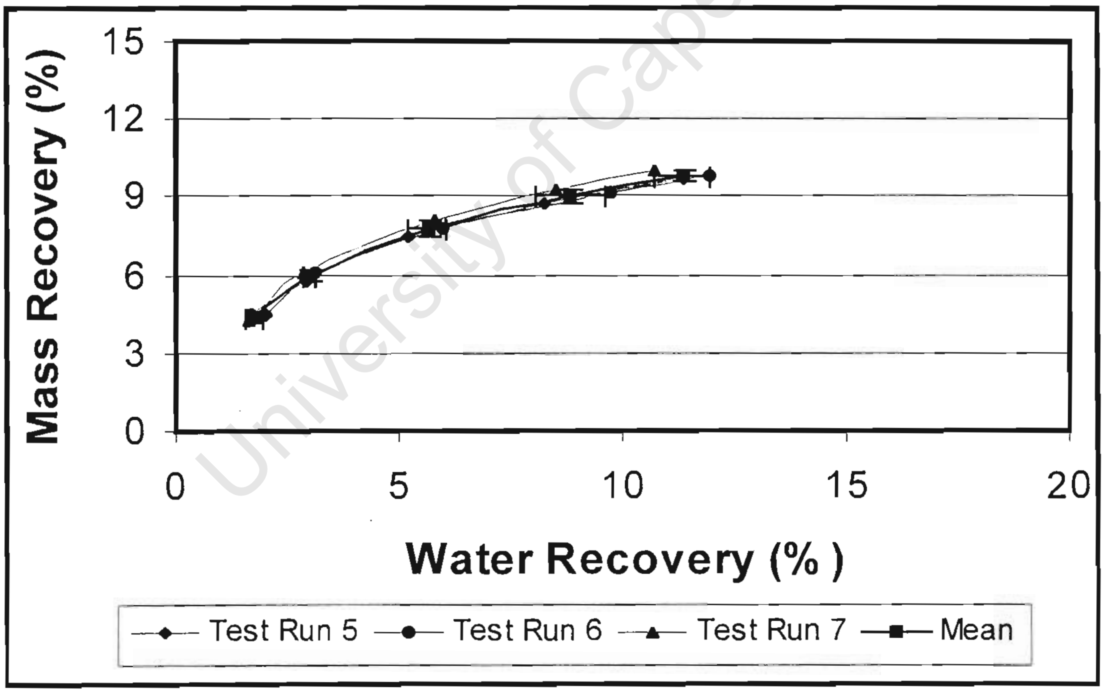


Figure 3.1 **The mass-water recovery relationships obtained with C2-X at a collector dosage of 0.139 mol/ton ore in the flotation of the OCC ore**

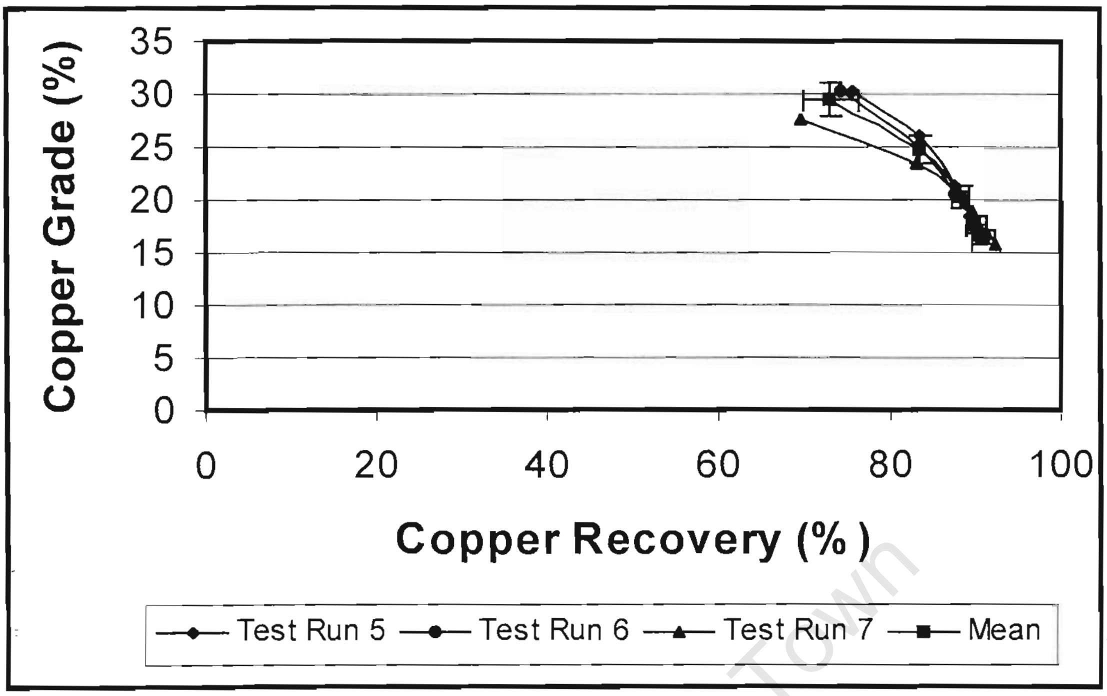


Figure 3.2 The cumulative copper grade-recovery relationships obtained with C2-X at a collector dosage of 0.139 mol/ton ore in the flotation of the OCC ore

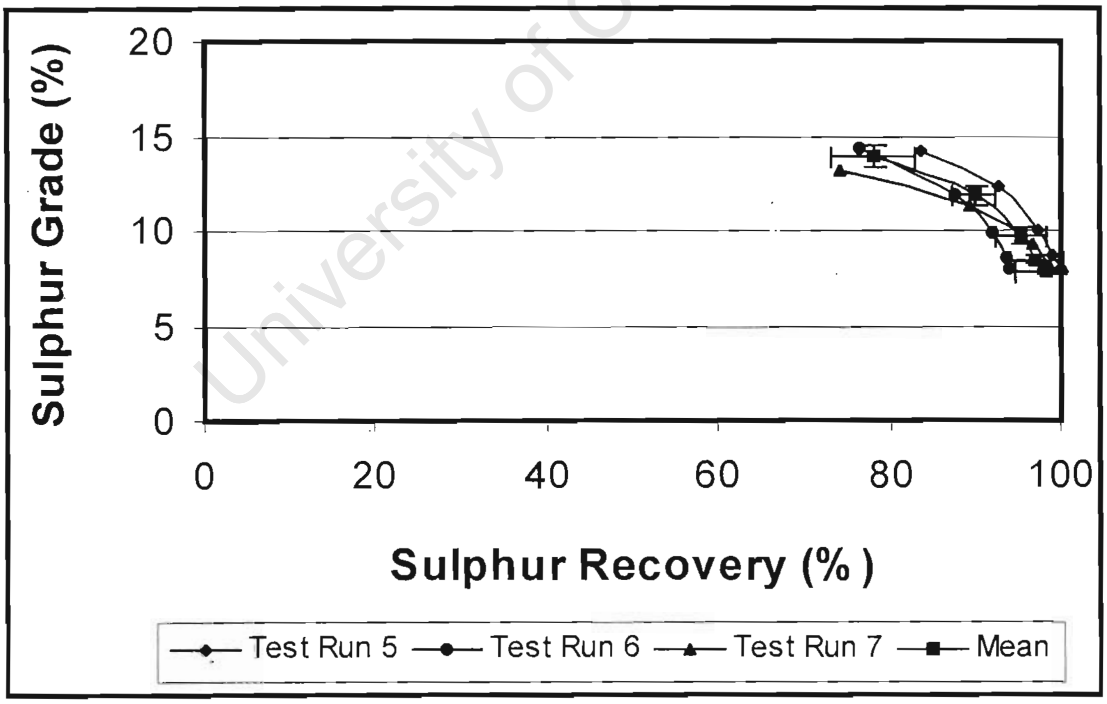


Figure 3.3 The cumulative sulphur grade-recovery relationships obtained with C2-X at a collector dosage of 0.139 mol/ton ore in the flotation of the OCC ore

Table 3.1 Standard deviations of the means (SD) obtained for test runs 5, 6, and 7 at a collector dosage of 0.139 mol C2-X/ton ore with Okiep Copper Company ore

Concentrate	Cumulative Water Recovery (%)		Cumulative Mass Recovery (%)		Cumulative Copper Recovery (%)		Cumulative Copper Grade (%)		Cumulative Sulphur Recovery (%)		Cumulative Sulphur Grade (%)	
Number	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	1.8	0.19	4.40	0.10	75.6	3.23	29.4	1.53	78.0	3.92	13.9	0.58
2	3.0	0.13	5.96	0.18	83.2	0.25	11.5	1.33	89.7	2.63	11.8	0.51
3	5.7	0.32	7.73	0.32	87.3	1.13	4.8	1.13	95.3	3.02	9.7	0.31
4	8.8	0.78	9.03	0.27	89.2	1.18	2.5	0.75	97.1	3.17	8.4	0.23
5	11.3	0.63	9.82	0.21	90.1	1.28	1.9	0.61	98.2	3.60	7.8	0.15

Table 3.2 Summary table of results obtained with the Okiep Copper Company ore

Test Run	**Collector**	**Mole Ratio of Mixture**	**Dosage (mol/ton ore)**	**Cumulative Concentrate Mass (%)**		**Cumulative Water (%)**		**Cumulative Copper Recovery (%)**		**Cumulative Copper Grade (%)**		**Cumulative Sulphur Recovery (%)**		**Cumulative Sulphur Grade (%)**		**Klimpel Constants**	
				1 min	20 min	1 min	20 min	1 min	20 min	1 min	20 min	1 min	20 min	1 min	20 min	k (min^{-1})	R (%)
1	No Collector		0	2.2	5.9	1.9	12.8	5.5	17.9	4.6	5.6	6.8	21.1	2.7	3.1	0.61	19.0
2	C2-X		0.0348	3.6	9.2	1.8	12.1	45.6	73.8	22.2	14.2	47.3	76.2	11.0	7.0	2.28	72.1
3	C2-X		0.0695	4.5	10.8	2.2	18.4	67.7	88.9	24.7	13.4	69.1	89.9	12.8	6.9	3.97	89.4
4	C2-X		0.0695	4.4	10.2	2.2	16.6	73.6	92.4	26.3	14.3	80.0	99.6	13.9	7.5	4.71	92.6
5	C2-X		0.139	4.5	9.6	2.0	11.3	75.6	90.1	30.3	16.8	83.5	100	14.2	7.9	6.06	89.8
6	C2-X		0.139	4.4	9.8	1.7	12.0	74.1	90.0	30.3	16.7	76.6	94.1	14.3	8.0	5.45	90.2
7	C2-X		0.139	4.3	10.0	1.6	10.7	69.3	92.3	27.6	15.7	74.0	100	13.3	7.7	3.78	92.8
8	C2-X		0.209	4.9	9.8	2.5	11.5	73.9	87.7	26.8	16.0	84.3	98.6	14.2	8.4	6.24	87.5
9	di-C2-DTP		0.0348	4.5	11.6	1.5	18.8	70.4	91.5	28.9	14.6	72.1	96.2	14.1	6.8	4.11	91.9
10	di-C2-DTP		0.0348	4.7	11.5	2.3	19.2	64.5	87.5	23.8	13.3	79.4	100	13.0	6.7	3.56	88.6

Table 3.2 (continued) Summary table of results obtained with the Okiep Copper Company ore

Test Run	Collector	Mole Ratio of Mixture	Dosage (g/ton ore)	Cumulative Concentrate Mass (%)		Cumulative Water (%)		Cumulative Copper Recovery (%)		Cumulative Copper Grade (%)		Cumulative Sulphur Recovery (%)		Cumulative Sulphur Grade (%)		Klimpel Constants	
				1 min	20 min	1 min	20 min	1 min	20 min	1 min	20 min	1 min	20 min	1 min	20 min	k (min^{-1})	R (%)
11	di-C2-DTP		0.0695	4.6	10.9	2.1	15.2	71.8	90.9	28.3	15.3	78.8	99.6	13.6	7.3	4.54	91.0
12*	di-C2-DTP		0.0695	4.9	10.9	2.1	12.9	76.0	94.3	27.0	15.1	78.8	99.9	12.6	7.2	4.99	94.4
13	di-C2-DTP		0.139	4.5	11.2	1.8	12.7	69.7	91.4	28.7	15.3	76.3	100	14.3	7.6	3.96	91.8
14	di-C2-DTP		0.139	5.2	11.8	2.4	16.8	77.8	95.2	24.9	13.4	77.1	95.8	12.0	6.5	5.28	95.5
15	di-C2-DTC		0.0348	2.4	7.6	1.5	13.6	15.1	37.7	11.8	9.3	19.1	44.1	6.6	4.9	0.98	39.6
16*	di-C2-DTC		0.0695	2.6	8.5	1.7	15.4	22.5	53.5	15.8	11.7	24.4	54.0	8.2	5.7	1.12	56.3
17	di-C2-DTC		0.0695	2.9	8.9	2.1	16.5	17.9	47.7	10.3	9.0	21.4	48.1	5.7	4.3	0.97	50.7
18	di-C2-DTC		0.139	2.9	8.3	1.7	11.1	30.0	63.2	18.0	13.1	34.5	70.6	9.3	6.6	1.29	65.4
19	di-C2-DTC		0.139	2.8	8.6	1.6	12.7	24.7	56.4	14.8	10.8	27.3	61.2	8.1	5.8	0.96	59.5
20	C2-X:di-C2-DTP	90:10	0.0695	4.5	10.9	2.1	17.6	72.6	94.6	26.7	14.3	76.4	99.9	13.4	7.2	4.06	95.1
21	C2-X:di-C2-DTP	90:10	0.0695	4.0	10.0	1.6	14.0	69.3	93.9	29.3	15.7	72.1	100	14.2	7.8	3.53	93.9
22	C2-X:di-C2-DTP	90:10	0.139	5.0	11.0	2.5	16.4	78.0	94.3	25.5	14.2	82.0	99.6	12.8	7.2	5.64	94.3
23	C2-X:di-C2-DTP	90:10	0.139	4.5	10.8	2.1	16.4	73.5	94.1	24.7	13.3	79.0	99.8	13.7	7.3	4.36	94.3
24	C2-X:di-C2-DTC	90:10	0.0695	4.5	9.9	2.3	17.4	75.5	92.5	28.3	15.7	74.1	91.6	13.7	7.7	5.27	92.6
25	C2-X:di-C2-DTC	90:10	0.0695	4.5	9.6	2.3	14.3	71.7	91.7	26.1	15.5	79.0	98.5	13.7	7.9	4.36	92.5
26	C2-X:di-C2-DTC	90:10	0.139	4.2	10.1	1.8	16.4	76.9	94.2	29.5	15.1	81.0	100	14.7	7.6	5.23	94.8
27	C2-X:di-C2-DTC	90:10	0.139	4.8	10.0	2.9	17.7	78.1	93.6	24.0	13.8	85.1	99.2	13.8	7.7	5.80	94.0

* First concentrates of Test runs 12 and 16 for mineralogy

3.1.3. The Effect of the Dosage of the Collector on the Froth Flotation Performance of the Okiep Copper Company Ore

Reported in this in this section of the thesis are the effects of the dosage of C2-X (Figures 3.4 to 3.7), di-C2-DTP (Figures 3.7 to 3.10) and di-C2-DTC (Figures 3.7 and 3.11 to 3.13) respectively on mass and water recoveries; cumulative copper recoveries and grades; cumulative sulphur recoveries and grades; and Klimpel rate constants.

3.1.3.1. The Froth Flotation Performance of the Okiep Copper Company Ore obtained with C2-X, at Collector Dosages of 0.0348, 0.0695, 0.139 and 0.209 mol/ton ore

The water and mass recoveries obtained at a dosage of 0.0695 mol/ton ore were significantly higher than those obtained at 0.139 mol/ton ore (Figures 3.4, 3.14 and 3.15, Appendix D, Table D12 and D13); showing that the froth structure was affected at a collector dosage of 0.0695 mol/ton ore. The cumulative copper and sulphur grades obtained at a dosage of at 0.139 were significantly higher than those obtained at 0.0695 mol/ton ore (Appendix D, Tables D9 and D11); indicating that there was less entrainment and that the froth was better drained at the higher dosage (Dippenaar, 1978 and Bradshaw et al, 1998).

The cumulative copper recoveries by flotation were 73.8, 90.6, 90.8 and 87.7% at collector dosages of 0.0348, 0.0695, 0.139 and 0.209 mol/ton ore respectively (Figure 3.16). As the recovery declined when the dosage was increased to 0.209, the upper limit of the collector dosage was 0.139 mol/ton ore in all tests (Figure 3.16).

The cumulative copper and cumulative sulphur recoveries obtained with C2-X at a dosage of 0.0348 mol/ton ore were less than with the other dosages tested (Figures 3.5 and 3.6); showing that this was near the starvation dosage.

Furthermore, once "enough" of the collector was present, increased dosage did not give increased cumulative copper recovery (Figure 3.16).
The copper grade obtained at a dosage of 0.209 mol/ton ore was marginally lower than that obtained at 0.139 mol/ton ore; 16.0% and 16.4% respectively (Figure 3.5 and Table 3.2). This was accompanied by a marginally higher water recovery obtained with a dosage of 0.209 mol/ton ore; 11.5 as opposed to 11.3.

Higher collector dosages contributed to higher Klimpel rate constants for copper recovery (Figures 3.7), although cumulative copper recoveries were not greatly different at dosages of 0.0695, 0.139 and 0.209 mol/ton ore (Figure 3.16).

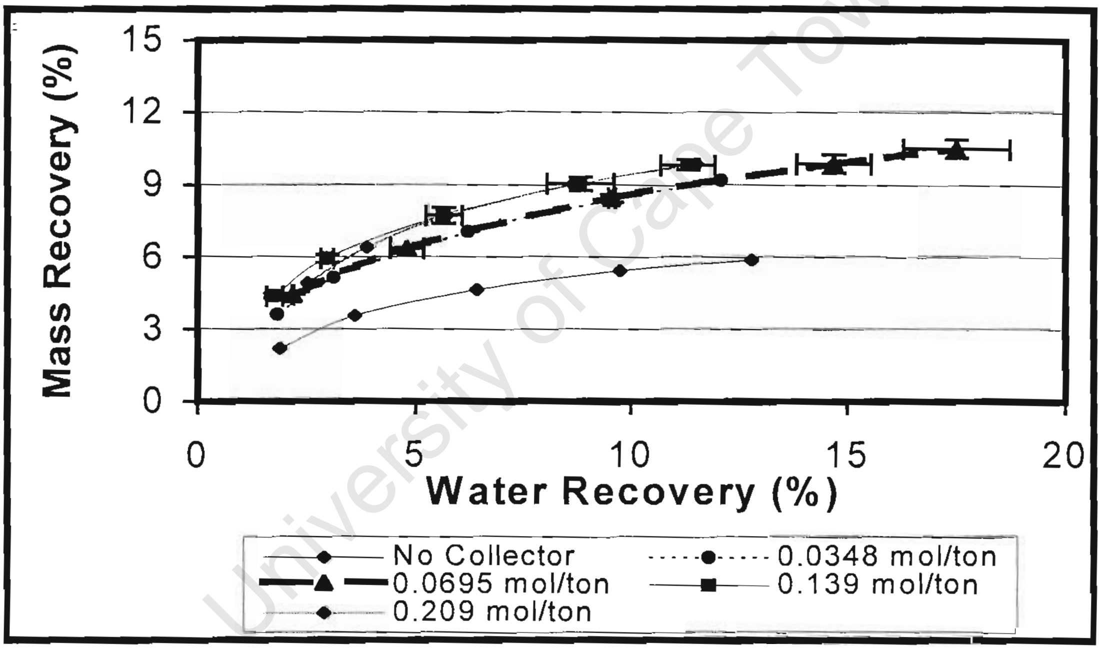


Figure 3.4 **The mass-water recovery relationships obtained with different dosages of C2-X in the flotation of the OCC ore**

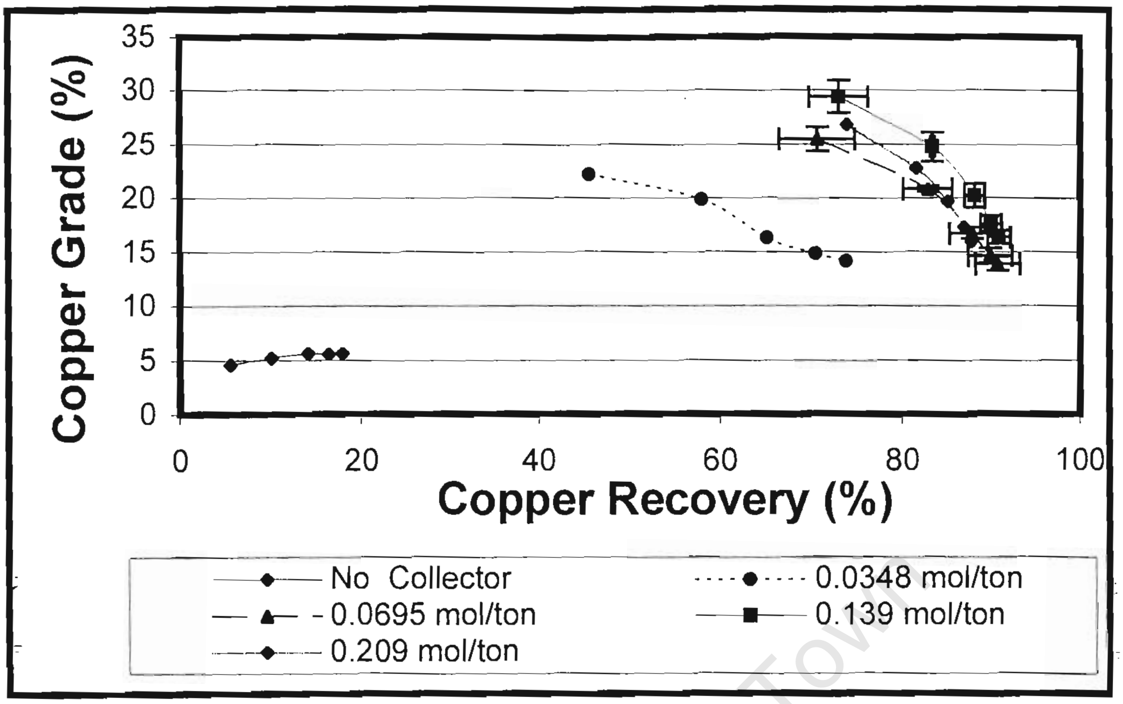


Figure 3.5 The cumulative copper grade-recovery relationships obtained with different dosages of C2-X in the flotation of the OCC ore

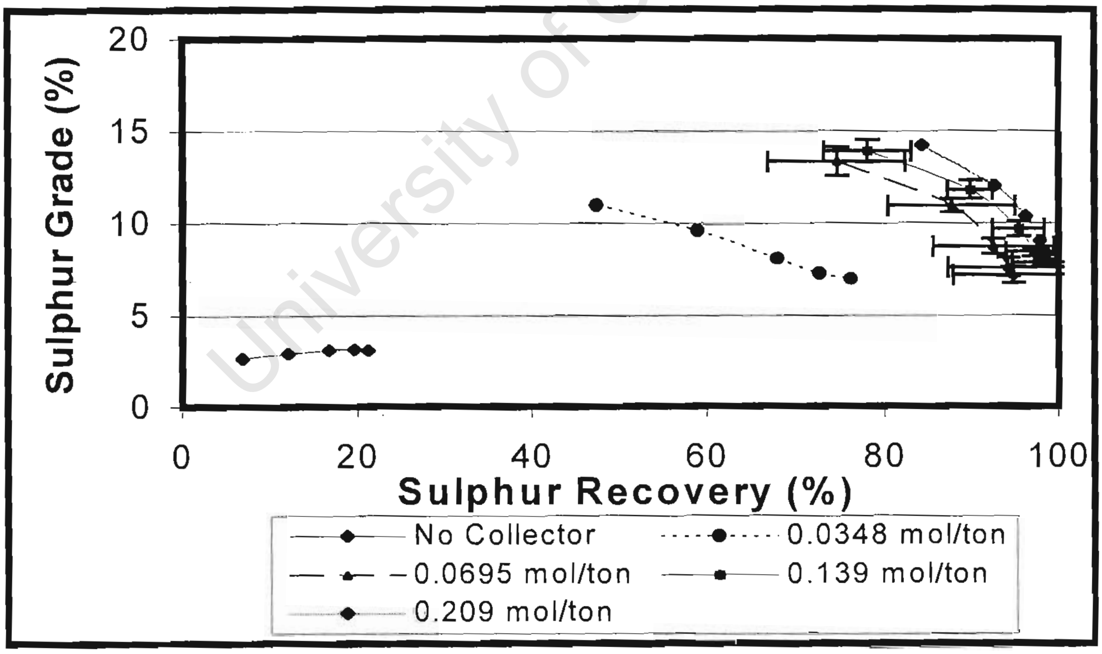


Figure 3.6 The cumulative sulphur grade-recovery relationships obtained with different dosages of C2-X in the flotation of the OCC ore

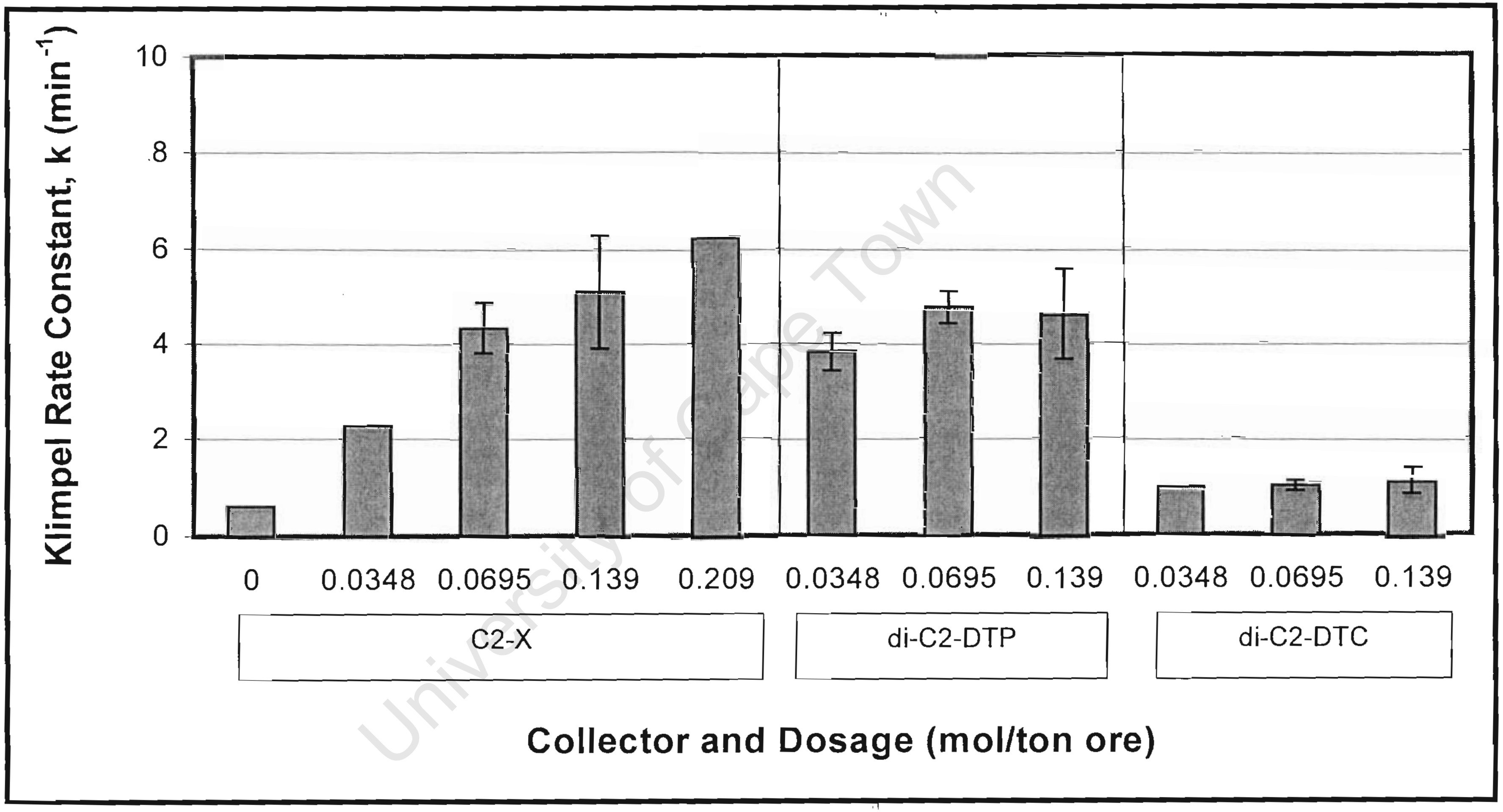


Figure 3.7 **The Klimpel rate constants for copper recovery obtained with different dosages of C2-X, di-C2-DTP and di-C2-DTC in the flotation of the OCC ore**

3.1.3.2. The Froth Flotation Performance of the Okiep Copper Company Ore obtained with di-C2-DTP at Collector Dosages of 0.0348, 0.0695 and 0.139 mol/ton ore

Mass and water recoveries obtained at a collector dosage of 0.0348 mol/ton ore were significantly higher than those at 0.0695 mol/ton ore (Figure 3.8 and Appendix D, Tables D12 and D13); indicating contribution to froth stability by di-C2-DTP and beneficial frother-collector interaction (Dai et al, 2001). This was accompanied by a significantly lower sulphur grade at 0.0348 mol/ton ore compared to that obtained at 0.695 mol/ton ore (Figure 3.10 and Appendix D, Table D11); attributable to the entrainment of hydrophilic non-sulphide gangue due to the higher water recovery.

The cumulative copper recoveries by flotation were 87.6%, 92.6% and 93.3% at collector dosages of 0.0348, 0.0695 and 0.139 mol/ton ore respectively (Figure 3.16); showing the established trend of increased recovery with increased collector dosage (Somasundaran, 1975 and Smar et al, 1994).

The Klimpel rate constants were 3.8, 4.8 and 4.6 min^{-1} at collector dosages of 0.0348, 0.0695 and 0.139 mol/ton ore respectively i.e. the rate constants increased as the dosage was increased until a maximum rate of copper recovery was attained after which they declined. This trend agrees with Smar et al, (1994).

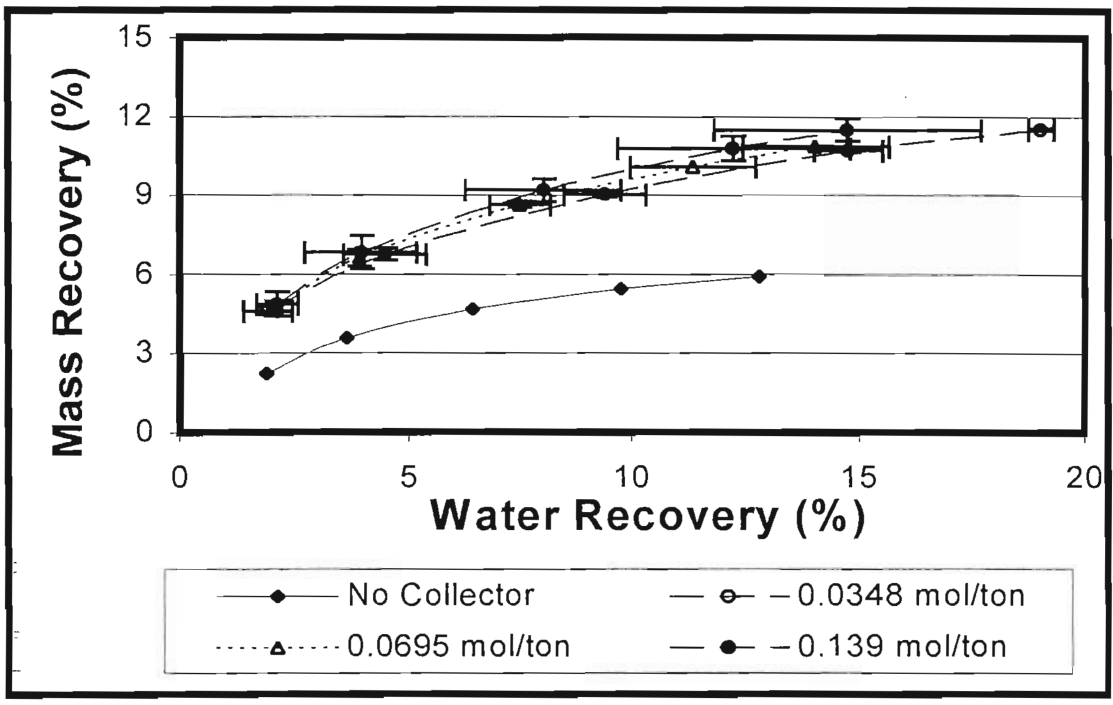


Figure 3.8 The mass-water recovery relationships obtained with different dosages of di-C2-DTP in the flotation of the OCC ore

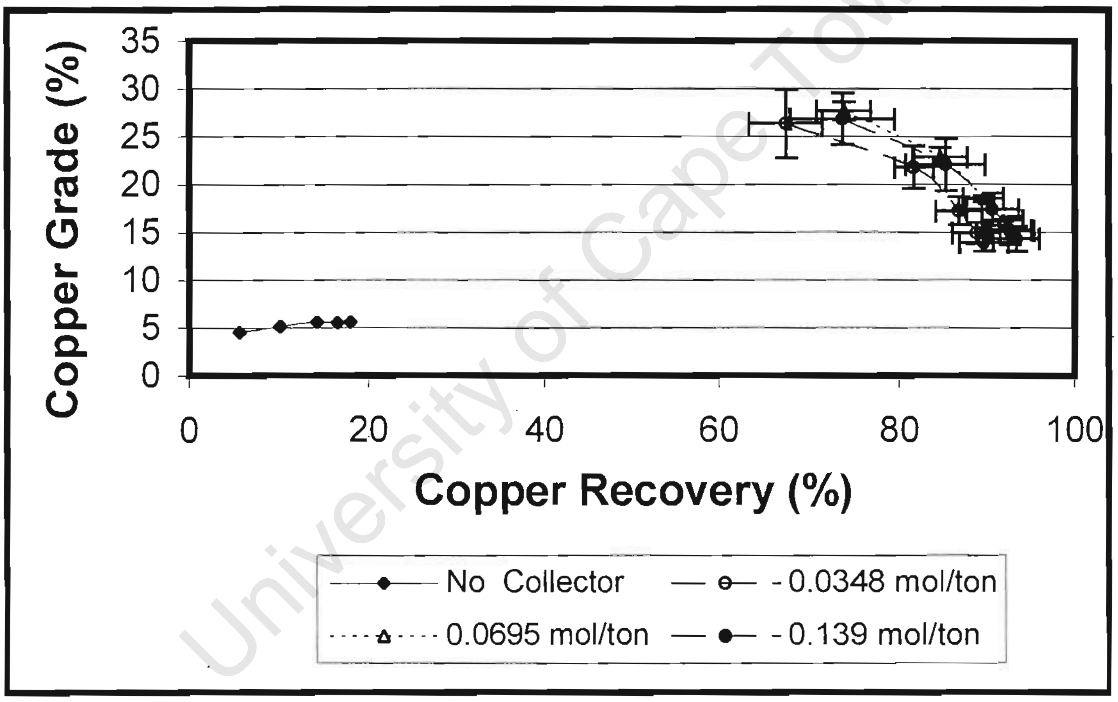


Figure 3.9 The cumulative copper grade-recovery relationships obtained with different dosages of di-C2-DTP in the flotation of the OCC ore

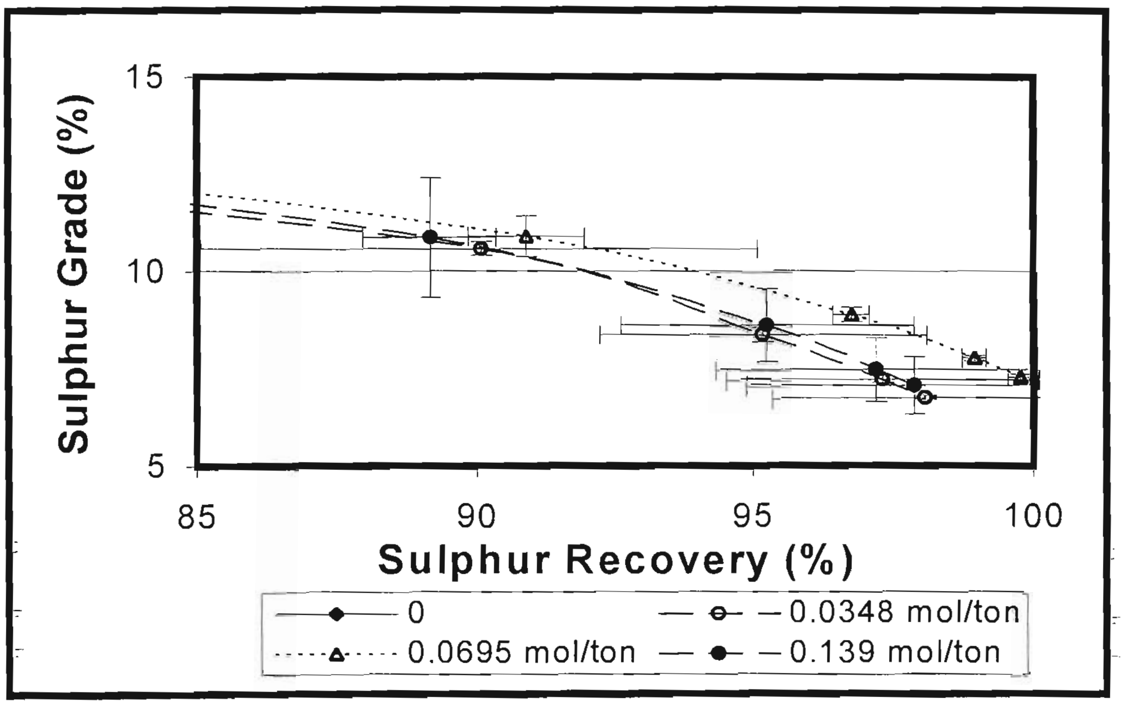


Figure 3.10 **Segment of the cumulative sulphur grade-recovery relationships obtained with different dosages of di-C2-DTP in the flotation of the OCC ore**

3.1.3.3. The Froth Flotation Performance of the Okiep Copper Company Ore obtained with di-C2-DTC at Dosages of 0.0348, 0.0695 and 0.139 mol/ton ore

The water recovery at an equivalent collector dosage of 0.0695 mol/ton ore was significantly higher than that obtained at a collector dosage of 0.139 mol/ton ore (Figure 3.11 and Appendix D, Table D12); possibly indicating lower froth stability at the higher collector dosage attributable to the presence hydrophobic particles that ruptured the froth films (Dippenaar, 1978).

The cumulative copper recovery by flotation increased from 37.7%, at a collector dosage of 0.0348 mol/ton ore to 50.6 % at a dosage of 0.0695 mol/ton ore to a maximum of 59.8% at 0.139 mol/ton ore (Figure 3.16). This was substantially lower than recovered with C2-X and di-C2-DTP (Figures 3.5 and 3.9).

The cumulative copper recovery vs dosage relationship for di-C2-DTC shows an upward trend compared to the relationships for the other two collectors (Figure 3.16). This may suggest that the optimum dosage for maximum copper recovery had not been reached at a di-C2-DTC dosage of 0.139 mol/ton ore.

Klimpel rate constants for copper recovery were 0.98, 1.04 and 1.12 min^{-1} at di-C2-DTC dosages of 0.0348, 0.0695 and 0.139 mol/ton ore respectively i.e. they were generally not sensitive to di-C2-DTC dosage (Figure 3.7). Furthermore, they were not much larger than when no collector was used (Figure 3.7).

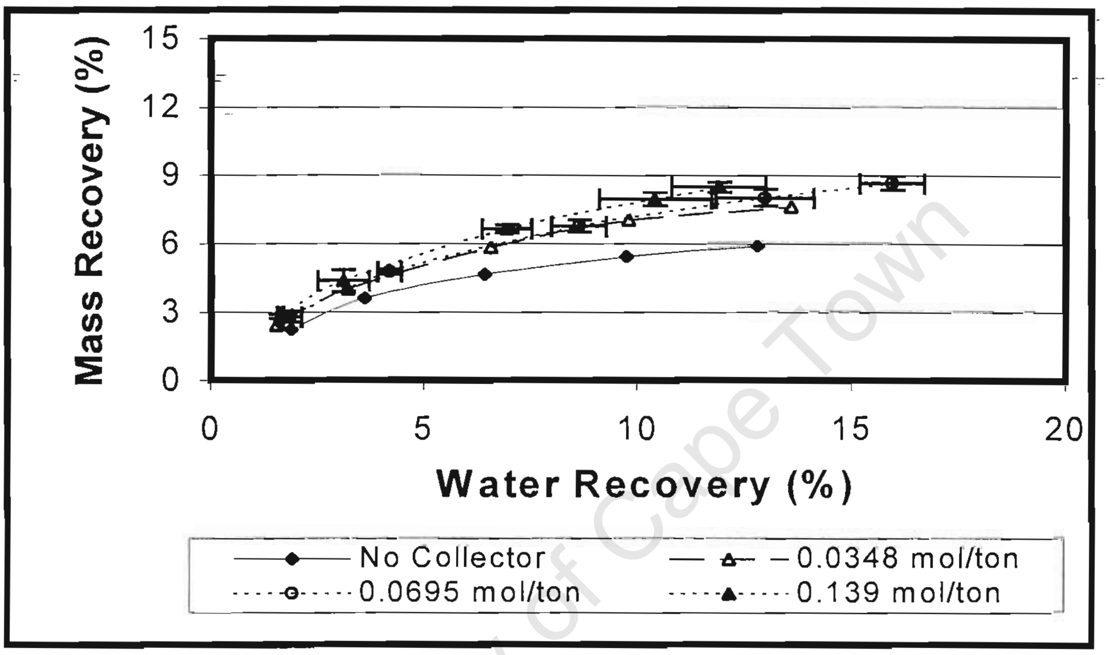


Figure 3.11 **The mass-water recovery relationships obtained with different dosages of di-C2-DTC in the flotation of the OCC ore**

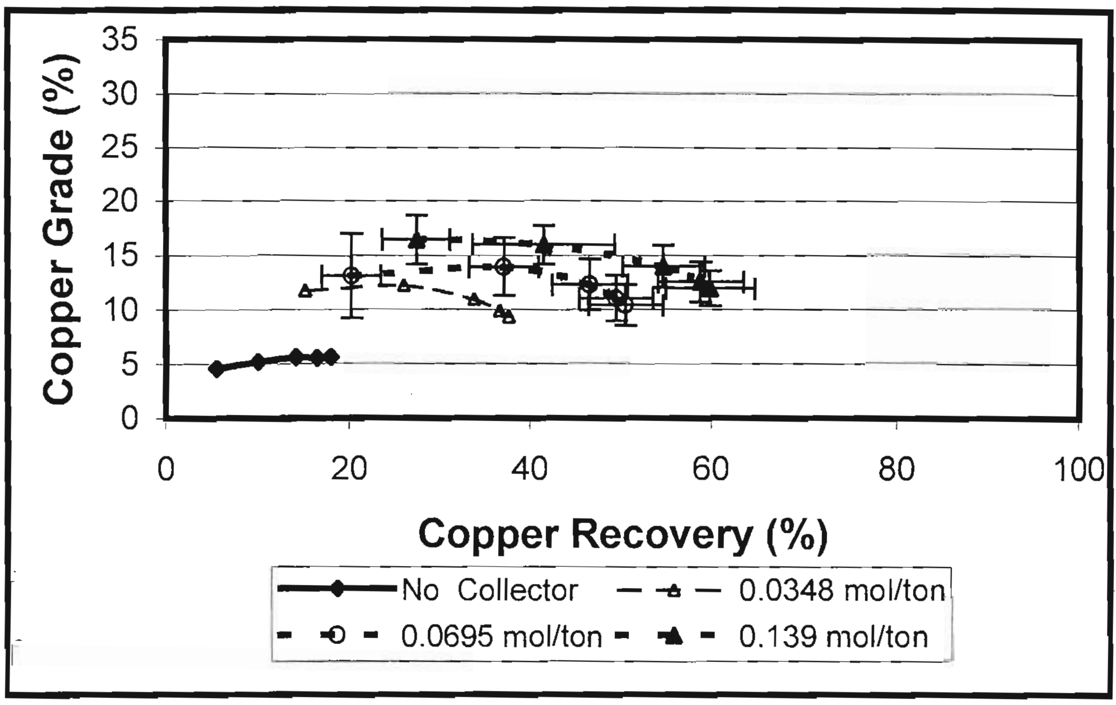


Figure 3.12 The cumulative copper grade-recovery relationships obtained with different dosages of di-C2-DTC in the flotation of the OCC ore

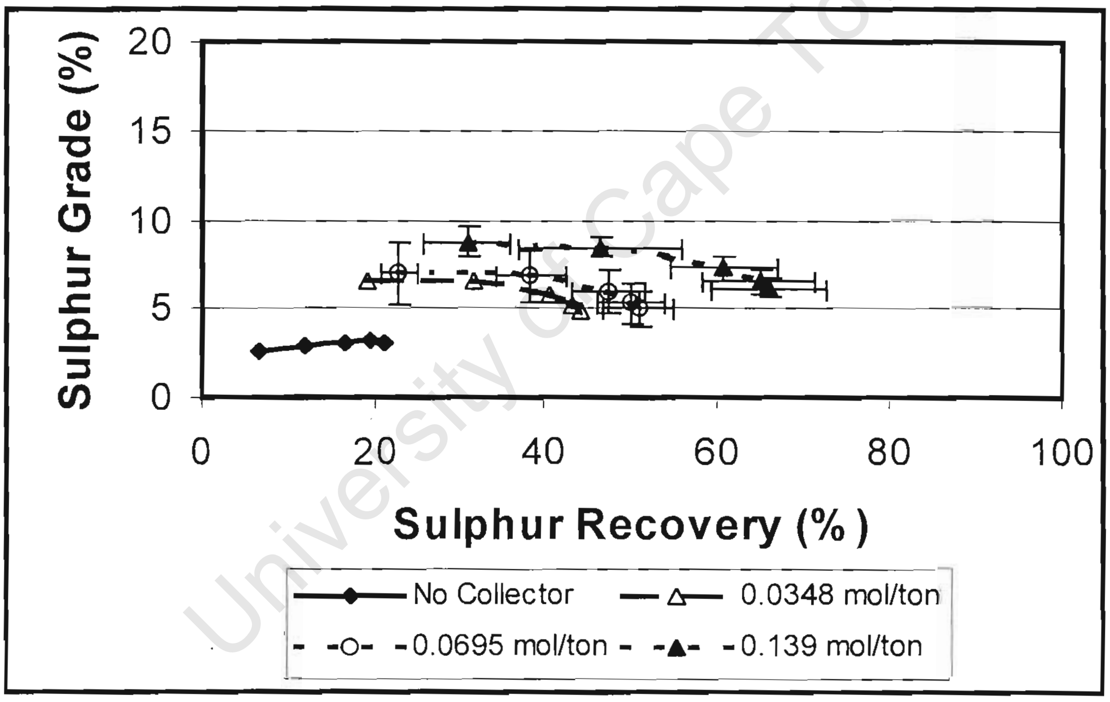


Figure 3.13 The cumulative sulphur grade-recovery relationships obtained with different dosages of di-C2-DTC in the flotation of the OCC ore

3.1.3.4 Comparison of the Relationships between Mass, Water, Cumulative Copper and Sulphur Recoveries and Collector Dosage obtained with C2-X, di-C2-DTP and di-C2-DTC in the Froth Flotation of the Okiep Copper Company Ore

When mass and water recoveries were expressed as a function of collector dosage, local maxima in recoveries were obtained with each collector (Figures 3.14 and 3.15). This may be attributed to hydrophobic breaking of the froth at dosages that exceed those corresponding to the maxima (Dippenaar, 1978).

Significantly lower mass, copper and sulphur recoveries were obtained with di-C2-DTC at all dosages compared to those obtained with C2-X and di-C2-DTP (Figures 3.14, 3.16 and 3.17).

The effect of the dosage of di-C2-DTP on cumulative copper recoveries and cumulative sulphur recoveries and grades was not as pronounced as the effect of the dosage of C2-X (Figures 3.6, 3.10, 3.16 and 3.17). This implied that "sufficient" hydrophobicity of the mineral surface was achieved at lower dosages of di-C2-DTP compared to C2-X. This may be attributed to the added hydrophobicity imparted by the second ethyl group of the di-C2-DTP.

Klimpel rate constants obtained with di-C2-DTC were low compared to those obtained with C2-X or di-C2-DTP (Figures 3.7). In the case of di-C2-DTP, they followed the established trend with respect to collector dosage (Smar et al, 1994). With C2-X, the rate increased as the collector dosage was increased (Figure 3.7).

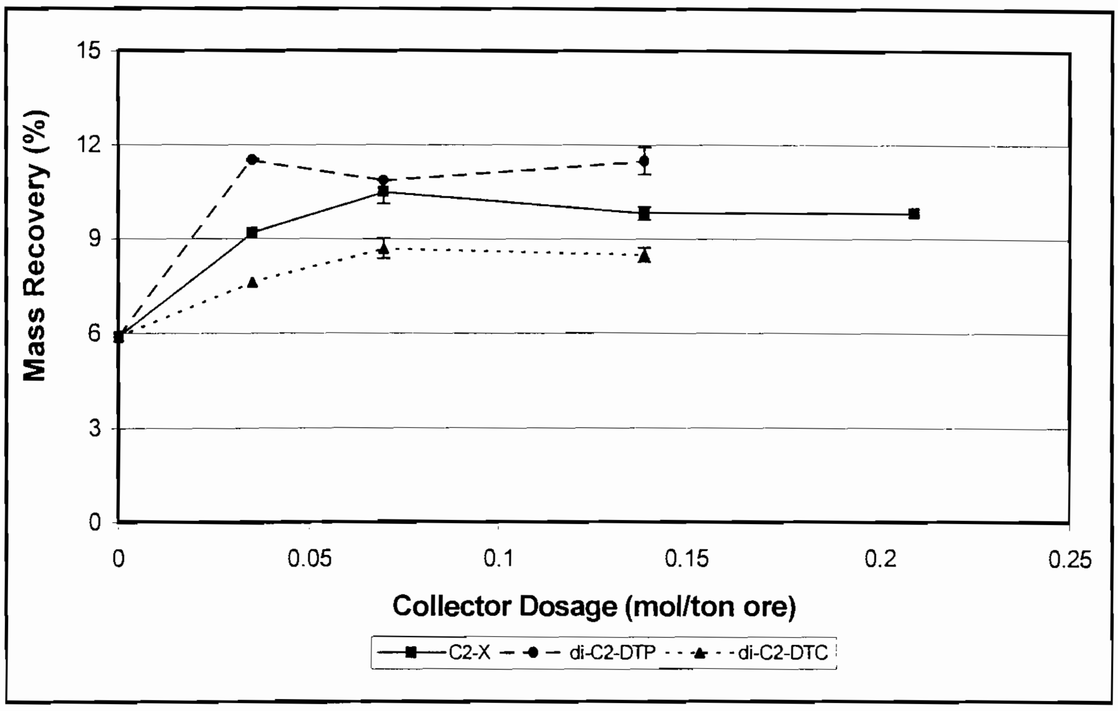


Figure 3.14 **The final cumulative mass recovery vs collector dosage obtained with C2-X, di-C2-DTP and di-C2-DTC in the flotation of the OCC ore**

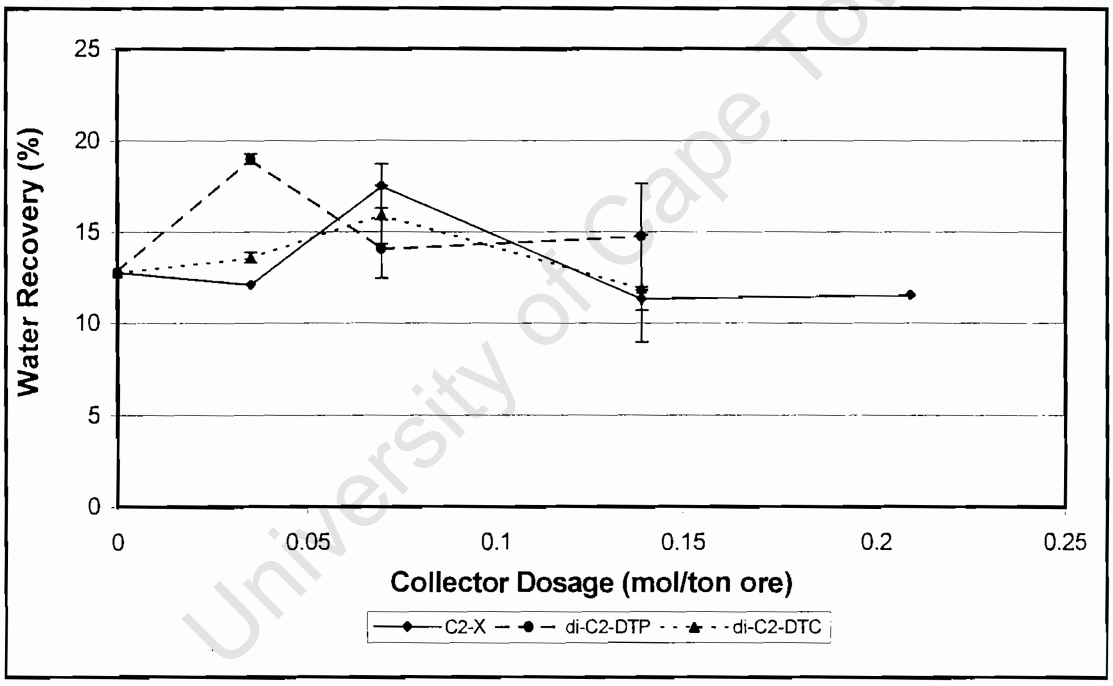


Figure 3.15 **The final cumulative water recovery vs collector dosage obtained with C2-X, di-C2-DTP and di-C2-DTC in the flotation of the OCC ore**

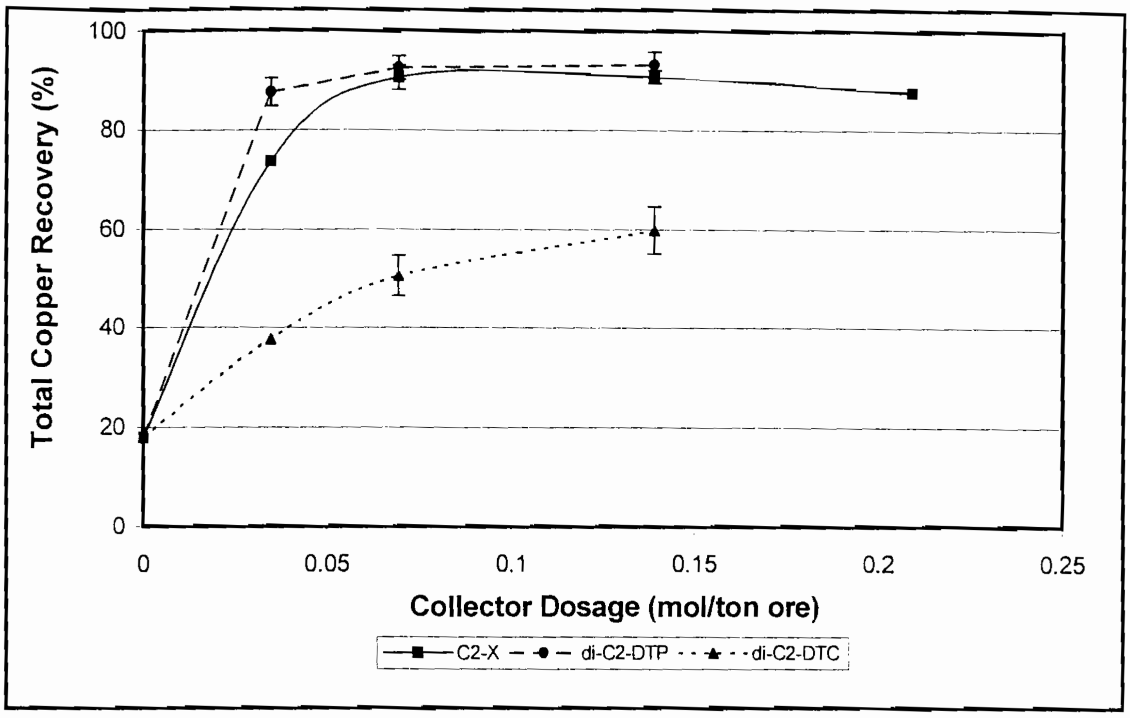


Figure 3.16 **The final cumulative copper recovery vs collector dosage obtained with C2-X, di-C2-DTP and di-C2-DTC in the flotation of the OCC ore**

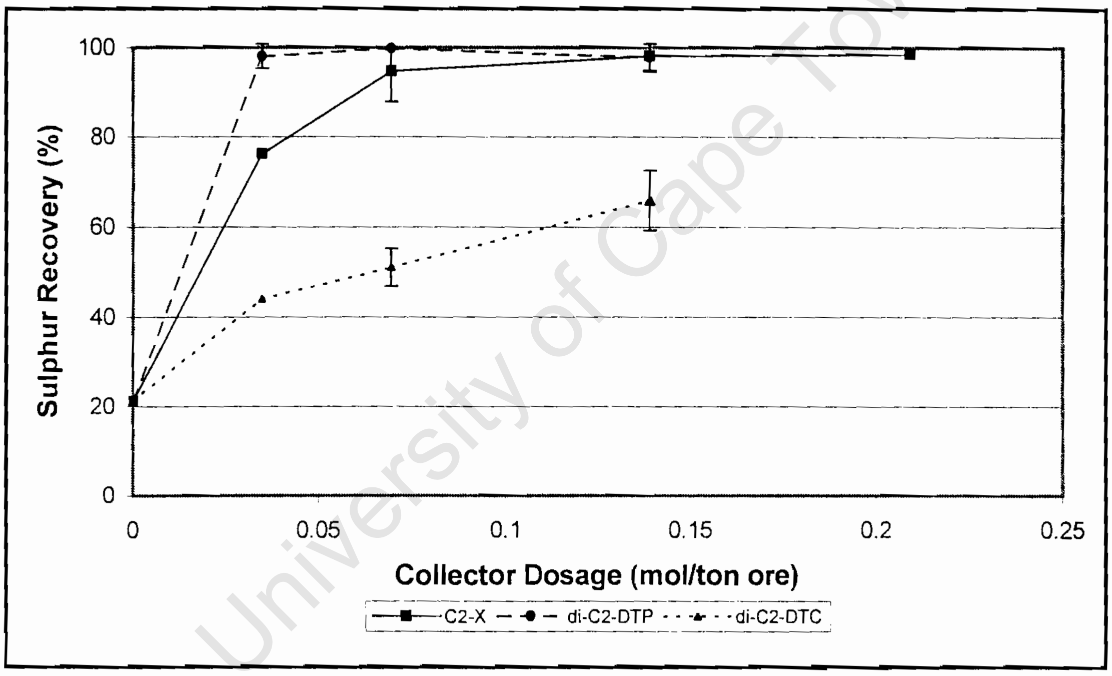


Figure 3.17 **The final cumulative sulphur recovery vs collector dosage obtained with C2-X, di-C2-DTP and di-C2-DTC in the flotation of the OCC ore**

3.1.4. The Effect of Functional Group of the Collector on the Flotation Performance of the Okiep Copper Company Ore

The cumulative mass recoveries (Figure 3.14); cumulative copper recoveries (Figure 3.16) and grades (Figures 3.5, 3.9 and 3.12); sulphur recoveries (Figure 3.17) and Klimpel rate constants for copper recovery (Figure 3.7) obtained with di-C2-DTC at dosages of 0.0695 or 0.139 mol/ton ore were significantly lower than with C2-X or di-C2-DTP each compared at the same dosage (Appendix D, Tables D1 to D7). In addition, the sulphur grade obtained with di-C2-DTC at 0.139 mol/ton ore was significantly lower than with C2-X at the same dosage (Appendix D, Table D4). The mass recovery obtained with di-C2-DTP was significantly higher than that obtained with C2-X at a dosage of 0.139 mol/ton ore (Appendix D, Table D6)

Although the lowest mass pulls were obtained with the di-C2-DTC (Figure 3.14), the reduction was less than the reduction in the cumulative copper (Figure 3.16) and cumulative sulphur recoveries (Figure 3.17) e.g. at a collector dosage of 0.0695 mol/ton ore, the di-C2-DTC recovered 83% of the mass and only 42% of copper and 45% of sulphur that the C2-X did (Table 3.2). These results suggest that di-C2-DTC was the weakest and least selective of the collectors tested. Furthermore, different mechanisms may have been responsible in the collection of copper sulphide minerals with di-C2-DTC compared to those with the other two collectors (Figures 3.16 and 3.17).

The mass pulls and water recoveries obtained with the dithiophosphate were higher than with the xanthate (Figures 3.14 and 3.15) at the tested dosages. The cumulative copper and cumulative sulphur recoveries obtained with di-C2-DTP were higher than those obtained with C2-X at an equivalent collector dosage of 0.0348 mol/ton ore (Figures 3.17 and 3.16). However, the final cumulative copper recoveries obtained were similar at equivalent collector dosages of 0.0695 and 0.139 mol/ton ore (Figure 3.16). The rate of copper recovery obtained with di-C2-DTP was higher than with C2-X at an equivalent collector dosage of 0.0348 mol/ton ore (Figures 3.7). This could be attributed to frothing properties of di-C2-DTP (Dai et al, 2001).

3.1.5 The Effect of Mixtures of Collectors on the Froth Flotation Performance of the Okiep Copper Company Ore

In order to establish the effect of mixtures of collectors and their dosages on the flotation performance of the OCC ore, two collector mixtures consisting of 90 mol% C2-X with 10 mol% di-C2-DTP (90% C2-X:10% di-C2-DTP) and 90 mol% C2-X with 10 mol% di-C2-DTC (90% C2-X:10% di-C2-DTC) were compared to the performance of pure C2-X at equivalent collector dosages of 0.0695 and 0.139 mol/ton ore respectively.

3.1.5.1. The Froth Flotation Performances of C2-X, 90% C2-X:10% di-C2-DTP and 90% C2-X:10% di-C2-DTC Collector Mixtures at an Equivalent Collector Dosage of 0.0695 mol/ton ore

The copper recovery obtained with 90% C2-X:10% di-C2-DTP was significantly higher than with 90% C2-X:10% di-C2-DTC (Figure 3.19 and Appendix D, Table D22).

The cumulative copper grade obtained with 90% C2-X:10% di-C2-DTC was significantly higher than with C2-X (Figure 3.19 Appendix D, Tables D15 to D18). In addition, higher cumulative copper and cumulative sulphur recoveries and grades were obtained with the collector mixtures compared to pure C2-X (Figures 3.19 and 3.20). These phenomena may signify that some degree of synergism between the components of the collector mixtures was present.

The performances of the collector mixtures with regard to mass and water recoveries (Figure 3.18) and the Klimpel rate constants for copper recovery (Figure 3.21) were similar to that obtained with C2-X.

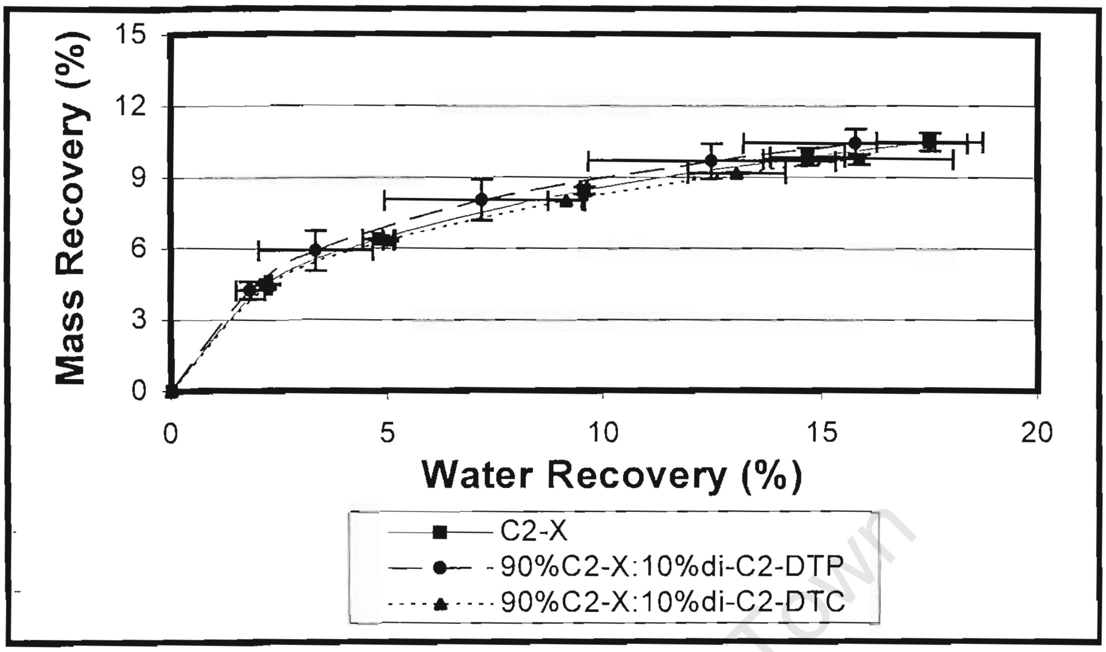


Figure 3.18 The mass-water recovery relationships obtained with C2-X, 90% C2-X:10% di-C2-DTP and 90% C2-X:10% di-C2-DTC collector mixtures at an equivalent collector dosage of 0.0695 mol/ton ore in the flotation of the OCC ore

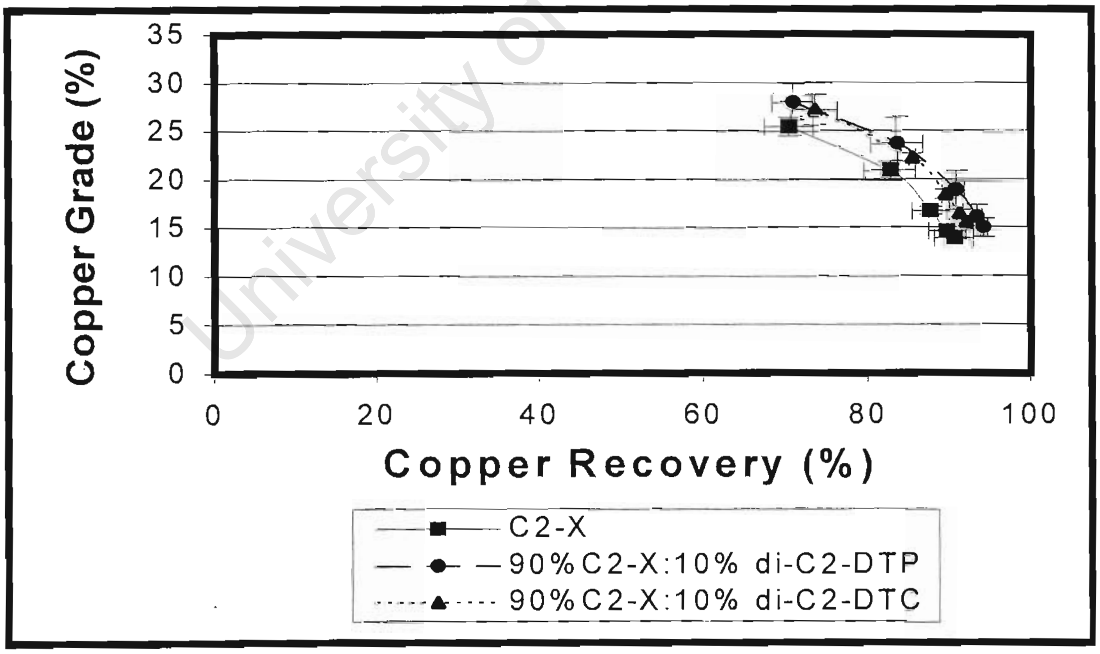


Figure 3.19 The cumulative copper grade-recovery relationships obtained with C2-X, 90% C2-X:10% di-C2-DTP and 90% C2-X:10% di-C2-DTC collector mixtures at an equivalent collector dosage of 0.0695 mol/ton ore in the flotation of the OCC ore

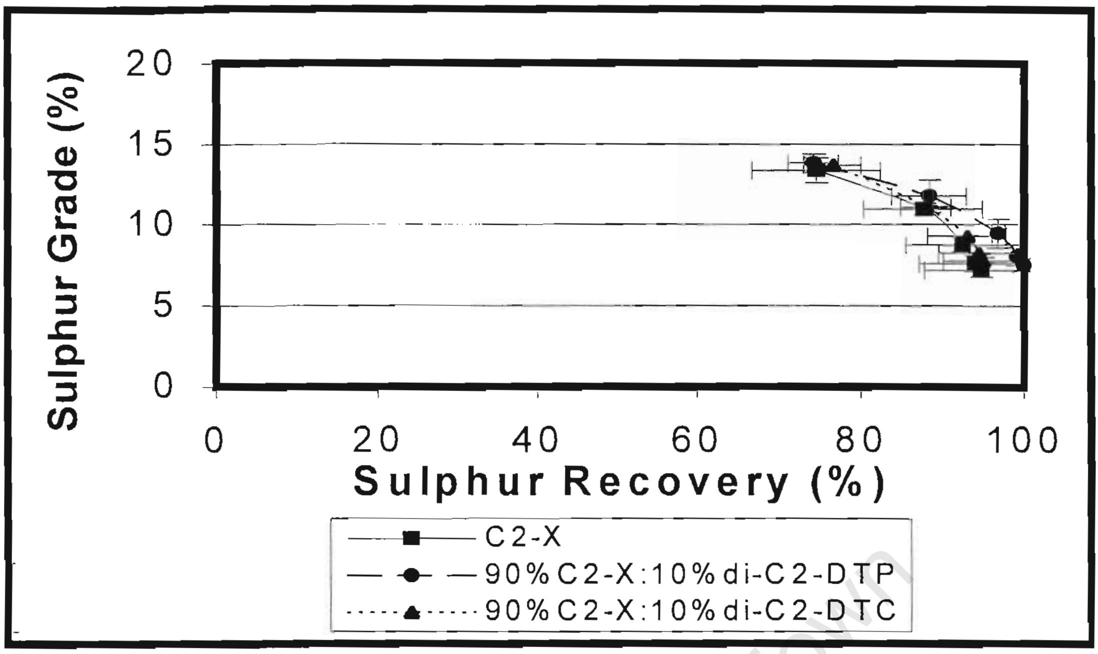


Figure 3.20 The cumulative sulphur grade-recovery relationships obtained with C2-X, 90% C2-X:10% di-C2-DTP and 90% C2-X:10% di-C2-DTC collector mixtures at an equivalent collector dosage of 0.0695 mol/ton in the flotation of the OCC ore

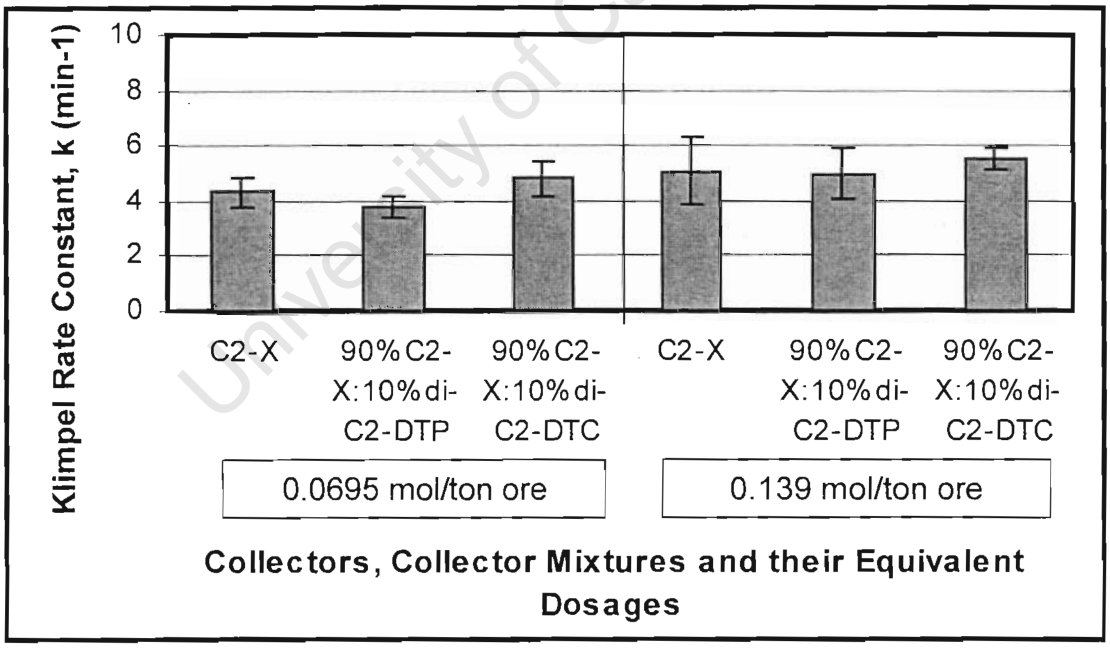


Figure 3.21 The Klimpel rate constants for copper recovery obtained with C2-X, 90% C2-X:10% di-C2-DTP and 90% C2-X:10% di-C2-DTC collector mixtures at equivalent collector dosages of 0.0695 and 0.139 mol/ton ore in the flotation of the OCC ore

3.1.5.2. The Froth Flotation Performances of C2-X, 90% C2-X:10% di-C2-DTP and 90% C2-X:10% di-C2-DTC collector mixtures at an Equivalent Collector Dosage of 0.139 mol/ton ore

Cumulative copper recoveries obtained with the collector mixtures were each 3% higher than the recovery obtained with C2-X (Figure 3.23 and Table 3.2); findings that were statistically significant (Appendix D, Table D15). The copper recovery obtained with 90% C2-X:10% di-C2-DTC at 0.139 mol/ton ore was significantly higher than at 0.0695 mol/ton ore (Figures 3.19 and 3.23, Appendix D, Table D29)

Both 90% C2-X:10% di-C2-DTC and C2-X gave significantly superior sulphur grades compared to 90% C2-X:10% di-C2-DTP (Figure 3.24 and Appendix D, Tables D18 and D25).

The water recoveries obtained with 90% C2-X:10% di-C2-DTP and 90% C2-X:10% di-C2-DTC were significantly greater (Figure 3.22, Appendix D, Table D19) than those obtained with C2-X (Figure 3.22); 5% and 6% greater respectively. The higher water recovery was accompanied by a significantly higher mass recovery in the case of 90% C2-X:10% di-C2-DTP (Figure 3.22, Appendix D, Table D20) and by significantly lower cumulative copper grades with 90% C2-X:10% di-C2-DTP and 90% C2-X:10% di-C2-DTC; 3% and 2% lower respectively (Table 3.2, Appendix D, Table D16). The lower copper grades may be attributed to entrainment of gangue material due to the elevated water recoveries (Subrahmanyam and Forssberg, 1988 & Kelly and Spottiswood, 1982). The elevated water recoveries suggest that the froth characteristics were more stable with the mixtures compared to C2-X.

The mass recovery obtained with 90% C2-X:10% di-C2-DTP was significantly higher than that obtained with 90% C2-X:10% di-C2-DTC (Figures 3.22, Appendix D, Table D27)

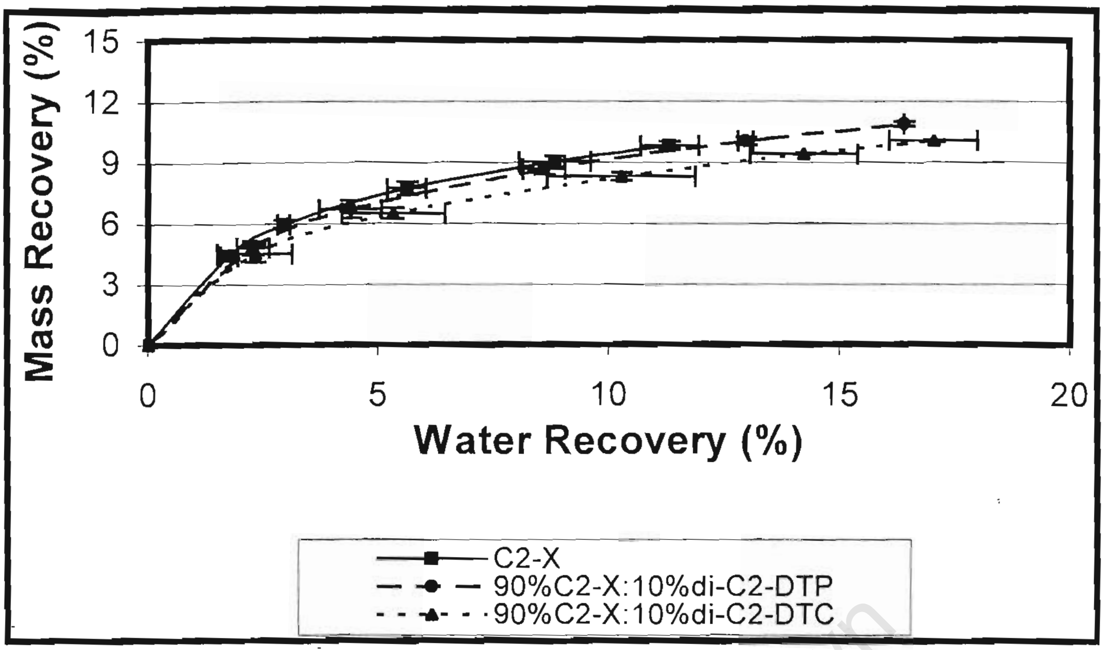


Figure 3.22 The mass-water recovery relationships obtained with C2-X, 90% C2-X:10% di-C2-DTP and 90% C2-X:10% di-C2-DTC collector mixtures at an equivalent collector dosage of 0.139 mol/ton ore in the flotation of the OCC ore

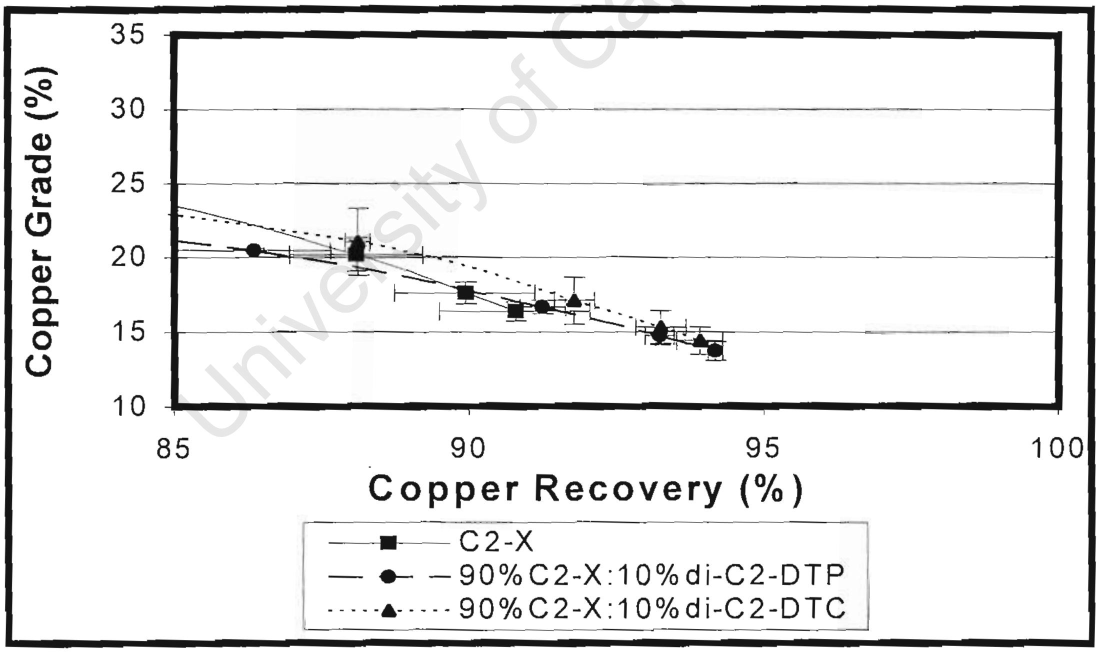


Figure 3.23 Segment of the cumulative copper grade-recovery relationships obtained with C2-X, 90% C2-X:10% di-C2-DTP and 90% C2-X:10% di-C2-DTC collector mixtures at an equivalent collector dosage of 0.139 mol/ton ore in the flotation of the OCC ore

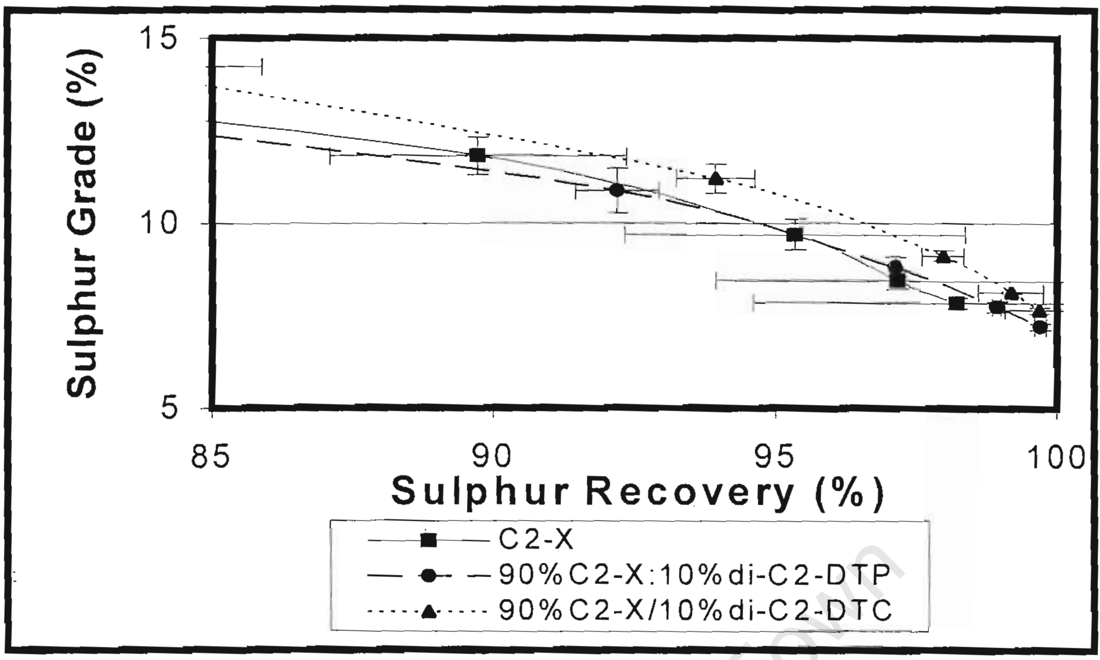


Figure 3.24 **Segment of the cumulative sulphur grade-recovery relationships obtained with C2-X, 90% C2-X:10% di-C2-DTP and 90% C2-X:10% di-C2-DTC mixtures at an equivalent collector dosage of 0.139 mol/ton ore in the flotation of the OCC ore**

3.1.6. The Mineralogical Assessment of the Okiep Copper Company Ore

3.1.6.1. The Mineralogy of the Ore

Although the main copper sulphide mineral in the copper ores from the Okiep area are chalcopyrite with a feed grade of 1.65% copper (Guilbert and Park, 1999), the mineralogy of a feed sample showed that the main copper sulphide was bornite. Furthermore, the actual average feed copper grade, determined by acid digestion was 1.8%.

Besides bornite, other copper sulphides reported in the mineralogy were chalcopyrite, chalcocite, digenite and possibly enargite. Pyrite was the main sulphide gangue mineral. The chief silicate gangue phases were pyroxene, quartz and K-feldspar. Mica, a complex aluminium silicate, was a minor constituent with biotite and phlogopite being the examples present. There were traces of talc, magnetite, hematite and ilmenite. The chemical formulae of the above minerals are given in Appendix E.

3.1.6.2. The Mineralogy of the First Concentrates

Mineralogical assessments were done on the first concentrates of test runs 12 and 16 (Table 3.3) where di-C2-DTP and di-C2-DTC respectively were the collectors used; each at a dosage of 0.0695 mol/ton ore. The most significant difference in the performance of the collectors was in the recovery of bornite (Table 3.3); in that 17.27 g vs 5.68 g was recovered with the dithiophosphate compared to the dithiocarbamate. The mass of the total sulphides recovered was higher with the dithiophosphate than with the dithiocarbamate; 20.18 g as opposed to 6.98 g (Table 3.3). Also, there was a larger recovery of gangue with the dithiophosphate; 26.78 g as opposed to 18.11 g (Table 3.3).

The grain-size distributions of sulphide and iron oxide particles were measured for the first concentrates from test runs 12 and 16. With the dithiocarbamate, 53.9, 38.2, 5.5 and 1 (v/v)% of the particles fell in the size ranges 0-20, 20-30, 30-60 and 60-80 μm respectively while 0.63 % of the particles were greater than 80 μm in size (Figure 3.25). With the dithiophosphate, 37.5, 38.5, 13.9 and 6.9 (v/v)% of the particles fell in the size ranges 0-20, 20-30, 30-60 and 60-80 μm respectively while 1.8 % of the particles were greater than 80 μm in size (Figure 3.26). A comparison of Figures 3.25 and 3.26 shows that there was a greater proportional contribution of finer particles recovered with the dithiocarbamate compared to that recovered with the dithiophosphate. This implies that the dithiocarbamate was the weaker collector and that with it there was a greater contribution to recovery by entrainment. Further evidence of the weakness of the dithiocarbamate is provided by the poor mass, copper and sulphur recoveries relative to those obtained with the dithiophosphate and the xanthate (Figures 3.14, 3.16 and 3.17).

Table 3.3 The mineralogy of the first concentrates obtained with di-C2-DTP and di-C2-DTC as collectors each at an equivalent dosage of 0.0695 mol/ton ore

Mineral		di-C2-DTP		di-C2-DTC	
Common Name	Chemical Formula	Mass Percentage (%)	Mass in Concentrate (g)	Mass Percentage (%)	Mass in Concentrate (g)
bornite	Cu_5FeS_4	35.6	17.27	21.9	5.68
chalcocite	Cu_2S	2.5	1.21	1.2	0.31
chalcopyrite	$CuFeS_2$	2.3	1.12	3.3	0.86
digenite	Cu_9S_5	0.1	0.05	0.1	0.03
pyrite	FeS_2	0.5	0.24	0.1	0.03
other sulphides		0.6	0.29	0.3	0.08
total sulphides		41.6	20.18	26.9	6.98
Fe oxide	Fe_2O_3	3.2	1.55	3.4	0.88
gangue		55.2	26.78	69.8	18.11
Total		100.0	48.51	100.0	25.97

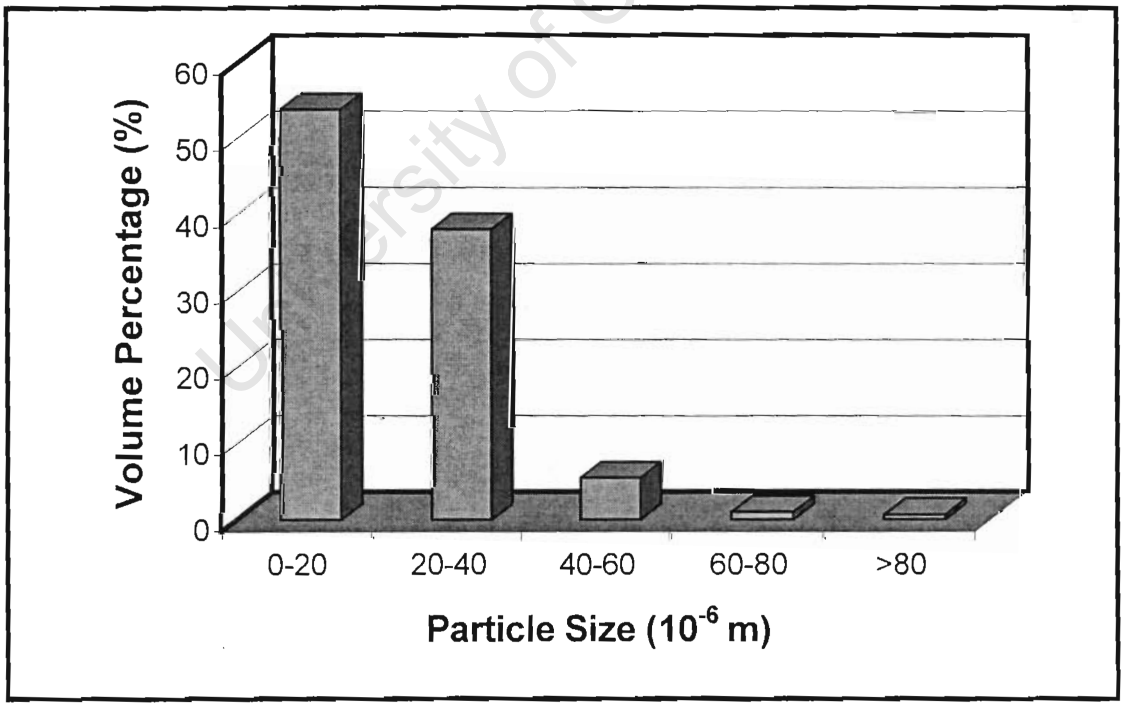


Figure 3.25 The grain size distribution of sulphide and iron oxide particles of a first concentrate obtained with di-C2-DTC at a collector dosage of 0.0695 mol/ton ore of in the flotation of the OCC ore

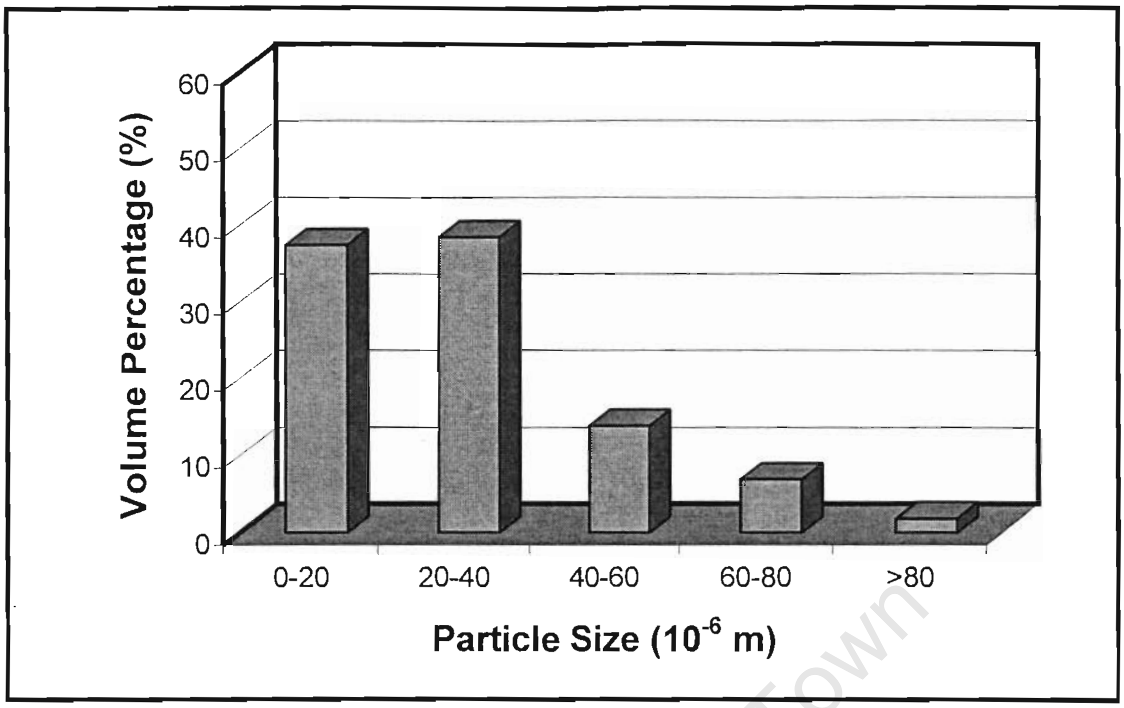


Figure 3.26 **The grain size distribution of sulphide and iron oxide particles of a first concentrate obtained with di-C2-DTP at a collector dosage of 0.0695 mol/ton ore of in the flotation of the OCC ore**

3.2. Palaborwa Mining Company Ore

The summary table of the results obtained with the PMC ore are presented in Table 3.4 and Appendix B contains the experimental results obtained.

3.2.1. Milling Relationship obtained with the Palaborwa Mining Company Ore

From the milling curve for the PMC ore (Appendix A), a milling time of 5 minutes gave 56.4% of particles below 75μ in size. With the OCC ore, a milling time of 9 minutes was required to achieve approximately the same degree of milling. Appendix A also contains a sieve analysis of a PMC ore sample that had been milled for 5 minutes.

Table 3.4 Summary table of the results obtained with the Palaborwa Mining Company ore

Test Run	Collector	Mole Ratio of Mixture	Dosage (mol/ton ore)	Cumulative Concentrate Mass (%)		Cumulative Water (%)		Cumulative Copper Recovery (%)		Cumulative Copper Grade (%)		Cumulative Acid Soluble Copper Recovery (%)		Cumulative Acid Soluble Copper Grade (%)		Klimpel Constants	
				1 min	20 min	1 min	20 min	1 min	20 min	1 min	20 min	1 min	20 min	1 min	20 min	k(min^{-1})	R(%)
28	No Collector		0	1.7	5.3	5.1	15.2	7.3	21.2	2.5	2.4	6.9	25.5	0.25	0.30	0.7	22.5
29	C2-X		0.0695	1.9	5.3	4.6	13.1	33.9	53.4	11.4	6.4	13.5	38.9	0.43	0.44	2.4	53.2
30	C2-X		0.139	2.0	6.3	4.7	14.0	33.5	60.7	10.2	6.0	13.0	43.6	0.39	0.46	1.7	61
31	C2-X		0.139	2.0	6.5	4.7	16.0	34.8	59.9	10.5	5.5					1.9	60.6
32	C2-X		0.139	2.1	6.0	5.1	15.4	36.9	56.1	10.4	5.6					2.6	55.8
33	C2-X		0.209	2.1	5.9	5.1	15.3	38.2	55.8	11.0	5.9	15.1	40.8	0.42	0.42	2.8	55.3
34	di-C2-DTP		0.0348	2.3	6.0	6.1	16.4	19.3	36.0	5.5	3.9	10.4	30.4	0.27	0.30	1.6	36.4
35	di-C2-DTP		0.0695	2.1	6.0	5.7	16.8	20.2	38.7	6.2	4.1	10.2	32.4	0.27	0.30	1.5	39.1
37	di-C2-DTC		0.0695	2.0	5.5	4.7	13.7	24.8	43.4	7.4	4.6	11.2	31.8	0.30	0.31	1.8	43.7
38	di-C2-DTC		0.139	1.9	5.4	4.7	14.2	25.2	43.9	7.4	4.5	10.9	32.0	0.31	0.32	1.8	44.0
39	iC4-X		0.139	2.8	6.7	6.3	16.8	44.8	64.7	10.0	6.0	18.8	45.7	0.37	0.37	3.0	64.7
40	iC4-X		0.139	2.6	6.5	5.1	14.4	42.9	64.0	11.0	6.6	17.4	44.8	0.34	0.36	2.7	64.6
41	90% C2-X:10% di-C2-DTP	90:10	0.139	2.7	6.5	5.6	14.7	44.7	63.3	11.6	6.8	15.2	42.0	0.32	0.37	3.1	62.7
42	90% C2-X:10% di-C2-DTP	90:10	0.139	2.2	5.9	4.9	13.9	34.7	57.8	9.76	5.9	13.3	39.6	0.33	0.36	2.1	58.0
43	90% C2-X:10% di-C2-DTC	90:10	0.139	2.1	5.5	4.5	11.5	40.3	60.2	12.02	6.9	13.1	37.1	0.34	0.37	2.7	60.0
44	90% C2-X:10% di-C2-DTC	90:10	0.139	2.0	5.1	4.5	11.4	36.5	55.8	10.64	6.4	14.5	37.6	0.37	0.38	2.5	56.1
45	iC4-X:di-C2-DTC	90:10	0.139	2.3	6.2	4.8	15.3	44.9	63.4	11.90	6.1	18.6	48.0	0.49	0.46	3.2	63.1
46	iC4-X:di-C2-DTC	90:10	0.139	2.7	6.8	6.0	17.3	39.2	61.7	8.95	5.7	15.6	40.6	0.32	0.33	2.4	62.1

3.2.2. Reproducibility Study on the Palaborwa Mining Company Ore

The collector used in the reproducibility study on the PMC ore was C2-X at a dosage of 0.139 mol/ton ore. The mass-water recovery relationships (Figure 3.27) and the copper concentrate grade-recovery relationships (Figure 3.28) for test runs 30, 31 and 32 are in close agreement with one another.

Standard deviations for the data for Figures 3.27 and 3.28 are given in Table 3.5. The standard deviations for the water recoveries range from 0.21 to 1.02%. This was deemed acceptable for water recovery measurements.

Table 3.5 Standard deviations of the means (SD) obtained for test runs 30, 31 and 32 at a collector dosage of 0.139 mol C2-X/ton ore with Okiep ore

Cumulative Water Recovery (%)		Cumulative Mass Recovery (%)		Cumulative Copper Recovery (%)		Cumulative Copper Grade (%)	
Mean	SD	Mean	SD	Mean	SD	Mean	SD
4.82	0.21	2.05	0.06	35.1	1.7	10.4	0.15
9.02	0.36	3.67	0.13	47.3	0.8	7.8	0.23
12.92	0.36	5.06	0.28	54.1	1.9	6.5	0.33
14.71	0.88	5.90	0.29	57.6	2.4	5.9	0.26
15.14	1.02	6.26	0.28	58.9	2.4	5.7	0.25

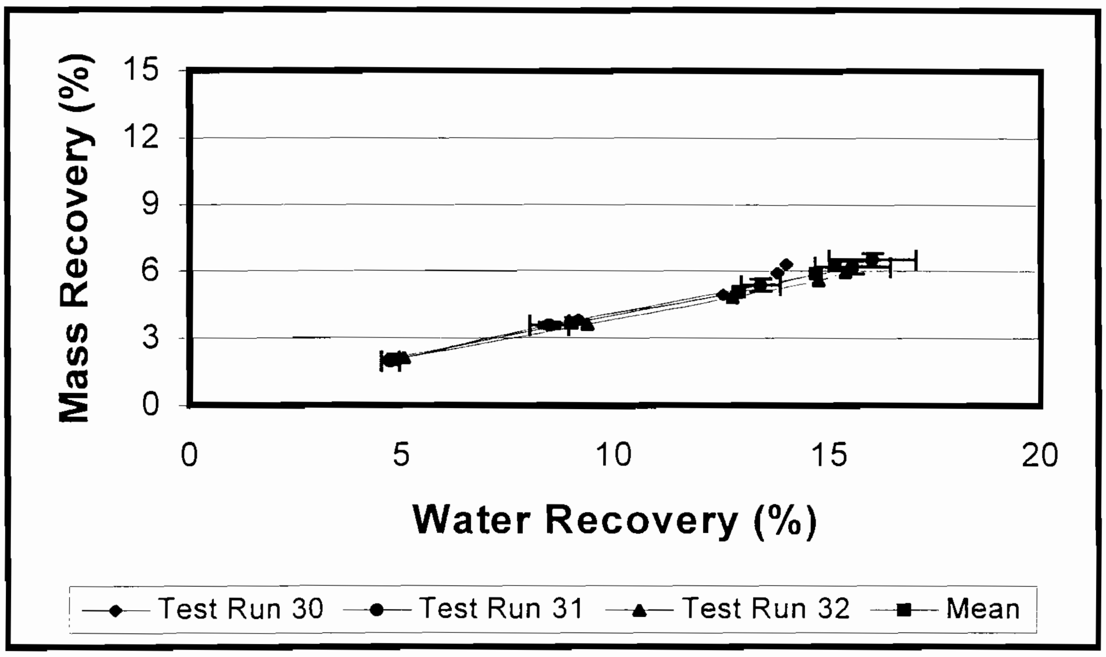


Figure 3.27 The mass-water recovery relationship obtained with C2-X at a collector dosage of 0.139 mol/ton ore in the flotation of the PMC ore

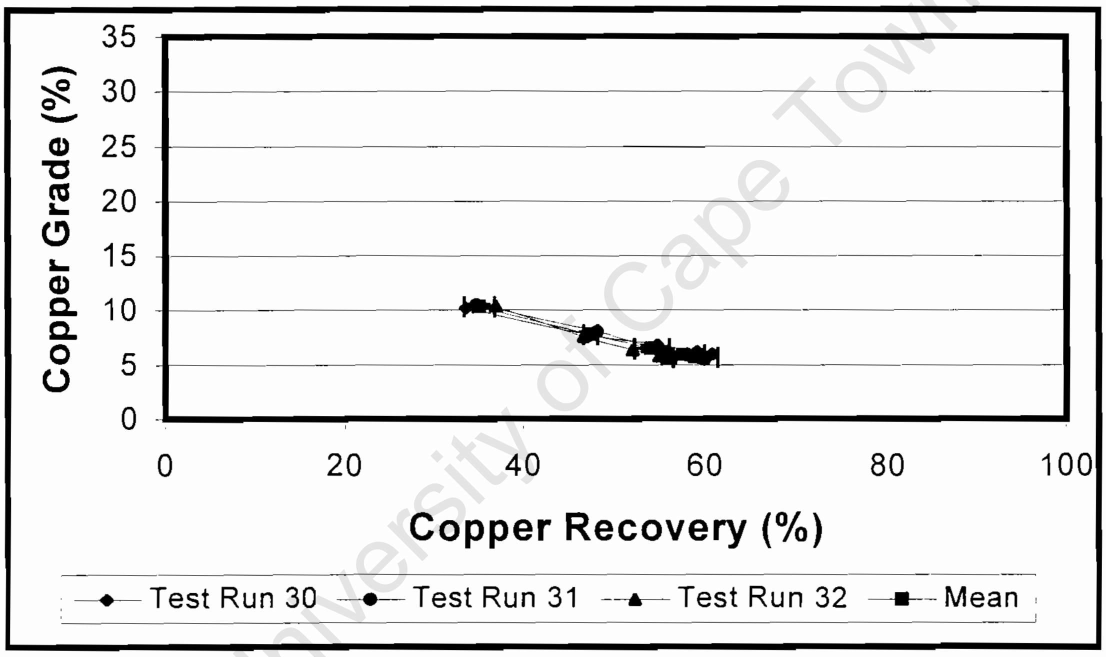


Figure 3.28 The cumulative copper grade-recovery relationship obtained with 0.139 mol C2-X/ton ore in the flotation of the PMC ore

3.2.3. The Effect of the Dosage of the Collector on the Froth Flotation Performance of the Palaborwa Mining Company Ore

In order to establish the effect of the dosage of the collectors on the flotation of the PMC ore, the performance of C2-X was tested at collector dosages of 0695, 0.139 and 0.209 mol/ton ore (Figures 3.29 to 3.32 and 3.39). The performance of di-C2-DTP was tested at collector dosages of 0.0348 and 0.0695 mol/ton ore (Figures 3.32 to 3.35 and 3.39), while that of the di-C2-DTC was tested at collector dosages of 0.0695 and 0.139 mol/ton ore (Figures 3.32 and 3.36 to 3.39).

3.2.3.1. The Froth Flotation Performance obtained with C2-X at dosages of 0.0695, 0.139 and 0.209 mol/ton ore in the Froth Flotation of the Palaborwa Mining Company Ore

The dosage of the collector had no effect on the mass and water recoveries (Figure 3.29).

The cumulative copper recovery obtained with C2-X increased from 53% at a collector dosage of 0.0695 mol/ton ore to a maximum of 59% at 0.139 mol/ton ore and decreased to 56% at 0.209 mol/ton ore (Figures 3.30 and 3.39). There were no significant differences in the cumulative copper grades obtained (Figure 3.30 and Table 3.4).

There were no discernable differences observed in the cumulative acid soluble copper grade-recovery relationships (Figure 3.31) and the mass-water recovery relationships obtained (Figure 3.29). In addition, there were no significant differences in the rates of cumulative copper recovery obtained at collector dosages of 0.0695 and 0.139 mol/ton ore (Figure 3.32). The results suggest that the rate of cumulative copper recovery obtained at 0.209 mol/ton ore was higher than at the other two dosages tested (Figure 3.32).

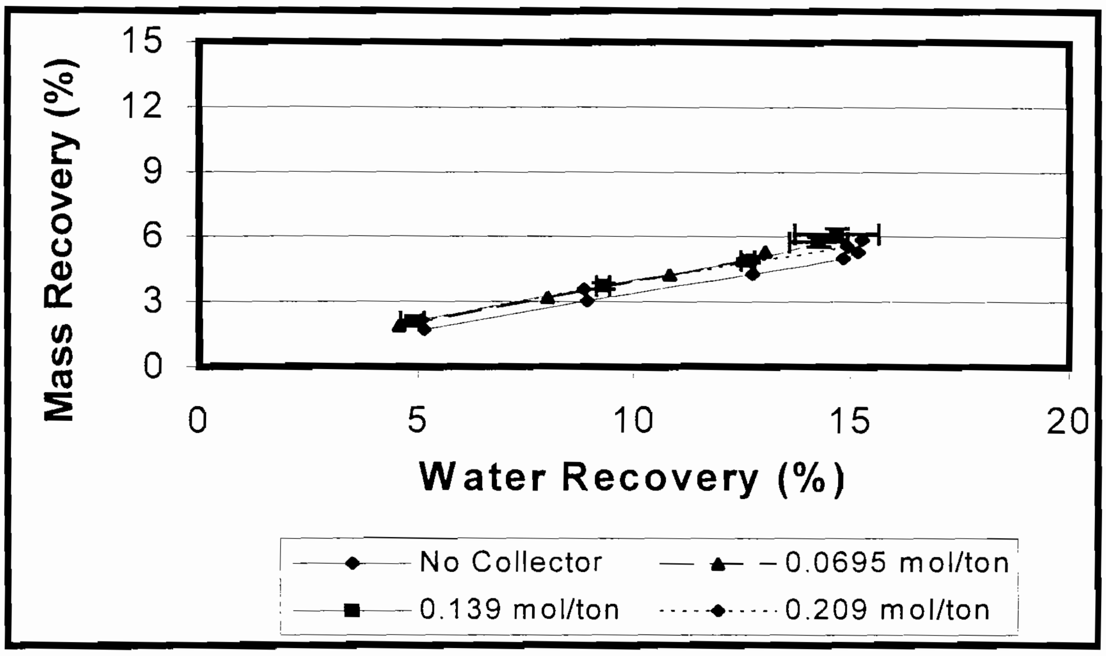


Figure 3.29 The mass-water recovery relationships obtained with C2-X at dosages of 0.0695, 0.139 and 0.209 mol/ton ore in the flotation of the PMC ore

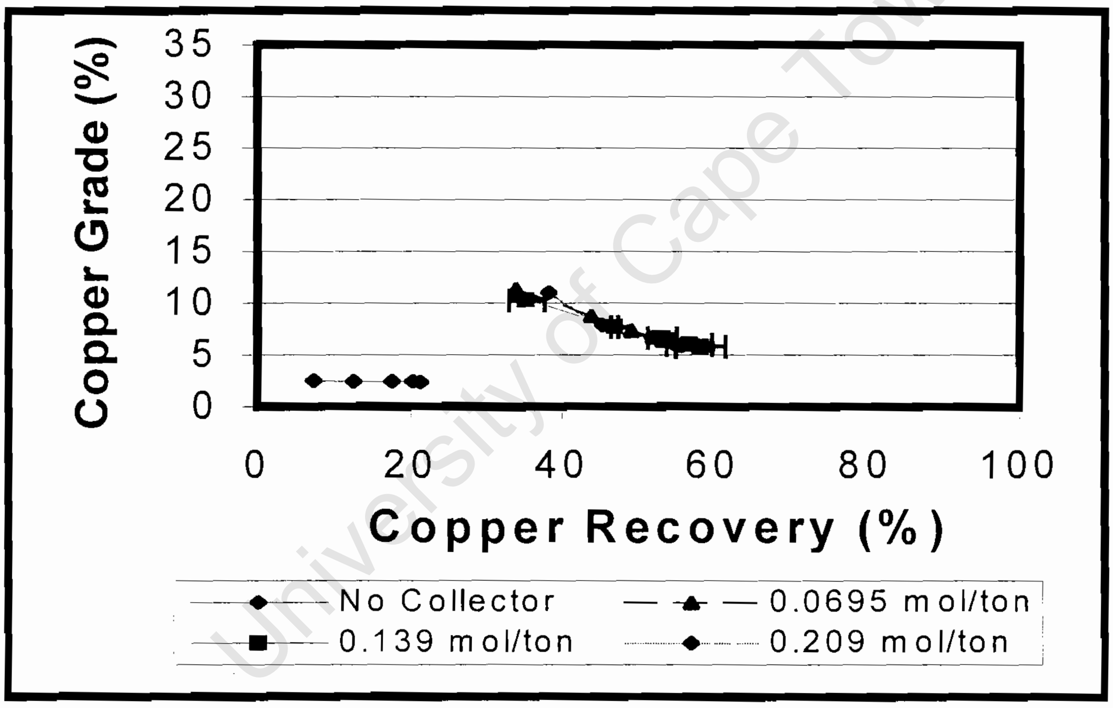


Figure 3.30 The cumulative copper grade-recovery relationships obtained with C2-X at collector dosages of 0.0695, 0.139 and 0.209 mol/ton ore in the flotation of the PMC ore

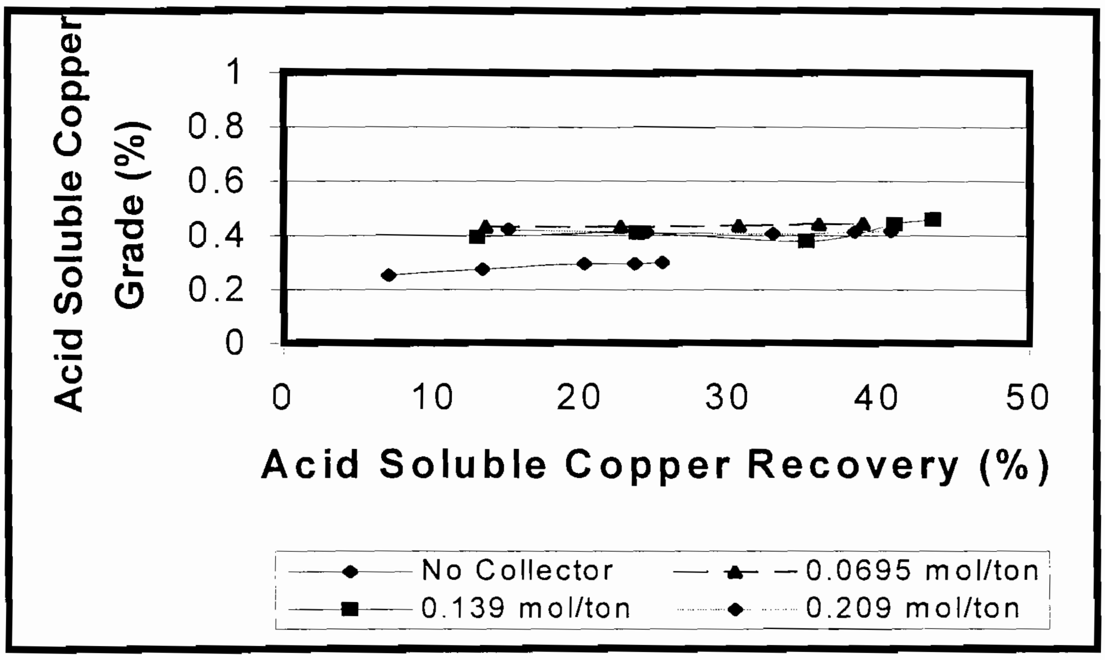


Figure 3.31 The cumulative acid soluble copper grade-recovery relationships obtained with C2-X at dosages of 0.0695, 0.139 and 0.209 mol/ton ore in the flotation of the PMC ore

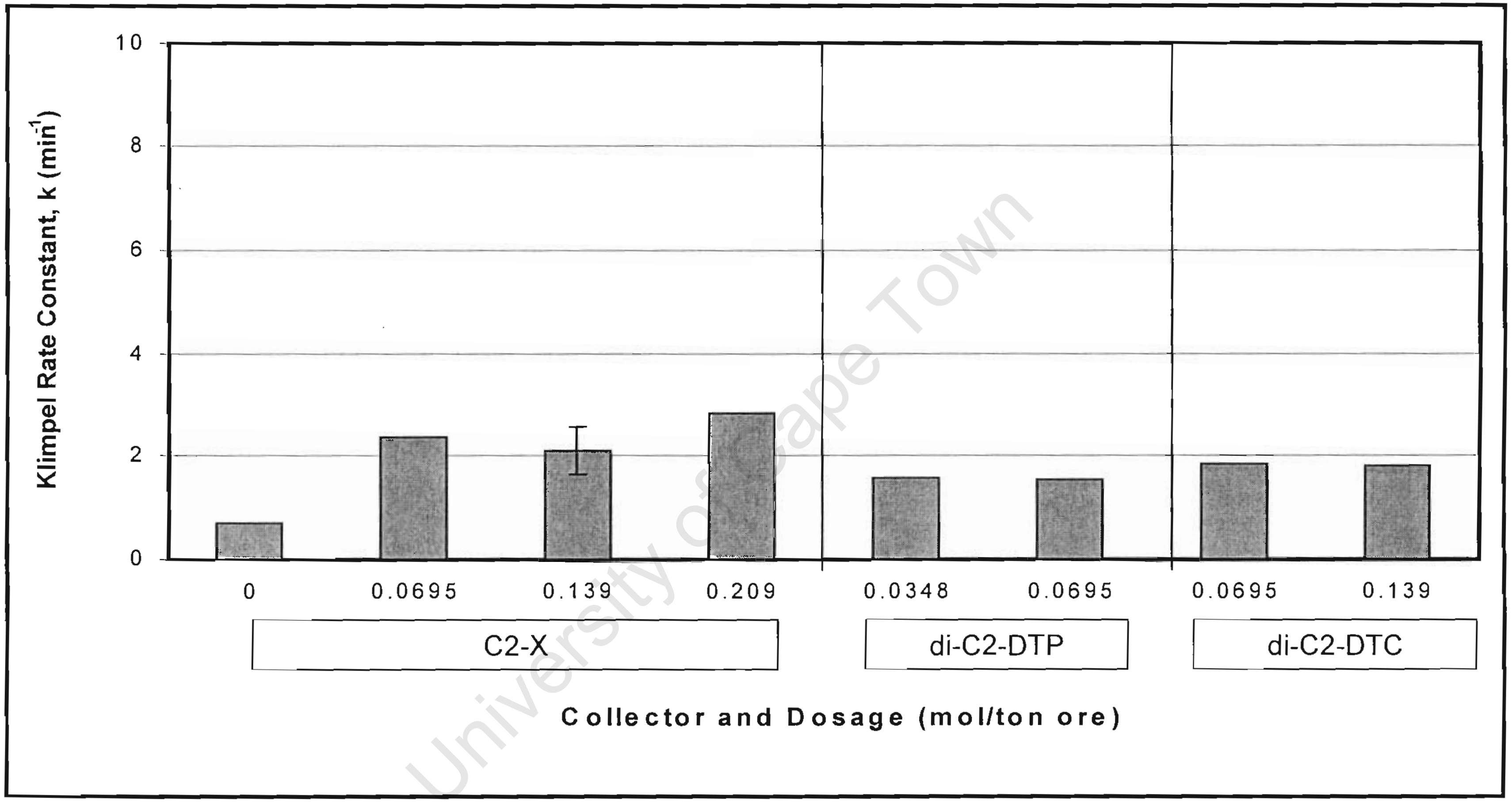


Figure 3.32 The Klimpel rate constants for cumulative copper recovery obtained with C2-X, di-C2-DTP and di-C2-DTC at various dosages in the flotation of the PMC ore

3.2.3.2. The Froth Flotation Performance of Palaborwa Mining Company Ore obtained with di-C2-DTP at Dosages of 0.0348 and 0.0695 mol/ton ore

There were no discernible differences in the mass-water recovery relationships obtained when no collector and dosages of 0.0348 or 0.0695 mol/ton ore were tested (Figure 3.33).

The cumulative copper recovery by flotation increased from 36.0% with 0.0348 mol/ton ore to 38.7% at 0.0695 mol/ton ore (Figures 3.34 and 3.39). The change in dosage of the collector had no discernible effect on the cumulative copper grades, cumulative copper recoveries (Figure 3.34), the cumulative acid soluble copper grades and the cumulative acid soluble copper recoveries obtained (Figure 3.35).

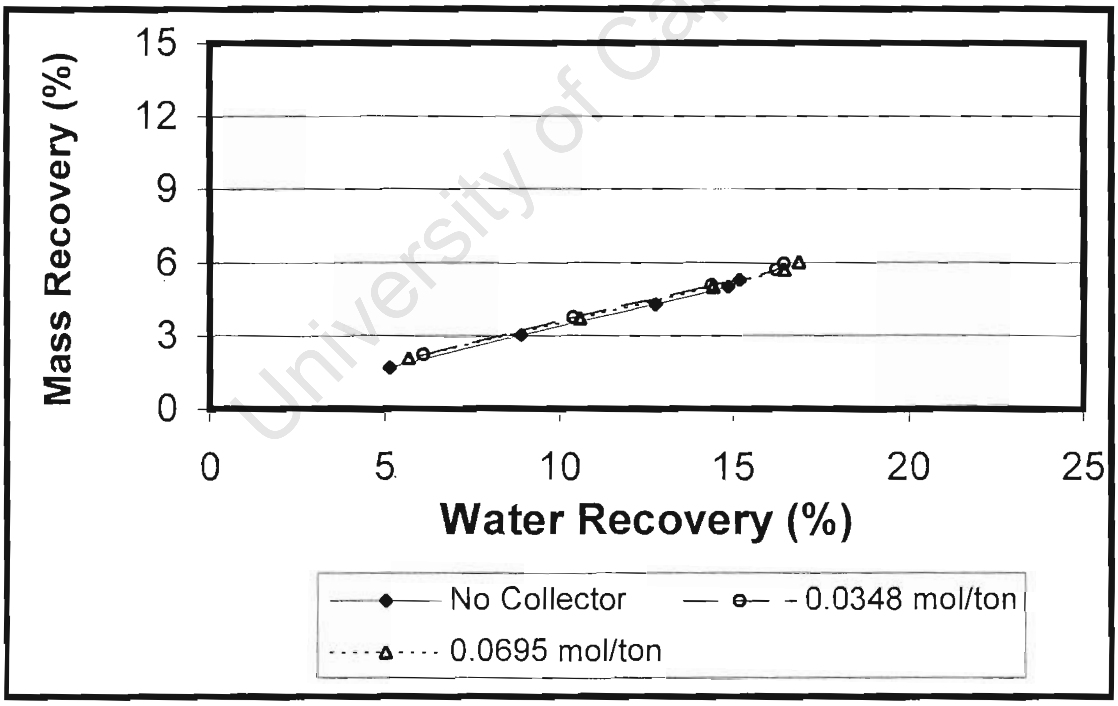


Figure 3.33 The mass-water recovery relationships obtained with different dosages of di-C2-DTP in the flotation of the PMC ore

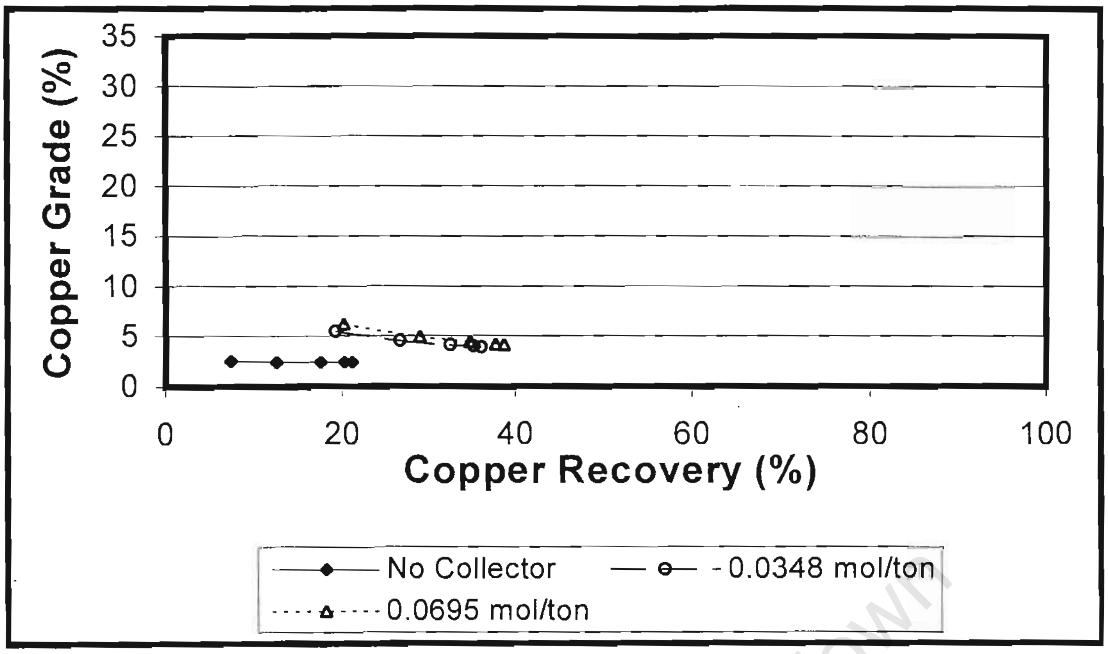


Figure 3.34 The cumulative copper grade-recovery relationships obtained with different dosages of di-C2-DTP in the flotation of the PMC ore

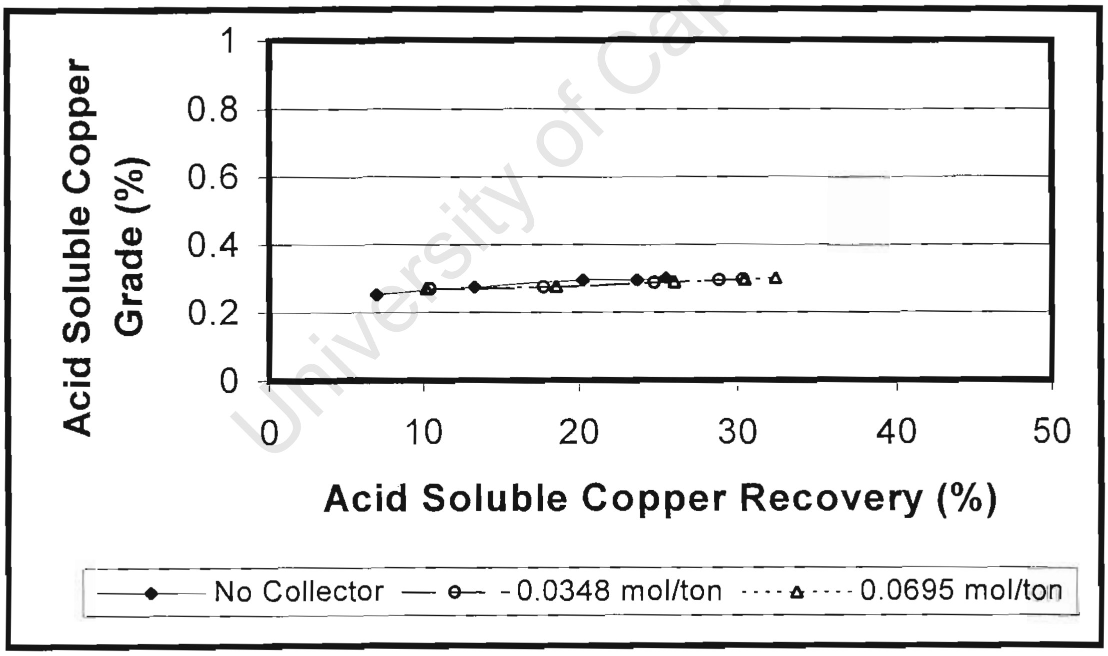


Figure 3.35 The cumulative acid soluble copper grade-recovery relationships obtained with different dosages of di-C2-DTP in the flotation of the PMC ore

3.2.3.3. The Froth Flotation Performance of Palaborwa Mining Company Ore obtained with di-C2-DTC at Collector Dosages of 0.0695 and 0.139 mol/ton ore

The flotation performances of the PMC ore were compared at di-C2-DTC dosages of 0.0695 and 0.139 mol/ton ore. No discernible differences were observed in the water-mass recovery, copper grade-recovery, acid soluble copper grade-recovery relationships and Klimpel rate constants obtained (Figures 3.36 to 3.39 and 3.32).

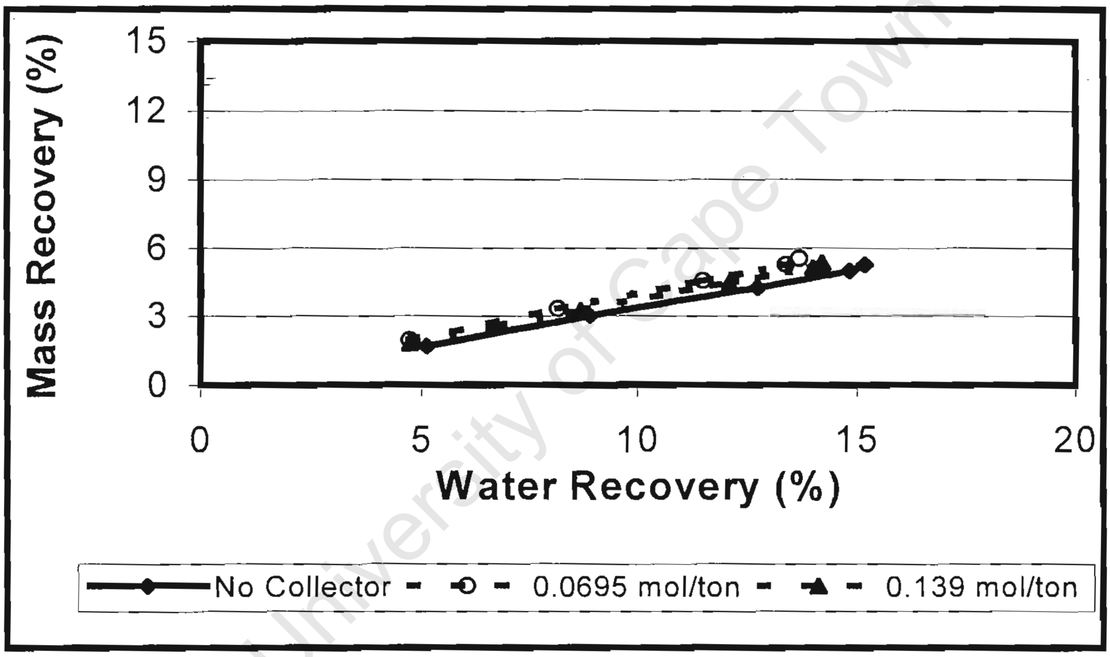


Figure 3.36 The mass-water recovery relationships obtained with different dosages of di-C2-DTC in the flotation of the PMC ore

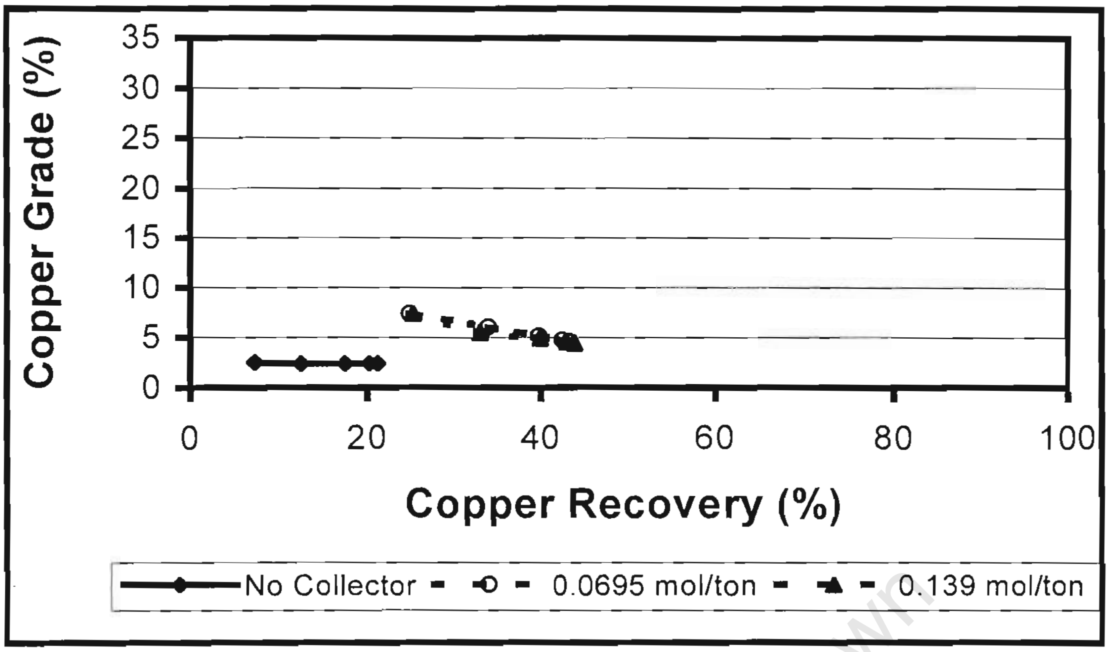


Figure 3.37 The cumulative copper grade-recovery relationships obtained with different dosages of di-C2-DTC in the flotation of the PMC ore

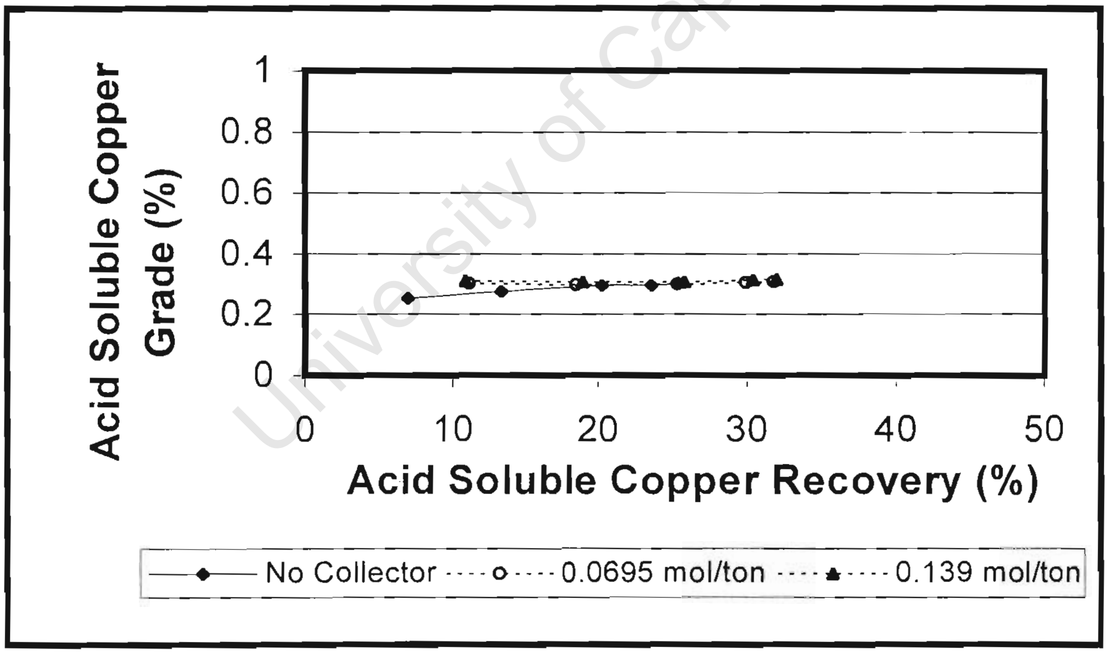


Figure 3.38 The cumulative acid soluble copper grade-recovery relationships obtained with different dosages of di-C2-DTC in the flotation of the PMC ore

3.2.3.4. The Relationships between Cumulative Copper Recovery and Collector Dosage obtained with C2-X, di-C2-DTP and di-C2-DTC in the Froth Flotation of the Palaborwa Mining Company ore

Superior cumulative copper recoveries were obtained with the xanthate compared to those obtained with the dithiophosphate or the dithiocarbamate at all dosages tested (Figure 3.39).

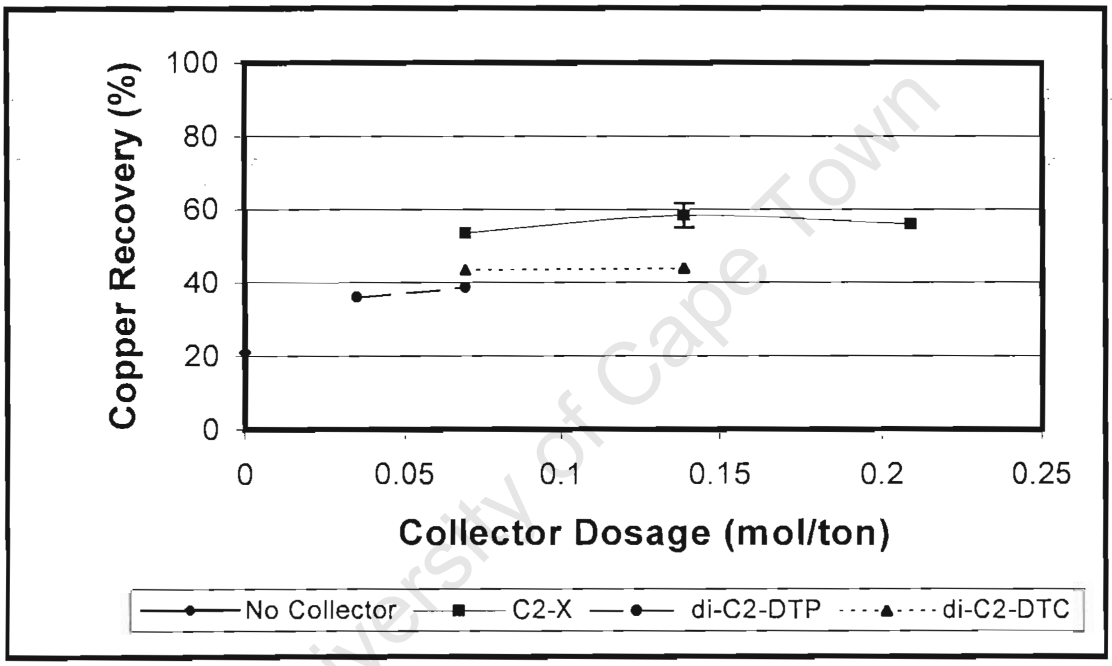


Figure 3.39 **The cumulative copper recovery vs collector dosage obtained with C2-X, di-C2-DTP and di-C2-DTC respectively in the flotation of the PMC ore**

3.2.4. The Effect of the Functional Group of the Collector on the Froth Flotation Performance of the Palaborwa Mining Company Ore

In order to establish the effect of the functional group of the collector on the flotation performance of the PMC ore, C2-X, di-C2-DTP and di-C2-DTC were each tested at a collector dosage of 0.0695 mol/ton ore, while C2-X and di-C2-DTC were tested at 0.139 mol/ton ore.

The xanthate gave superior cumulative copper (Figure 3.39) and copper oxide recoveries (Figures 3.31, 3.35 and 3.38) and grades (Figures 3.30 and 3.34; 3.30 and 3.37 and 3.31, 3.35 and 3.38) compared to those obtained with the dithiophosphate or the dithiocarbamate at equivalent collector dosages. At a dosage of 0.139 mol/ton ore, the copper grades with the xanthate were higher than that obtained with the dithiocarbamate (Figures 3.30 and 3.37 and Table 3.4) despite a larger water recovery with the xanthate; indicating a greater selectivity towards copper minerals by the xanthate. However, at a dosage of 0.0695 mol/ton ore, a larger water recovery was obtained with dithiophosphate compared to those obtained with the xanthate or the dithiocarbamate (Figure 3.29, 3.33 and 3.36).

The cumulative copper grade-recovery relationships with the dithiophosphate (Figure 3.34) and the dithiocarbamate (Figure 3.37) were of lesser slope in comparison to that obtained with xanthate at the same equivalent dosages (Figure 3.30); indicating that non-selective entrainment of material was a more dominant process with the dithiophosphate and the dithiocarbamate.

The highest rates of copper recovery were obtained with the xanthate compared to those obtained with the dithiophosphate or the dithiocarbamate each at the same dosage (Figure 3.32).

3.2.5. The Effect of Collector Mixtures on the Froth Flotation Performance of the Palaborwa Mining Company ore

In order to establish the effect of mixtures of collectors on the flotation performance of the PMC ore, three collector mixtures were tested. The performance of pure C2-X was compared to that of 90 mol% C2-X with 10 mol% di-C2-DTP (90% C2-X:10% di-C2-DTP) and 90 mol% C2-X with 10 mol% di-C2-DTC (90% C2-X:10% di-C2-DTC). In addition, the performance of pure iC4-X was compared to that of a 90 mol% iC4-X with 10 mol% di-C2-DTC (90% iC4-

X:10% di-C2-DTC). All tests were done at an equivalent collector dosage of 0.139 mol/ton ore.

3.2.5.1. The Comparison of the Froth Flotation Performances obtained with C2-X, 90% C2-X:10% di-C2-DTP and 90% C2-X:10% di-C2-DTC

The water recovery obtained with C2-X was significantly greater than that obtained with the 90% C2-X:10% di-C2-DTC; 15.1% as opposed to 11.4%. Furthermore, a significantly greater water recovery was obtained with 90% C2-X:10% di-C2-DTP compared to that obtained with 90% C2-X:10% di-C2-DTC; 14.3% as opposed 11.4% (Figure 3.40 and Appendix D, Table D40).

The mass recovery obtained with C2-X, 6.3%, was significantly higher than the 5.3% obtained with the 90% C2-X:10% di-C2-DTC collector mixture (Figure 3.40 and Appendix D, Table D41).

The cumulative copper recovery and grade obtained with the 90% C2-X:10% di-C2-DTC were 58.0% and 6.6% respectively and for C2-X they were 58.9% and 5.7% respectively (Figure 3.41). The difference in copper grade was statistically significant (Figure 3.41 and Appendix D, Table D37).

The rate of copper recovery, as measured by the Klimpel rate constant, was larger with the collector mixtures; approximately 2.5 as opposed to 2.0 min^{-1} (Figure 3.43).

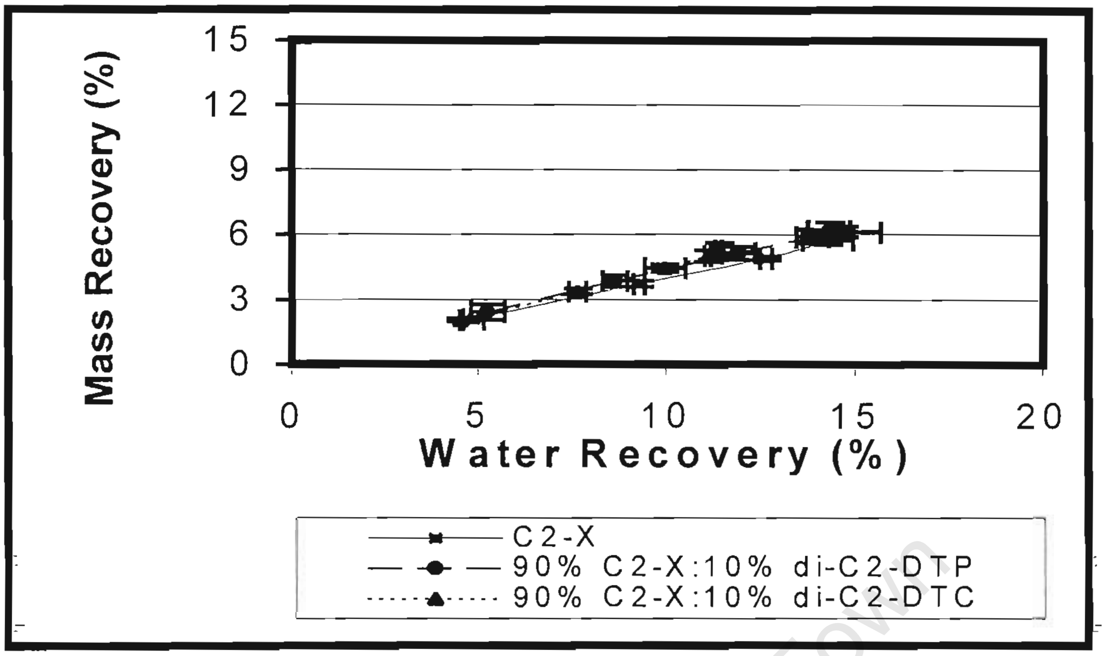


Figure 3.40 The mass-water recovery relationships obtained with C2-X, 90% C2-X:10% di-C2-DTP and 90% C2-X:10% di-C2-DTC at an equivalent collector dosage of 0.139 mol/ton ore in the flotation of the PMC ore

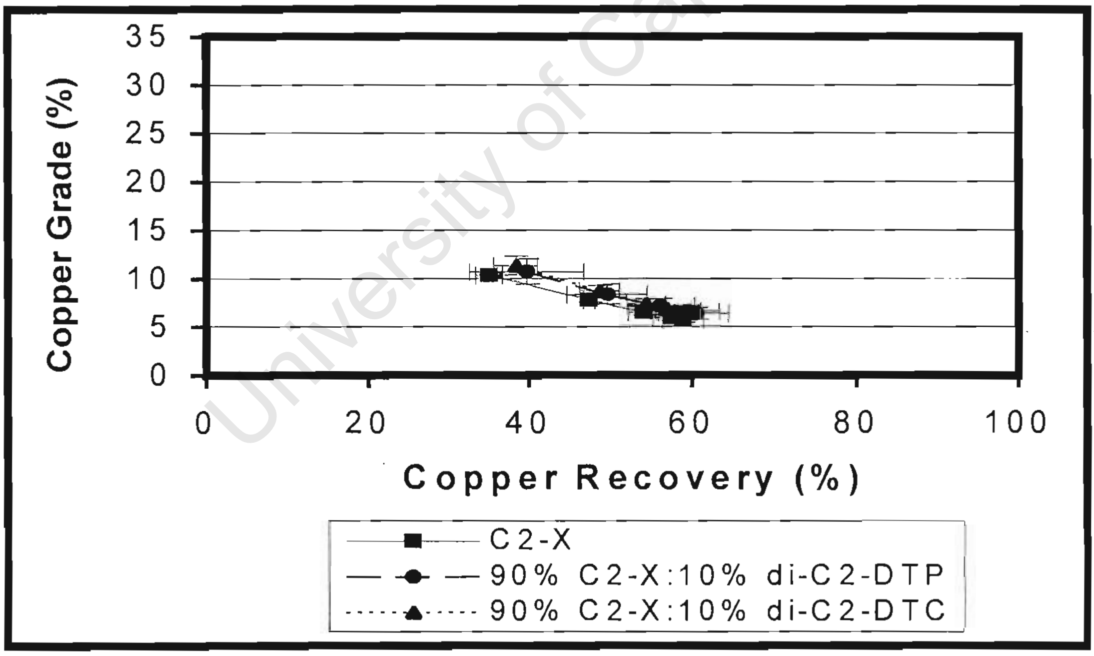


Figure 3.41 The cumulative copper grade-recovery relationships obtained with C2-X, 90% C2-X:10% di-C2-DTP and 90% C2-X:10% di-C2-DTC at an equivalent collector dosage of 139 mol/ton ore in the flotation of the PMC ore

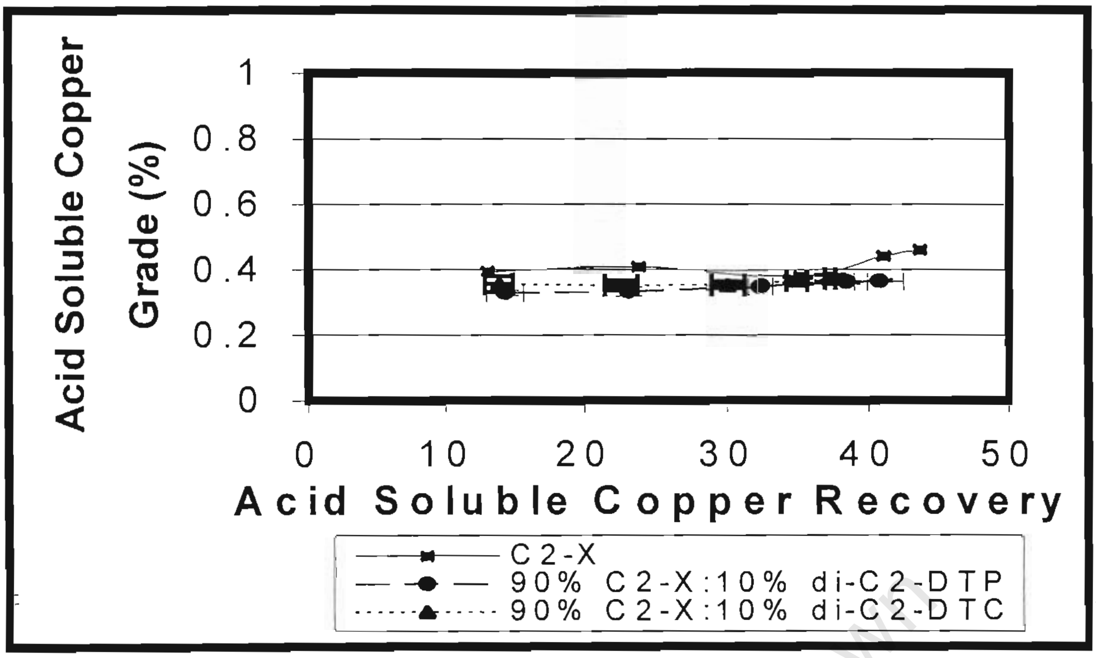


Figure 3.42 The cumulative acid soluble copper grade-recovery relationships obtained with C2-X, 90% C2-X:10% di-C2-DTP and 90% C2-X:10% di-C2-DTC at an equivalent collector dosage of 0.139 mol/ton ore in the flotation of the PMC ore

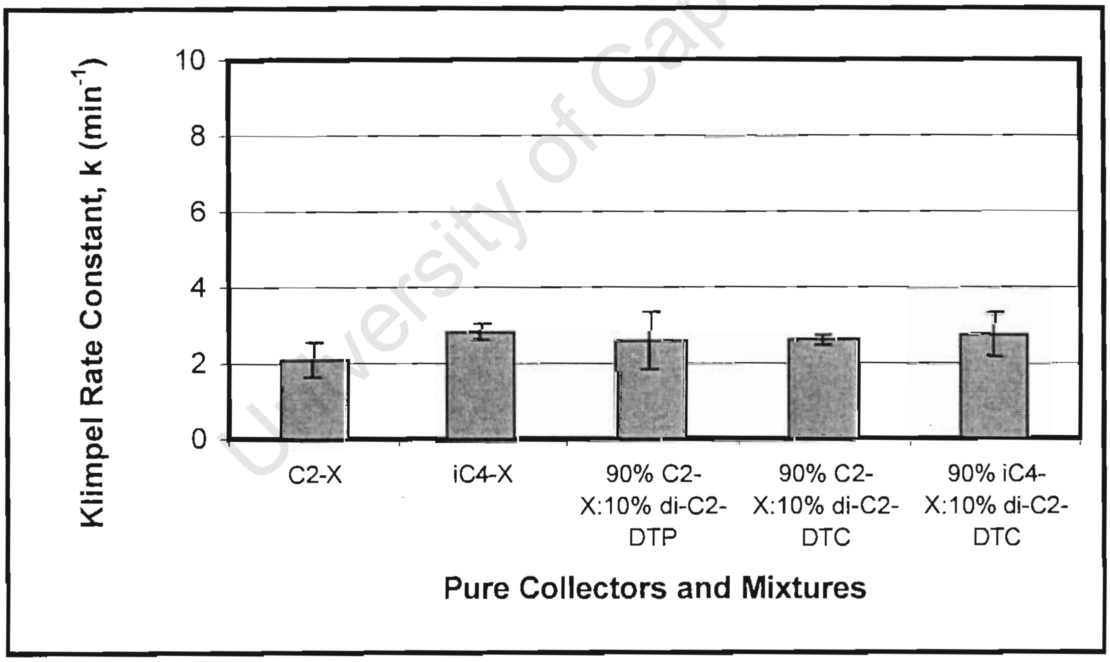


Figure 3.43 The Klimpel rate constants for copper recovery obtained with C2-X, iC4,. 90% C2-X:10% di-C2-DTP, 90% C2-X:10% di-C2-DTC and 90% iC4-X:10% di-C2-DTC at an equivalent collector dosage of 0.139 mol/ton ore in the flotation of the PMC ore

3.2.5.2. The Froth Flotation Performance of the Palaborwa Mining Company ore obtained with iC4-X and 90% iC4-X:10% di-C2-DTC

The cumulative copper grade-recovery; cumulative copper oxide grade-recovery and mass-water recovery relationships and the Klimpel rate constants for copper recovery obtained with iC4-X were indistinguishable from those of 90% iC4-X:10% di-C2-DTC (Figures 3.43. to 3.46).

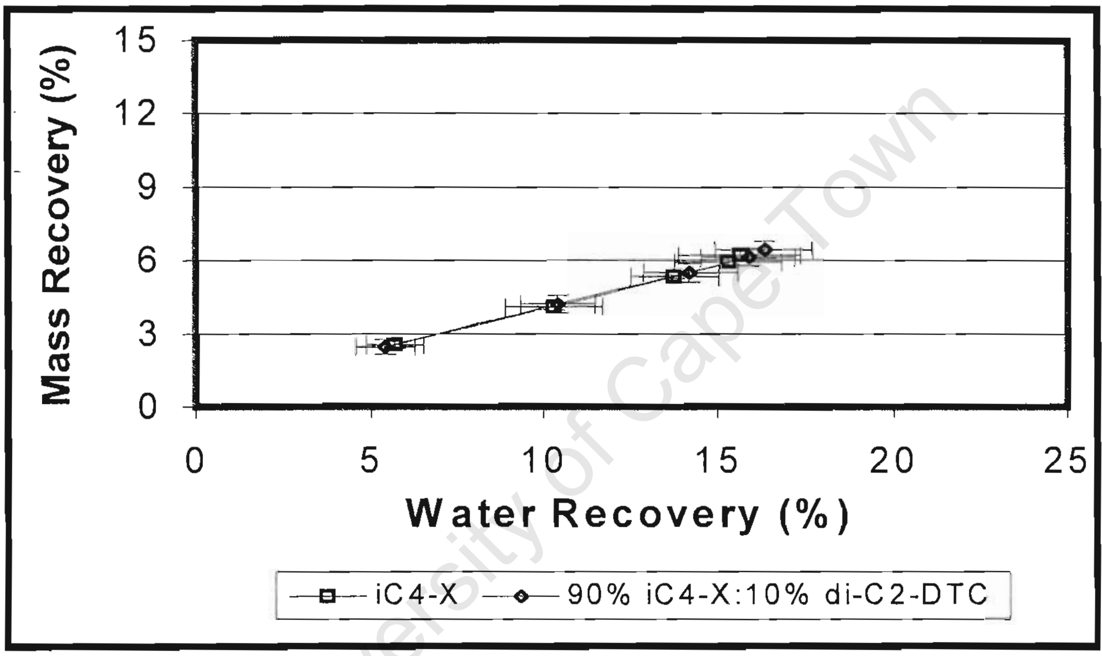


Figure 3.44 **The mass-water recovery relationships obtained with iC4-X and 90%iC4-X:10% di-C2-DTC, each at an equivalent collector dosage of 0.139 mol/ton ore, in the flotation of the PMC ore**

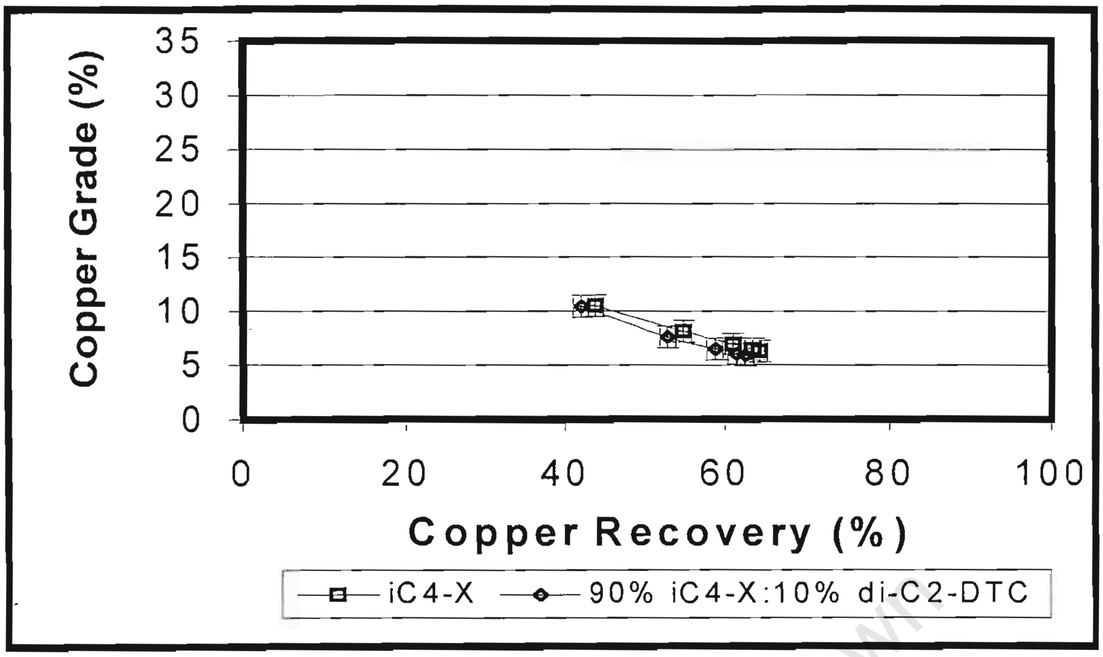


Figure 3.45 The cumulative copper grade-recovery relationships obtained with iC4-X and 90%iC4-X:10% di-C2-DTC, each at an equivalent collector dosage of 0.139 mol/ton ore, in the flotation of the PMC ore

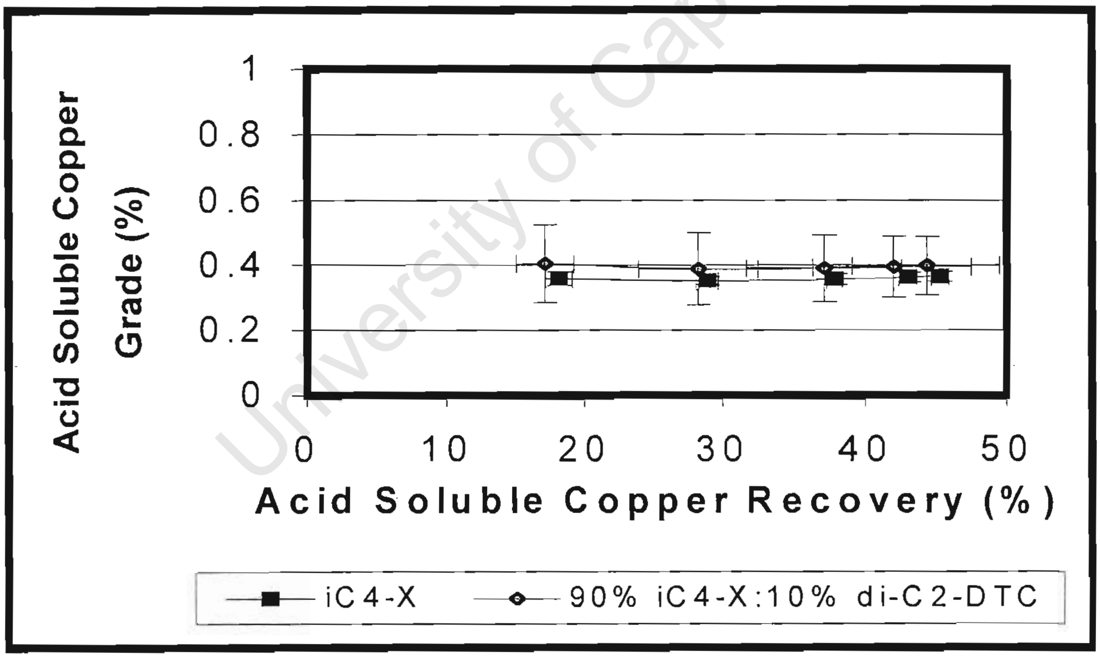


Figure 3.46 The cumulative acid soluble copper grade-recovery relationships obtained with iC4-X and 90%iC4-X:10% di-C2-DTC, each at an equivalent collector dosage of 0.139 mol/ton ore, in the flotation of the PMC ore

3.2.6. The Mineralogy of the Palaborwa Mining Company Ore

The PMC ore was "oxidised" and had a significant amount of copper oxide minerals (Palaborwa Mining Company). Furthermore, it was a "difficult" ore to float.

In the Palaborwa complex, copper minerals appear in transgressive carbonatite, banded carbonatite and Phoskorite. All carbonatites contain calcite, dolomite or siderite. Bornite, at grades averaging 0.5% copper, is the dominant copper mineral in the lower grade banded carbonatite. Magnetite, with 2 to 4% TiO_2, baddeleyite and vallerite, are present in transgressive carbonatite and banded carbonatite (Evans, 1992).

According to the feed ore mineralogy, bornite and chalcopyrite were the main sulphides. The accessory phases contained copper sulphide, pyrite, galena, cubanite, ilmenite. and baddeleyite. Carbonate (calcite and dolomite/ankerite) was the main gangue phase. Mica (biotite/phlogopite) was a minor constituent. Trace components were serpentine, magnetite and apatite. The minerals and their chemical formulae are given in Appendix E.

The mineralogy of the ore (Appendix E) agrees well with the above description of the banded carbonatite from the Palaborwa complex. It is therefore probable that the ore used in this work came from the banded carbonatite.

Vallerite in the banded carbonatite poses recovery problems, as recovery by flotation is less than 20%. In addition, it interferes with the flotation of other sulphides so causing copper losses (Evans, 1992). Vallerite was notably absent from the feed mineralogical analysis. No assessment of the concentrates was done.

4. DISCUSSION

The predominant copper sulphide in the Okiep Copper Company (OCC) ore was bornite (section 2.2.1 and Table 3.3), while bornite and chalcopyrite were the predominant copper sulphides in the Palaborwa Mining Company (PMC) ore (section 2.2.2). The OCC ore had a copper feed grade of 1.8%, while the feed grade of the PMC ore was 0.58%. Approximately 10% of the copper in the PMC ore was acid soluble copper oxides with an average feed grade of 0.06%.

4.1. The Effect of the Dosage of the Collector

The objectives in this part of the work were to establish the effect of the dosage of the collector on the flotation of a partially oxidised copper ore from Okiep and an oxidised copper ore from Palaborwa.

In the case of both the OCC and the PMC ores, the copper recovery obtained declined marginally when the C2-X dosage was increased from 0.139 to 0.209 mol/ton/ore (Figure 3.16 and 3.39). This decline suggested that a dosage of 0.209 mol/ton ore represented an excess of collector. Somasundaran (1975) proposed that an excess of collector reduced the flotation of minerals for the following reasons:

1. The adsorption of a second layer of collector on the mineral surface with the opposite orientation of the first layer.
2. The formation of micelles by the collector.

The second effect is not normally observed with short chain collectors of the type used in this work (Somasundaran, 1975). This then leaves the option that a second layer of collector was adsorbed with the opposite orientation of the first thus forming unstable, patchy multilayers of collector (Bradshaw and O'Connor, 1996). This would render particles less hydrophobic than those with a monolayer of collector and leave them more inclined to remain in the pulp phase (Taggart, 1951).

4.1.1. Okiep Copper Company Ore

The copper recovery by flotation was dependent on the dosage or concentration of C2-X, di-C2-DTP and di-C2-DTC (Figure 3.16).

In the case of the xanthate, the observed trend of copper recovery in relation to collector dosage (Figure 3.16) is in agreement with Somasundaran (1975) and Smar et al, (1994). However, as the copper recovery at collector dosages of 0.0695 and 0.139 mol/ton were not significantly different, the optimal coverage of the mineral surface for flotation recovery probably occurred nearer the lower dosage.

Part of a similar trend to that observed with C2-X with regard to copper recovery and collector dosage was observed with di-C2-DTP and di-C2-DTC (Figure 3.16). With di-C2-DTP, however, a decline in copper recovery was not observed at the highest collector dosage tested (Figure 3.16) and the copper recoveries obtained at all dosages tested were not significantly different (Figure 3.16). This implied that the optimal coverage of the mineral surface for flotation recovery probably occurred near a dosage of 0.0348 mol/ton ore in the case of di-C2-DTP (Figure 3.16). This speculation is supported by the observation that the sulphur grade-recovery relationships were almost co-incident at all dosages of di-C2-DTP tested (Figure 3.10); implying that total coverage of the sulphide mineral surface had been achieved at the lower dosages. This was not the case for C2-X (Figure 3.6) or di-C2-DTC (Figure 3.13). Furthermore, as the di-C2-DTP had an additional alkyl group compared to C2-X, it is reasonable to assume that once adsorbed on the mineral surface, it imparted a greater hydrophobicity than the same molar amount of C2-X. This then implies that the optimal coverage of the mineral surface would have occurred at lower molar concentrations of the di-C2-

DTP than C2-X; as indeed was observed. The maximum copper recovery possible with di-C2-DTC was probably not observed at a collector dosage of 0.139 mol/ton ore, the highest dosage tested with this collector (Figure 3.16).

From the discussion thus far, the optimal coverage of the mineral surface occurred near a collector dosage of 0.0695 mol/ton ore with C2-X and at 0.0348 mol/ton ore with di-C2-DTP. It may be assumed that these dosages of collector also produced a maximum in the surface hydrophobicity of the mineral. As hydrophobic particles may stabilise froths at sufficient concentrations (Harris, 1982), it may be assumed that the degree of hydrophobicity of the particles has some influence on froth stability. The observations that the water recovered with C2-X at a dosage of 0.0695 mol/ton ore (Figure 3.4) and with di-C2-DTP (Figure 3.8) at 0.0348 mol/ton ore were higher than at the other dosages tested support the assumption that maximum hydrophobicity and copper recovery corresponded to maximum froth stability.

Slightly hydrophobic particles, that may be present when excess collector molecules are adsorbed as a secondary layer on the mineral surface with the opposite orientation of the first layer (Somasundaran, 1975), could also stabilise the froth zone (Dippenaar, 1978) and reduce froth drainage leading to higher water recoveries and lower grades. The water recovery was indeed marginally higher accompanied by a marginally reduced copper grade at a xanthate dosage of 0.209 mol/ton ore compared to that obtained at 0.139 mol/ton ore (Figure 3.5 and 3.15). The higher collector dosage may then have contributed to a more stable froth relative to that obtained at the lower one.

In general, higher dosages of C2-X or di-C2-DTC (Figure 3.7) contributed to higher Klimpel rate constants and rates of copper recovery. With di-C2-DTP, the Klimpel rate constants increased as the collector dosage was increased until a maximum was reached after which there was a decrease. This follows a reported trend (Smar et al, 1994). It may be assumed that part of this trend was observed with

C2-X and di-C2-DTC and that the maximum rate with these collectors had not been reached.

4.1.2. Palaborwa Mining Company Ore

The changes in the results obtained for the various collector dosages of each collector was not significant for the copper recoveries and grades (Figures 3.30, 3.34 and 3.37), the acid soluble copper recoveries and grades (Figures 3.31, 3.35 and 3.38) and the mass and water recoveries (Figures 3.29, 3.33 and 3.36).

Some of the copper minerals may have been rendered unavailable to collector action attributable to presence of surface oxidation products on the mineral surface (Barzyk et al, 1981 and Grano et al, 1997). This could explain the insensitivity of the performance of the collectors to the changes in their dosages (Figures 3.30, 3.34 and 3.37). In this case, the complete reaction of all available copper minerals may have occurred at the lower collector dosages and the effect of increasing the dosage would then consequently have been minimal; as was observed. Alternative treatment such as sulphidisation of the oxidised mineral surface is recommended.

4.2 The Role of the Functional Group of the Collector

4.2.1 Okiep Copper Company Ore

Superior copper recoveries and grades; sulphur recoveries and grades; mass recoveries and Klimpel rate constants for copper recovery were obtained with di-C2-DTP and C2-X compared to those obtained with di-C2-DTC at dosages of 0.0348, 0.0695 and 0.139 mol/ton ore (Figures 3.4 to 3.17). These results imply that of the collectors tested, di-C2-DTC was the weakest collector of sulphide minerals in general and copper sulphide minerals in particular. They agree with Bradshaw and O'Connor (1994) but contradict the order of collector strength for sulphide minerals identified by Nagaraj (1988): dithiocarbamate > xanthate > dithiophosphate. They also question the statement of Bhaskar Raju and Forsling (1991) that "dithiocarbamates are particularly selective and exhibit several advantages as collectors for copper minerals". Neither a superior selectivity, as would have been evidenced by a superior copper grade, nor other advantages were observed in this work.

The differences in final copper recoveries obtained with di-C2-DTC compared to those obtained with C2-X or di-C2-DTP (Figures 3.16) were disproportionately large compared to the differences in mass recoveries obtained in each respective case (Figures 3.14). Also, the di-C2-DTC recovered a lower percentage of total sulphides and copper sulphides in a first concentrate obtained at a collector dosage of 0.0695 mol/ton ore (Table 3.3). It is therefore reasonable to assume that the poor copper recoveries obtained with di-C2-DTC were not solely attributable to the poor mass recoveries obtained. Possibly, there were differences in the chemical reactions at the mineral surface; particularly dithiolate formation or the lack thereof in the case of di-C2-DTC (Finkelstein and Poling, 1977).

Generally, the dithiolate can be assumed responsible for the flotation of copper minerals with di-C2-DTC and di-C2-DTP (Table 1.3). An exception was chalcopyrite after reaction with di-C2-DTC where the cuprous thiolate was reported (Mangalam and Khangoankar, 1985 and Bhaskar Raju and Khangaonkar, 1984), while another was oxidised chalcocite where the cuprous thiolate and cupric dithiolate were formed after reaction with di-C2-DTP (Chander and Fuestenau, 1974). This information relates to the thermodynamics of the systems examined. For the most part therefore, the formation of the cupric dithiolate was thermodynamically feasible with di-C2-DTP and di-C2-DTC. The thermodynamic feasibility of a process does not, however, guarantee that it does indeed occur as its kinetics also plays a role (Woods, 1984).

The di-C2-DTC concentration that corresponded to the optimal adsorption density in the chalopyrite-di-C2-DTC system was 8.3 × 10^{-4} mol/L at a pH of 9 (Mangalam and Khangoankar, 1985). Furthermore, maximum copper recoveries occurred at a collector concentration in the region of 5 × 10^{-4} mol/L (Bhaskar Raju and Khangoankar, 1984). This suggests that the optimal concentration of di-C2-DTC for maximum copper recovery lies in the range 5 to 8.3 × 10^{-4} mol/L. The maximum dosage of di-C2-DTC used in this work was 4.6×10^{-5} mol/L. This dosage was an order of magnitude below the lowest in the range. It is therefore proposed that the poor performance of di-C2-DTC observed was in part attributable to the less than optimal dosage used for this collector. Furthermore, the dosage was too low for the formation of the cupric dithiolate and this would have compromised the floatability of the minerals (Finkelstein and Poling, 1977).

From the comparison of the grain size distributions of the first concentrates obtained with di-C2-DTP and di-C2-DTC each at a collector dosage of 0.0695 mol/ton ore (Figures 3.25 & 3.26), it is evident that di-C2-DTP was able to carry over greater percentages of the larger particles compared to di-C2-DTC. This also demonstrates that the dithiocarbamate was the weaker collector. Furthermore, in general di-C2-DTP recovered larger masses of the sulphide minerals and the copper sulphide minerals than di-C2-DTC. The mass of chalcopyrite recovered was, however, almost the same for both collectors (Table 3.3). This could be attributed to the high natural floatability of chalcopyrite and not to the action of collectors (Guy and Trahar, 1985).

The higher mass and water recoveries obtained with di-C2-DTP compared to those obtained with C2-X or di-C2-DTC, each at dosages of 0.0348 or 0.139 mol/ton ore (Figures 3.14 and 3.15), suggested that the froth properties were different with the di-C2-DTP. These differences may be attributed to the frothing properties of the dithiophosphate and synergistic interactions between it and the frother (Dai et al, 2001). The improved copper recoveries (Figures 3.16) and rates of copper recovery (Figure 3.7) obtained with di-C2-DTP at collector dosages of 0.0348 and 0.0695 mol/ton ore may also result from these interactions (Dai et al, 2001).

4.2.2. Palaborwa Mining Company Ore

All three collectors tested were responsible for raising the grades and recoveries above that obtained with collectorless flotation (Figures 3.30, 3.34 and 3.37). This implied that the collectors reacted with the copper minerals and enhanced their hydrophobicity.

Oxidised bornite and chalcocite display no natural floatability (Buckley et al, 1985, Guy and Trahar, 1984 and Woods, 1984), as their surface oxidation products in alkaline solutions are neither a sulphur-rich, nor a metal deficient species (Guy and Trahar, 1985). However, chalcopyrite and covellite, upon oxidation, become naturally floatable attributable to the deposition of sulphur on the mineral surface (Guy and Trahar, 1985). This implies that in this work, the initial recoveries and grades obtained with all three collectors could have been raised by the self-induced floatability of oxidised chalcopyrite and oxidised covellite (Figures 3.30, 3.34 and 3.37).

The rate of copper recovery was higher with the xanthate compared to those obtained with the dithiophosphate and the dithiocarbamate (Figure 3.32). Furthermore, the initial copper grade was higher with the xanthate (Figures 3.30, 3.34 and 3.37). This suggested that a greater percentage of the copper minerals was recovered by flotation after reaction with this collector and recovery was not solely attributable to the natural floatability of certain minerals. However, copper recoveries were low compared to those obtained with the OCC ore under the same conditions (Figures 3.16 and 3.39). This was perhaps attributable to a collector concentration that was too low to recover minerals that may have been oxidised (Barzyk et al, 1981).

The superior performance obtained with the xanthate compared to those obtained with the dithiophosphate or the dithiocarbamate (Figures 3.30, 3.34 and 3.37) could have been attributable to adsorption mechanisms similar to those established for oxidised chalcocite. These are anodic oxidation in the presence of oxygen and ion exchange with the previously formed oxidised species (Barzyk et al, 1981, Richardson et al, 1984 and Chander & Fuestenau, 1974). Another view is that the electrochemical mechanism may result in the formation of cuprous xanthate (Yoon and Basilio, 1993).

When di-C2-DTP was used as a collector, the copper recoveries were lower with the PMC ore (Figure 3.39) compared to those obtained with the OCC ore (Figure 3.16). If the chalcopyrite in the PMC ore had been oxidised, a hydrated iron oxyhydroxide oxidation product would have hampered the adsorption of the dithiophosphate (Grano et al, 1997). Given the poor copper recovery from the PMC ore, this may indeed have been the case.

As the copper oxides are not conductors or semi-conductors, they do not tend to react with thiol collectors (Chabuka and Witika, 2001) and collector adsorption densities sufficient for flotation are not as readily achieved as for sulphide minerals (Bhaskar Raju and Forsling, 1991). The acid-soluble copper recoveries obtained with all collectors at all dosages tested were however, higher than when no collector was used (Figures 3.31, 3.35 and 3.38 and Table 3.4). It is then concluded that the low recoveries with the collectors may be attributed to insufficient adsorption densities of the collector on the mineral surface. Furthermore, non-conductors may conduct electrical charge to a small degree and it is therefore possible that the catalytic oxidation of collectors took place on the oxide mineral surface resulting in dithiolate formation; the species responsible for the limited floatability of the copper oxides.

It is known that approximately 1.5% of chalcocite and 2% of bornite is acid soluble copper (Siame et al, 2002). The recovery of these oxidised copper minerals with the xanthate (Barzyk et al, 1981, Richardson et al, 1984 and Chander & Fuestenau, 1974) may therefore have contributed in some small measure to the superior acid soluble copper grades and recoveries obtained with C2-X compared to those obtained with di-C2-DTP or di-C2-DTC (Figures 3.31, 3.35 and 3.38),

As the copper oxides are inherently hydrophilic in nature (Chabuka and Witika, 2001), it was expected that there would have been a direct relationship between their recovery and water recovery. This relationship was observed to be linear with C2-X, di-C2-DTP and di-C2-DTC at the collector dosages tested (Appendix G). In addition, there was a linear relationship between copper and water recoveries obtained (Appendix F). It may therefore be suggested that one of the mechanisms by which the copper sulphides and hydrophilic copper oxides were recovered was by entrainment in the water of the froth phase. The contribution to copper and copper oxide recovery by entrainment may be estimated by ignoring the natural floatability of oxidised copper sulphides such as chalcopyrite and calculating the ratio of total recovery without collectors to that obtained with the collectors. Approximately 38, 57 and 49% of copper and 62, 81 and 80% of copper oxide recovery was by entrainment with the xanthate, dithiophosphate and the dithiocarbamate respectively (Appendix F).

The presence of di-C2-DTP contributed to more watery froths than those obtained with C2-X and di-C2-DTC at a dosage of 0.0695 mol/ton ore (Figures 3.29, 3.33 and 3.36). This higher water recovery contributed to the entrainment of fine hydrophilic material (Subrahmanyam and Forssberg, 1988 & Kelly and Spottiswood, 1982) and this led to a marginally lower copper grade compared to those obtained with the other collectors (Figures 3.30, 3.34 and 3.37 and Table 3.5).

4.3. The Effect of Collector Mixtures on the Flotation Performance

The objective in this part of this work was to establish the effect of collector mixtures on the flotation of the OCC and PMC ores. The benefits of the use of collector mixtures over pure collectors include lower dosage requirements, improved selectivity, rates and recovery and an increase in the recovery of coarse particles (Bradshaw et al, 1998).

Not all of the differences in the performances of the collector mixtures compared to the pure major component of the mixtures were statistically significant. An observation of general trends, however, makes discussion possible.

4.3.1. Okiep Copper Company Ore

The performances obtained with C2-X at collector dosages of 0.0695 and 0.139 mol/ton ore were compared to those obtained with 90%C2-X:10% di-C2-DTP and 90%C2-X:10% di-C2-DTC at the same equivalent collector dosages respectively (Figures 3.18 to 3.24).

A significantly superior grade to that obtained with C2-X was observed with 90% C2-X:10% di-C2-DTC collector mixture at an equivalent collector dosage of 0.0695 mol/ton ore (Figure 3.19 and Appendix D, Table D16). Earlier it was suggested that the maximum hydrophobicity of the mineral surface occurred near a collector dosage of 0.0695 mol/ton ore with C2-X. It is therefore reasonable to propose that the maximum hydrophobicity with the collector mixtures would also have occurred near this dosage. In the case of the mixtures, however, the mineral surface would have been more hydrophobic attributable to the adsorption of either di-C2-DTP or di-C2-DTC instead of C2-X at some of the adsorption sites. The presence of small extremely hydrophobic solids that were less than 37μm in size could have led to froth destabilisation (Dippenaar, 1978). A sieve analysis showed that approximately 33 mass% of the milled ore was in this size range (Appendix A, Table A1). These small highly hydrophobic particles could have destabilised the froth; leading to better froth drainage and improved selectivity and grades (Bradshaw et al, 1998).

The significantly superior copper recoveries obtained with the collector mixtures compared to that obtained with C2-X at a collector dosage of 0.139 mol/ton ore (Appendix D, Table D15, Figure 3.23 and Table 3.2) were accompanied by significantly greater water recoveries (Figure 3.22) and consequently significantly lower copper grades (Figure 3.23). This suggested that the froths obtained with the mixtures were more stable than with C2-X and less drained (Bradshaw, 1998). This may be attributable to the presence of moderately hydrophobic particles that stabilised the froths (Harris, 1982). These may have been present due to the lowering of the hydrophobicity of the particles by the adsorption of collectors in patchy multilayers on the mineral surface (Bradshaw and O'Connor, 1996). Other factors at work at a collector dosage of 0.139 mol/ton ore could have been that the excess of either di-C2-DTC (Jiwu et al, 1984) or di-C2-DTP (Dai et al, 2001) could have stabilised the froths.

The processes that affected the hydrophobicity of the particles and consequently affected copper recovery and grade may have been the selective adsorption of the different collectors on particular sites or changes in the orientation of the alkyl chains resulting in superior surface coverage (Bradshaw and O'Connor, 1994). In addition, for a mixture of xanthate and dithiophosphate there may have been enhanced co-adsorption of collectors at low collector concentrations (Wakamatsu and Numata, 1980). These phenomena played a role in determining the degree of hydrophobicity of the mineral surface and were therefore responsible for the differences in froth properties (Harris, 1982 and Dippenaar, 1978).

4.3.2. Palaborwa Mining Company Ore

The copper grade obtained with the 90% C2-X:10% di-C2-DTC collector mixture was 1% higher than that obtained with C2-X at a collector dosage of 0.139 mol/ton ore (Table 3.4 and Figure 3.41). The difference, though slight, was significant (Appendix D, Table D37). This advantage may be attributable to differences in the froth characteristics as the water recovery was 3.7% lower with the mixture (Table 3.4, Figure 3.40); a significant finding (Appendix D, Table D 40). As above, the presence of hydrophobic solids could have led to froth destabilisation and consequently better froth drainage and grades (Bradshaw et al, 1998). Furthermore, as the mass recovery was significantly lower with the mixture (Appendix D, Table D41, Table 3.4, and Figure 3.40), it may be stated that the mixture was more selective towards copper minerals than C2-X (Bradshaw et al, 1998).

The copper grade obtained with the C2-X:di-C2-DTC mixture in the flotation of the OCC ore was lower than that obtained with C2-X at a collector dosage of 0.139 mol/ton ore (Figure 3.23 and Table 3.2). In the flotation of the PMC ore under the same conditions, a superior copper grade was obtained with the mixture (Figure 3.41 and Table 3.4). As talc was present in the OCC ore and not the PMC ore (Appendix E, Tables E1 and E2), it may have exerted a stabilising effect on the froth obtained with the OCC ore (Robinson, 2002). This could have led to increased water recovery and a reduced copper grade (Bradshaw, 1998). The presence of the talc in the OCC ore therefore explains the difference in the performances obtained with the C2-X:di-C2-DTC collector mixture in the flotation of the OCC and PMC ores.

At an equivalent collector dosage of 0.139 mol/ton ore, there were no significant differences in the performances of iC4-X and the 90% iC4-X:10% di-C2-DTC collector mixture (Figures 3.43 to 3.46). This implied that there were no collector:collector or collector:frother synergistic interactions or indeed any other advantage of using the mixture. As the 90% C2-X:10% di-C2-DTC mixture gave the advantage of an improved copper grade over C2-X, the absence of this advantage with the 90% iC4-X:10% di-C2-DTC mixture over iC4-X requires explanation. As longer chained xanthates are less selective than shorter chained ones (Ackerman et al, 1984, Somasundaran, 1975), iC4-X was probably less selective than C2-X. This would have negated any likelihood of an improved grade with the 90% iC4-X:10% di-C2-DTC collector mixture.

A marginally higher copper oxide grade and recovery was obtained with C2-X compared to those obtained with 90% C2-X:10% di-C2-DTP and 90% C2-X:10% di-C2-DTC collector mixtures at an equivalent dosage of 0.139 mol/ton ore (Figure 3.42). This may have been attributable to the higher concentration of the C2-X in the flotation cell when pure C2-X was used and its superior collecting power compared to either di-C2-DTP or di-C2-DTC (Figure 3.39).

The use of collector mixtures (90%C2-X:10%di-C2-DTP and 90%C2-X:10%di-C2-DTC) may have given an enhanced rate of copper recovery compared to that obtained with C2-X (Figure 3.43). Other examples of enhanced kinetics obtained with collector mixtures consisting of a xanthate and a dithiophosphate in a batch flotation cell have been reported (Bradshaw et al, 1998).

4.4. The Effect of the Ore on the Flotation Performance

The copper recoveries, copper grades (Figures 3.16, 3.5, 3.9, 3.12, 3.30, 3.34, 3.37, 3.39), Klimpel rate constants for copper recovery (Figures 3.7 and 3.32) and mass recoveries (Figures 3.14, 3.29, 3.33 and 3.36) obtained with the OCC ore were generally higher than those obtained with the PMC ore.

In the flotation of the OCC ore, bornite was the major copper sulphide in the concentrates obtained with di-C2-DTP and di-C2-DTC each at a dosage of 0.0695 mol/ton ore (Table 3.3). This and the fact that it is slower floating than other copper sulphides (Ackerman et al, 1984) implied that it was the major copper sulphide in the feed. This was confirmed by the feed ore mineralogy. From the test results, the copper to sulphur mole ratios of the concentrates mentioned above were 1.08 and 0.97 respectively. They were close to that of bornite, which is 1.25 (Table E1). This provides some further support for bornite having been the main copper sulphide in the concentrates.

The mineralogy of the PMC ore suggested that bornite and chalcopyrite were the main copper sulphides present. There was no way of corroborating this as no sulphur analyses were done on the feed, concentrates or tailings of the PMC ore.

The products of oxidation on the chalcopyrite surface may have been ferrous hydroxide, cupric hydroxide (Woods, 1984) or hydrated iron oxyhydroxide (Grano et al, 1997). These impaired the reactions between collectors and minerals that were oxidised and this led to reduced copper recovery by flotation (Grano et al, 1997, Guy and Trahar, 1985, Richardson et al, 1984, Barzyk et al, 1981, Klymowsky and Salman, 1970). It is reasonable to suggest that similar processes were at work in the case of other oxidised copper sulphide minerals. The consequences of these phenomena were perhaps observed in this work as inferior copper recoveries and grades that were obtained with the PMC ore (Figures 3.30, 3.34, 3.37 and 3.39) compared to those obtained with the OCC ore (Figures 3.16 and 3.5, 3.9, 3.12). This suggested that the PMC ore might have been more oxidised than the OCC ore.

Xanthate could adsorb on chalcocite by anodic oxidation in the presence of oxygen and by ion exchange with the previously formed oxidised species (Barzyk et al, 1981 and Richardson et al, 1984). However, to achieve the same flotation recovery, greater xanthate coverage was required with the most heavily oxidised mineral compared to the coverage required for the least oxidised mineral (Barzyk et al, 1981). Generally, the xanthate and dithiophosphate collector dosages used in this work were suitable to obtain high copper recoveries from the OCC ore. For more oxidised ores, as the PMC ore may have been, higher collector dosages would have been required to improve copper recovery (Barzyk et al, 1981).

The mass-water recovery relationships obtained with each collector at each of the dosages tested in the flotation of the PMC ore was not significantly different from those obtained with no collector (Figures 3.29, 3.33 and 3.36). This indicated that the action of the collector had no significant effect on the mass pull and the froth properties. This was not the case with the OCC ore (Figures 3.4, 3.8 and 3.11). In addition, the relationships between the mass and water recoveries obtained with the PMC ore were linear compared to those obtained with the OCC ore (Figures 3.4, 3.8, 3.11, 3.29, 3.33 and 3.36); perhaps confirming the limited degree of reaction between the collectors and minerals. This indicated that the entrainment of hydrophilic material in the water of the froth was a more dominant process in the case of the PMC ore (Kelly and Spottiswood, 1982). This further explains the poor copper recoveries and grades obtained with the PMC ore (Figures 3.30, 3.34 and 3.37) compared to those obtained with the OCC ore (Figures 3.16 and 3.5, 3.9, 3.12).

In summary, the PMC ore was probably more oxidised than the OCC ore. This implied that surface products of oxidation could have impaired thiol collector adsorption. The consequently low hydrophobicity of the particles in the pulp phase ensured that they did not attach to rising air bubbles and that they were instead entrained in the water of the froth phase. These factors accounted for the generally lower copper recoveries and grades obtained with the PMC ore despite having had a similar spectrum of copper sulphide minerals as the OCC ore.

5. CONCLUSIONS

The Role of the Functional Group of the Collector

The order of collector strength for the copper sulphide minerals in the Okiep Copper Company (OCC) ore at the collector dosages tested was:

di-C2-DTC <<< C2-X < di-C2-DTP.

This was attributed to the lack of dithiolate formation in the case of di-C2-DTC and the frothing properties of the collector and synergistic interactions between the collector and frother in the case of di-C2-DTP.

The xanthate, C2-X, was significantly better at collecting the copper sulphide and copper oxide minerals in the Palaborwa Mining Company (PMC) ore than the dithiophosphate, di-C2-DTP, and the dithiocarbamate, di-C2-DTC. Also, the rate of copper recovery with the xanthate was higher than with the other collectors.

Generally, when di-C2-DTP was used, it contributed to froths that were more watery and caused increased entrainment of gangue minerals with a consequent loss of grade.

The Effect of the Dosage of the Collector

The effect of collector dosage with regard to copper recovery and rate of copper recovery was confirmed with the OCC ore. Generally, higher dosages led to higher copper recoveries and rates until some maximum value was reached in the case of each collector. When collector dosages in excess of this maximum were used, copper recovery and rates of copper recovery declined.

The maxima in water recoveries obtained in the flotation of the OCC ore with C2-X and di-C2-DTP occurred at the maximum in hydrophobicity of the mineral surface in each case in that the copper recoveries were not significantly different at collector dosages higher than those corresponding to maximum water recovery.

The Effect of Collector Mixtures on the Froth Flotation Performance

There was a slight but significant enhancement of copper recovery and loss of copper grade obtained with the C2-X:di-C2-DTP and C2-X:di-C2-DTC collector mixtures relative to those obtained with pure C2-X at an equivalent collector dosage of 0.139 mol/ton ore in the flotation of the OCC ore.

The dosage of the collector mixtures had significant effects on the froth properties in the flotation of the OCC ore. This was attributed to froth destabilisation by small highly hydrophobic particles at a collector dosage of 0.0695 mol/ton ore and froth stabilisation by moderately hydrophobic particles with patchy multilayers of adsorbed collectors at 0.139 mol/ton ore.

Slight enhancements of copper grades were obtained with the C2-X:di-C2-DTC collector mixture relative to those obtained with pure C2-X at an equivalent collector dosage of 0.695 mol/ton ore in the flotation of the OCC ore and at 0.139 mol/ton ore in the flotation of the PMC ore.

The Effect of the Ore on the Froth Flotation Performance

A linear relationship was obtained between copper recovery and water recovery in the flotation of the PMC ore; indicating that froth stability and entrainment played a significant role.

The flotation performance of the PMC ore was poor relative to that obtained with the OCC ore. This may be attributed to limited reaction between the minerals and collectors and the lower feed grade of the PMC ore.

6. RECOMMENDATIONS

Recommendations for future work are:

1. The poor performance of the dithiocarbamate was attributed to the less than optimal dosages used. This should be tested by using this collector in the range of dosages suggested by the literature for copper sulphide minerals (Bhaskar Raju and Khangaonkar, 1984 and Mangalam and Khangoankar, 1985). Should this collector live up to its reputation of being more selective than the others tested (Bhaskar Raju and Forsling, 1991), the added reagent cost may be outweighed by the potential improvement in copper grade. Also, once the optimal dosage of the dithiocarbamate has been established, the flotation performance of collector mixtures with it as the principal collector should be tested.

2. The poor flotation performance of the Palaborwa Mining Company (PMC) ore was attributed to its greater degree of oxidation (Grano et al, 1997, Guy and Trahar, 1985, Richardson et al, 1984, Barzyk et al, 1981, Klymowsky and Salman, 1970) and its lower feed grade compared to the Okiep Copper Company (OCC) ore. However, the degree of oxidation of the mineral surface was not quantified. This should be addressed in order to establish the relationship between the nature of the surface oxidation products and their impact on the reactions between the collectors and minerals.

3. The froth stability should be measured and quantified as it had strong effects on the copper grade. Furthermore, factors that influence it such as collector dosage and collector type should be further examined.

4. Hallimond tube experiments should be used to measure copper recovery with the same collectors at the same dosages as tested in this study. This would assist in separating the effects of the froth from the effects of the collectors in the flotation recovery of the copper minerals. It may then be possible to establish how the mineral hydrophobicity impacts upon the froth stability and water recovery.

5. The effect of collectors and their mixtures on the flotation of oxidised copper sulphide and copper oxide ores that have been sulphidised should be further investigated.

6. The synergistic effects observed with the collector mixtures although not definitive, do show promise. The effects of different mole ratios of the components of the collector mixtures in the flotation of copper sulphide minerals should therefore be further explored.

7. The effect of xanthate, dithiophosphate and dithiocarbamate dosages on the flotation performance of heavily oxidised copper sulphide or copper oxide ores that have been sulphidised should be further explored.

8. Adsorption studies should be undertaken to better understand the relationship between collector concentration and the nature of the surface coverage by the collector and how this relates to surface hydrophobicity and floatability.

9. The nature of the reaction products between collectors and minerals depends upon thermodynamic and kinetic considerations (Woods, 1984). Those factors that influence the kinetics of the surface reactions, such as system temperature concentration of reagents, should be further explored.

10. It is probable that the formation of the dithiolate was responsible for the superior performance of the xanthate compared to that obtained with the dithiophosphate in the flotation of the PMC ore. This should be established by means of spectroscopy. If indeed the dithiolate was less likely to form with the dithiophosphate, the mechanisms of these phenomena should be further explored.

11. The influence of the gangue material on the froth properties and collector action should be quantified.

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APPENDIX A: Milling Curves and Sieve Analyses of the Okiep Copper Company (OCC) and Palaborwa Mining Company (PMC) Ores

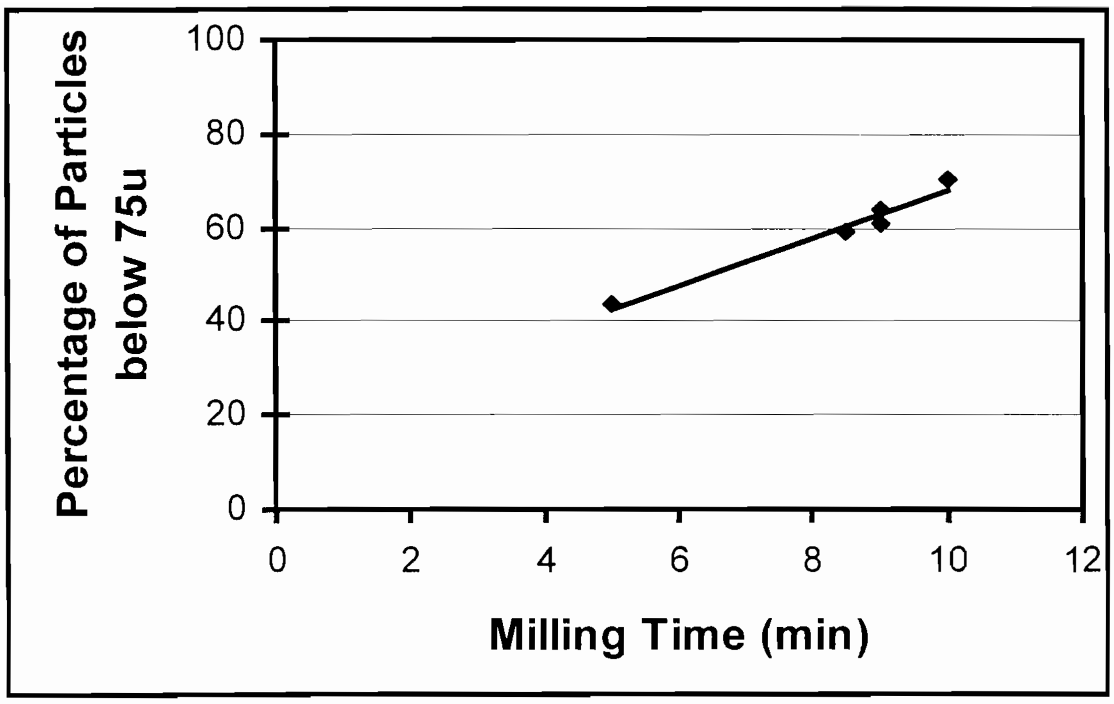

Figure A1 Milling curve for the OCC ore

Table A1 Sieve analysis of the OCC ore after 9 minutes of milling

Particle Size Range (μm)	Mass% of Feed Sample
(+)212	0.06
(-)212(+)150	2.16
(-)150(+)106	12.42
(-)106(+)75	23.08
(-)75(+)53	15.96
(-)53(+)38	13.18
(-)38	33.17
TOTAL(%)	100.01
%(-)75	62.30

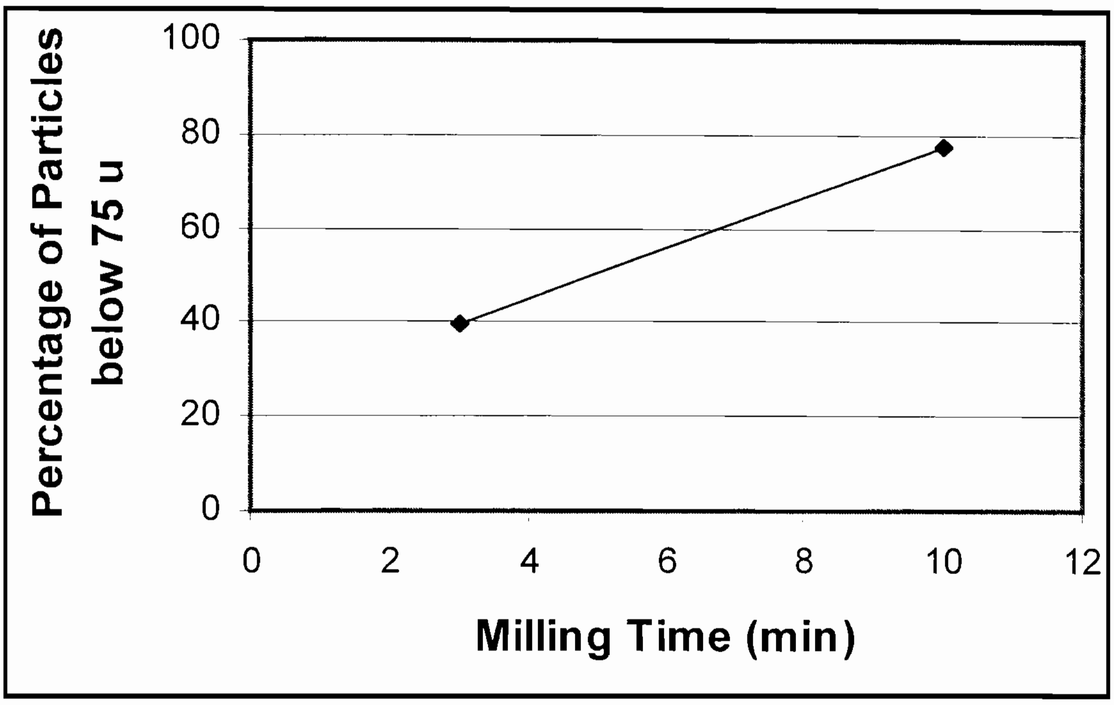

Figure A2 Milling curve for the PMC ore

Table A2 Sieve analysis of the PMC ore after 5 minutes of milling

Particle Size Range (μm)	Mass% of Feed Sample
(+)106	24.13
(-)106(+)75	19.52
(-)75(+)53	14.16
(-)53(+)38	10.43
(-)38	31.75
TOTAL(%)	100.00
%(-)75	56.35

Appendix B: Experimental results obtained with the Okiep Copper Company (OCC) and Palaborwa Mining Company (PMC) ores

Table B1 Experimental results obtained with the OCC ore

Test Number	Collector	Collector Dosage (mol/ton ore)	Mole Ratio of Collector Mixture	Time (min)	Cum. Mass (g)	Cum. Water Rec. (g).	Cu Grade (%)	S Grade (%)	Cu Rec. (%)	Mass Balance (%)
1	No Collector			1	22.0	56.6	4.6	2.7	5.5	
				2	35.4	108.6	6.1	3.3	10.0	
				7	46.0	192.4	7.0	3.8	14.1	
				12	53.8	292.7	5.3	3.2	16.4	
				20	58.4	384.1	5.9	2.9	17.9	100.0
2	C2-X	0.0348		1	35.8	55.2	22.2	11.0	45.6	
				2	51.0	94.1	14.3	6.3	58.0	
				7	69.8	186.5	6.7	4.0	65.2	
				12	82.9	287.3	7.0	3.0	70.5	
				20	90.9	363.4	7.3	3.7	73.8	100.9
3	C2-X	0.0695		1	43.9	65.9	24.7	12.8	67.7	
				2	62.8	136.4	11.2	5.8	80.9	
				7	84.2	285.7	3.8	1.9	86.0	
				12	99.9	458.9	2.1	0.9	88.1	
				20	106.2	551.1	2.2	0.9	88.9	100.9
4	C2-X	0.0695		1	43.8	65.1	26.3	13.9	73.6	
				2	63.0	152.3	9.1	5.1	84.8	
				7	82.0	288.7	3.9	1.9	89.5	
				12	94.6	423.0	2.4	0.9	91.5	
				20	100.8	499.1	2.2	0.8	92.4	100.9
5	C2-X	0.139		1	44.6	59.7	30.3	14.2	75.6	
				2	57.3	88.1	10.8	5.4	83.2	
				7	73.6	155.4	4.5	2.2	87.3	
				12	87.0	247.7	2.5	1.0	89.2	
				20	95.9	340.0	1.8	0.7	90.1	100.0
6	C2-X	0.139		1	43.4	51.4	30.3	14.3	74.1	
				2	59.2	93.9	10.6	5.5	83.5	
				7	75.9	179.9	4.3	2.2	87.6	
				12	89.2	291.7	2.3	1.0	89.3	
				20	95.7	359.3	1.9	0.7	90.0	100.9
7	C2-X	0.139		1	42.3	48.7	27.6	13.3	69.3	
				2	60.1	85.6	13.0	6.5	83.1	
				7	79.4	173.1	5.5	3.0	89.4	
				12	91.4	255.7	2.7	1.2	91.3	
				20	99.2	321.1	2.1	1.7	92.3	100.9
8	C2-X	0.209		1	48.5	75.7	26.8	14.2	73.9	
				2	62.9	117.1	9.3	4.7	81.5	
				7	75.9	171.7	4.7	2.2	85.0	
				12	88.5	259.7	2.6	1.1	86.8	
				20	96.6	346.2	1.9	0.8	87.7	100.8
9	di-C2-DTP	0.0348		1	44.9	46.3	28.9	13.1	70.4	
				2	65.7	114.7	11.4	5.7	83.2	
				7	89.2	262.2	4.2	2.3	88.5	
				12	106.4	427.3	2.3	1.1	90.6	
				20	115.2	564.2	1.8	0.7	91.5	100.0

Table B1 (continued) Experimental results obtained with the OCC ore

Test Number	Collector	Collector Dosage (mol/ton ore)	Mole Ratio of Collector Mixture	Time (min)	Cum. Mass (g)	Cum. Water Rec. (g).	Cu Grade (%)	S Grade (%)	Cu Rec. (%)	Mass Balance (%)
10	di-C2-DTP	0.0348		1	46.5	68.6	23.8	13.0	64.5	
				2	68.2	153.8	12.4	5.0	80.1	
				7	90.0	301.5	3.7	1.3	84.8	
				12	105.5	458.5	2.2	1.0	86.8	
				20	113.2	576.2	1.7	0.7	87.5	100.9
11	di-C2-DTP	0.0695		1	46.4	63.4	28.3	13.6	71.8	
				2	64.1	115.5	11.0	5.1	82.4	
				7	85.7	238.5	4.6	2.4	87.9	
				12	101.2	369.9	2.6	1.2	90.1	
				20	108.7	455.3	2.0	0.9	90.9	100.9
12	di-C2-DTP	0.0695		1	48.5	63.3	27.0	12.6	76.0	
				2	67.5	118.7	9.7	5.3	86.7	
				7	86.1	209.9	4.1	2.2	91.2	
				12	99.4	311.0	2.8	1.2	93.4	
				20	107.2	387.7	2.1	0.8	94.3	100.9
13	di-C2-DTP	0.139		1	44.5	53.9	28.7	14.3	69.7	
				2	62.7	92.2	12.4	6.3	82.0	
				7	87.2	203.0	4.8	2.4	88.4	
				12	102.8	312.9	2.6	1.1	90.6	
				20	109.9	380.3	2.0	0.9	91.4	100.9
14	di-C2-DTP	0.139		1	51.2	72.9	24.9	12.0	77.8	
				2	72.0	144.8	8.3	4.3	88.4	
				7	93.8	277.4	3.2	1.9	92.6	
				12	109.9	422.1	1.9	0.9	94.5	
				20	116.6	504.0	1.6	0.7	95.2	100.9
15	di-C2-DTC	0.0348		1	23.9	46.2	11.8	6.6	15.1	
				2	39.5	96.7	12.8	6.7	26.0	
				7	57.4	196.7	8.1	4.1	33.8	
				12	69.1	294.0	4.6	1.9	36.7	
				20	75.0	407.6	3.1	1.3	37.7	100.9
16	di-C2-DTC	0.0695		1	25.9	50.2	15.8	8.2	22.5	
				2	46.1	120.3	15.7	7.4	39.8	
				7	65.1	245.0	9.4	4.2	49.6	
				12	76.8	365.4	4.5	1.9	52.4	
				20	83.7	461.9	2.8	1.2	53.5	100.9
17	di-C2-DTC	0.0695		1	29.1	61.8	10.3	5.7	17.9	
				2	47.7	131.8	14.8	5.9	34.4	
				7	68.7	272.6	7.4	3.3	43.7	
				12	82.0	413.7	3.7	1.7	46.7	
				20	87.9	493.9	2.8	1.2	47.7	101.0
18	di-C2-DTC	0.139		1	28.3	50.4	18.0	9.3	30.0	
				2	46.5	106.5	16.0	7.9	47.0	
				7	64.2	195.8	10.5	5.1	58.0	
				12	76.5	284.7	5.7	2.7	62.1	
				20	82.3	334.2	3.4	1.6	63.2	100.9

Table B1 (continued) Experimental results obtained with the OCC ore

Test Number	Collector	Collector Dosage (mol/ton ore)	Mole Ratio of Collector Mixture	Time (min)	Cum. Mass (g)	Cum. Water Rec. (g).	Cu Grade (%)	S Grade (%)	Cu Rec. (%)	Mass Balance (%)
19	di-C2-DTC	0.139		1	27.2	47.2	14.8	8.1	24.7	
				2	39.9	80.9	14.4	7.8	35.9	
				7	66.8	220.6	9.5	5.1	51.5	
				12	80.6	340.5	4.7	2.3	55.5	
				20	85.4	380.2	3.3	1.5	56.4	100.9
20	C2-X:di-C2-DTP	0.0695	90:10	1	44.2	61.6	26.7	13.4	72.6	
				2	64.2	128.3	10.8	5.9	85.9	
				7	85.4	265.6	4.4	2.2	91.6	
				12	100.4	435.1	2.4	1.0	93.8	
				20	107.2	528.4	1.8	0.7	94.6	100.9
21	C2-X:di-C2-DTP	0.0695	90:10	1	39.2	47.8	29.3	14.2	69.3	
				2	52.6	72.4	15.1	7.5	81.5	
				7	73.8	168.4	6.8	4.1	90.1	
				12	90.8	315.0	2.8	1.3	93.0	
				20	99.4	419.5	1.9	0.8	93.9	100.9
22	C2-X:di-C2-DTP	0.139	90:10	1	49.6	76.2	25.5	12.8	78.0	
				2	68.7	147.1	7.8	4.4	87.3	
				7	87.3	267.9	3.7	1.8	91.5	
				12	100.0	392.9	2.4	1.1	93.4	
				20	107.8	492.5	1.8	0.8	94.3	100.9
23	C2-X:di-C2-DTP	0.139	90:10	1	44.8	61.5	24.7	13.7	73.5	
				2	63.0	118.0	9.9	5.4	85.4	
				7	83.8	248.2	4.0	2.0	91.0	
				12	97.9	385.8	2.2	1.0	93.1	
				20	106.6	492.6	1.8	0.7	94.1	100.9
24	C2-X:di-C2-DTC	0.0695	90:10	1	44.2	69.0	28.3	13.7	75.5	
				2	62.9	153.6	9.0	5.1	85.7	
				7	79.1	284.0	4.2	1.9	89.9	
				12	90.4	415.8	2.5	1.0	91.6	
				20	97.7	522.1	2.2	0.7	92.5	100.9
25	C2-X:di-C2-DTC	0.0695	90:10	1	44.1	67.7	26.1	13.7	71.7	
				2	62.4	148.3	11.8	4.6	85.2	
				7	79.1	266.3	3.9	2.9	89.3	
				12	90.3	368.4	2.4	1.0	90.9	
				20	94.9	429.9	2.5	0.8	91.7	100.9
26	C2-X:di-C2-DTC	0.139	90:10	1	41.5	52.6	29.5	14.7	76.9	
				2	61.9	136.7	8.9	5.0	88.3	
				7	80.2	274.4	3.2	1.6	92.0	
				12	92.4	402.6	2.0	0.8	93.6	
				20	99.3	491.4	1.4	0.6	94.2	100.9
27	C2-X:di-C2-DTC	0.139	90:10	1	48.0	87.6	24.0	13.8	78.1	
				2	66.5	184.1	7.9	3.5	88.0	
				7	84.3	342.9	3.0	1.9	91.5	
				12	94.1	452.0	2.1	0.8	93.0	
				20	100.2	531.9	1.7	0.6	93.6	100.9

Table B2 Experimental results obtained with the PMC ore

Test Number	Collector	Collector Dosage (mol/ton ore)	Mole Ratio of Collector Mixture	Time (min)	Cum. Mass (g)	Cum. Water Rec. (g)	Cu Grade (%)	Cu Rec. (%)	Acid Soluble Cu Grade (%)	Acid Soluble Copper Rec. (%)	Mass Balance (%)
28	No Collector			1	17.5	153.9	2.5	7.3	0.3	6.9	
				2	31.0	267.2	2.3	12.4	0.3	13.3	
				7	43.7	383.0	2.4	17.5	0.3	20.2	
				12	51.2	445.4	2.2	20.2	0.3	23.6	
				20	54.1	455.1	2.0	21.2	0.4	25.5	100.0
29	C2-X	0.0695		1	18.9	136.6	11.4	33.9	0.4	13.5	
				2	31.8	239.3	4.9	43.8	0.4	22.7	
				7	42.5	325.3	3.3	49.3	0.5	30.7	
				12	49.3	375.8	2.6	52.1	0.5	36.0	
				20	53.0	392.0	2.2	53.4	0.5	38.9	100.0
30	C2-X	0.139		1	16.1	140.1	10.2	33.5			
				2	30.1	275.1	4.8	47.3			
				7	39.1	376.4	4.0	54.7			
				12	46.7	414.4	2.8	59.1			
				20	49.7	420.7	2.7	60.7			100.7
31	C2-X	0.139		1	20.1	142.0	10.5	34.8	0.4	13.0	
				2	36.2	255.2	5.0	48.1	0.4	23.8	
				7	54.4	402.8	2.5	55.6	0.4	35.2	
				12	62.5	467.0	2.4	58.8	0.4	41.1	
				20	65.9	480.7	1.9	59.9	0.5	43.6	100.0
32	C2-X	0.139		1	20.9	151.6	10.4	36.9			
				2	35.9	281.5	3.8	46.6			
				7	47.9	383.3	2.6	52.0			
				12	55.4	442.4	2.3	54.8			
				20	59.0	461.3	2.1	56.1			100.0
33	C2-X	0.209		1	22.3	151.9	10.4	36.9	0.4	15.1	
				2	37.2	264.8	3.8	46.6	0.4	24.4	
				7	50.4	382.0	2.6	52.0	0.4	32.9	
				12	58.0	448.0	2.3	54.8	0.5	38.4	
				20	61.0	458.0	2.1	56.1	0.5	40.8	100.0
34	di-C2-DTP	0.0348		1	23.6	183.6	5.5	19.3	0.3	10.4	
				2	39.4	311.9	3.2	26.8	0.3	17.8	
				7	52.8	430.8	2.9	32.6	0.3	24.8	
				12	59.7	486.0	2.6	35.2	0.4	28.9	
				20	62.2	493.0	2.2	36.0	0.4	30.4	100.0
35	di-C2-DTP	0.0695		1	21.9	170.8	6.2	20.2	0.3	10.2	
				2	39.1	317.8	3.4	29.0	0.3	18.5	
				7	52.6	432.4	2.9	34.8	0.3	26.0	
				12	60.0	492.6	2.6	37.7	0.4	30.5	
				20	63.2	505.4	2.2	38.7	0.4	32.4	100.0

Table B2 (continued) Experimental results obtained with the PMC ore

Test Number	Collector	Collector Dosage (mol/ton ore)	Mole Ratio of Collector Mixture	Time (min)	Cum. Mass (g)	Cum. Water Rec. (g)	Cu Grade (%)	Cu Rec. (%)	Acid Soluble Cu Grade (%)	Acid Soluble Copper Rec. (%).	Mass Balance (%)
37	di-C2-DTC	0.0695		1	20.1	142.1	7.4	24.8	0.3	11.2	
				2	33.9	244.7	4.0	34.0	0.3	18.5	
				7	46.3	345.7	2.8	39.8	0.3	25.4	
				12	53.6	402.5	2.3	42.5	0.3	30.0	
				20	56.3	411.5	1.9	43.4	0.4	31.8	100.0
38	di-C2-DTC	0.139		1	18.7	142.4	7.4	25.2	0.3	10.9	
				2	33.0	260.4	3.0	33.0	0.3	18.9	
				7	44.8	363.6	3.2	39.9	0.3	25.9	
				12	51.6	420.7	2.5	43.0	0.4	30.4	
				20	53.9	427.1	2.2	43.9	0.4	32.0	100.0
39	iC4-X	0.139		1	27.9	187.6	10.0	44.8	0.4	18.8	
				2	45.2	338.8	3.8	55.4	0.3	29.5	
				7	57.4	440.6	2.9	61.1	0.4	38.2	
				12	64.2	490.8	2.4	63.6	0.4	43.4	
				20	67.3	505.0	2.2	64.7	0.4	45.7	100.0
40	iC4-X	0.139		1	23.0	152.2	11.0	42.9	0.3	17.4	
				2	37.6	278.9	4.7	54.5	0.3	28.4	
				7	49.5	386.8	3.3	61.1	0.3	37.5	
				12	54.9	427.0	2.5	63.4	0.4	42.5	
				20	57.3	432.7	1.3	64.0	0.4	44.8	100.0
41	C2-X:di-C2-DTP	0.139	90:10	1	25.1	167.1	11.6	44.7	0.3	15.2	
				2	38.2	265.9	4.2	53.1	0.3	23.1	
				7	50.4	367.5	3.2	59.2	0.4	33.0	
				12	57.8	424.9	2.7	62.2	0.5	39.5	
				20	60.8	441.3	2.3	63.3	0.4	42.0	100.0
42	C2-X:di-C2-DTP	0.139	90:10	1	22.4	147.9	9.8	34.7	0.3	13.3	
				2	38.0	252.0	4.6	46.1	0.4	23.2	
				7	51.1	348.6	3.4	53.2	0.4	31.8	
				12	58.9	406.9	2.8	56.7	0.4	37.5	
				20	61.6	418.0	2.5	57.8	0.4	39.6	100.0
43	C2-X:di-C2-DTC	0.139	90:10	1	20.7	134.7	12.0	40.3	0.3	13.1	
				2	34.0	224.3	4.6	50.3	0.3	21.8	
				7	44.8	287.4	3.3	56.1	0.4	29.3	
				12	51.2	331.9	2.8	59.0	0.4	34.5	
				20	54.2	344.2	2.5	60.2	0.5	37.0	100.0

Table B2 (continued) Experimental results obtained with the PMC ore

Test Number	Collector	Collector Dosage (mol/ton ore)	Mole Ratio of Collector Mixture	Time (min)	Cum. Mass (g)	Cum. Water Rec. (g)	Cu Grade (%)	Cu Rec. (%)	Acid Soluble Cu Grade (%)	Acid Soluble Copper Rec. (%)	Mass Balance (%)
44	C2-X:di-C2-DTC	0.139	90:10	1	19.3	135.9	10.6	36.5	0.4	14.5	
				2	31.8	234.3	4.7	46.8	0.3	23.4	
				7	41.9	311.0	3.2	52.7	0.4	30.9	
				12	46.7	335.7	2.6	54.9	0.5	35.5	
				20	48.8	340.7	2.5	55.8	0.5	37.6	100.0
45	iC4-X:di-C2-DTC	0.139	90:10	1	23.3	144.1	11.9	44.9	0.5	18.6	
				2	41.3	289.2	3.2	54.2	0.4	31.3	
				7	54.4	398.4	2.5	59.6	0.5	41.0	
				12	61.2	448.0	2.5	62.4	0.4	45.8	
				20	64.0	460.0	2.2	63.4	0.5	47.9	100.0
46	iC4-X:di-C2-DTC	0.139	90:10	1	27.3	180.0	9.0	39.2	0.3	15.6	
				2	45.5	335.7	4.2	51.6	0.3	25.2	
				7	58.8	455.0	3.1	58.1	0.3	33.3	
				12	64.9	503.6	2.5	60.6	0.4	38.0	
				20	68.1	518.1	2.2	61.7	0.5	40.6	100.0

Appendix C: Methods of analyses

Leco standard method for sulphur analysis

Acid digestion method for copper analysis

Acid digestion method for acid-soluble copper analysis

Leco standard method for sulphur analysis

The Leco sulphur analyser analyses a sample for sulphur content by burning a known mass of sample at 1623 K in the presence of excess oxygen. The sulphur dioxide gas given off is drawn through the combustion chamber by a vacuum pump. The gas passes through a pair of moisture traps filled with anhydrous magnesium perchlorate. The gas flow is controlled by a flow controller and then passes through the infra red (IR) detector cell. The principle of measurement is that the reduction in IR generated by a nichrome wire at 1123K, at specified wavelength, is due to absorption of SO_2 and is proportional to the concentration of SO_2 given off. The sulphur content of the sample is automatically calculated from the concentration of SO_2 and the mass of the sample analysed.

The Leco is calibrated before measurement using samples of known sulphur concentration. The system is calibrated for different standard according to the sulphur content of the samples to be measured.

Acid digestion method for copper analysis (ex Karbochem R & D Lab)

Principle

The finely milled ore sample is dissolved in aqua regia with the addition of hydrofluoric acid and perchloric acid. The sample is made up to a known volume, filtered and read on the AA spectrophotometer.

Reagents

Hydrofluoric acid	CP	approximately 40%
Nitric acid	CP	approximately 60%
Perchloric acid	CP	concentrated
Hydrochloric acid	CP	approximately 30%

For use: Mix 4 parts HCl to 1 part HF per volume.

Sample preparation:
Samples should be finely ground.

Method

1. Sample is weighed out according to the type, into a 250 ml wide-mouthed Erlenmeyer flask as follows:

Concentrates	0.1 g
Tails and feed (head)	0.5 g

2. Digest
Add 10 ml of the HCl/HF mixture of sample and heat to boiling.
Add 10 ml HNO_3 to flask and boil until the sample is approximately 2 ml.
Add 5 ml $HClO_4$ to flask and boil until the sample is approximately 2 ml.
(A white cloud will form which will rise once the reaction has taken place.)

3. Make up to volume and filter:
Transfer the sample quantitatively to a 100 ml volumetric flask and make up to 100 ml with distilled water. Filter through Whatman No.1 paper into sample bottle. Filtrate to be read on AA. Store in fridge if reading is delayed.

4. Read on AA

5. Calculation:
e.g. %Cu in sample = R(in ppm)/100×a(sample mass

Acid digestion method for acid-soluble copper analysis

1. Weigh out 1.0 g into a plastic bottle.
2. Add 25 ml of leaching acid and swirl the contents of the bottle. Allow to stand for 1 minute for the gases to escape.
3. Stopper the bottle and shake samples on a mechanical shaker for 1 hour.
4. Filter through Whatman No 541 filter paper into a 100 ml volumetric flask and wash the bottle thoroughly into te filter paper with distilled or deionised water.
5. Wash the residue and the filter paper several times with water and finally dilute to the mark with distilled water.
6. Read the samples on the AAS.

Leaching acid

Add 400 ml of concentrated sulphuric acid slowly and with stirring to 1000 ml of distilled water in a 2 L boiling flask. Allow to cool. Add 72 g of sodium sulphite hypta-hydrate ($Na_2SO_3.7H_2O$) and when dissolved, dilute the solution to 8 L with distilled water. (OR add 35.987 g of anhydrous sodium sulphite.)

Appendix D: Results of the analysis of variance (ANOVA) of the experimental results

1. METHOD OF ANALYSIS OF VARIANCE (ANOVA)*

The sum of the squares due to the treatment, S_1, is:

$$S_1 = \sum_{i=1}^{k} n_i (\bar{x}_i - \bar{x})^2$$

where
k = number of treatments
$\bar{x}$ = overall data mean
$\bar{x}_i$ = mean of the i^{th} treatment
n_l = number of replicates of i^{th} treatment

The sum of the squares due to error, S_0, is:

$$S_0 = \sum_{j=1}^{n_i} (x_{1j} - \bar{x}_1)^2 + \ldots + \sum_{j=1}^{n_k} \left(x_{kj} - \bar{x}_k\right)^2$$

where x_{ij} is the j_{th} observation for the i^{th} treatment.

Degrees of Freedom (Df)

$Df_{treatment}$ = number of treatments – 1
Df_{total} = total number of The results – 1
$Df_{error} = Df_{total} - Df_{treatment}$

Now $MS_{treatment} = S_1/Df$ and
$MS_{error} = S_0/Df$

$F = MS_{treatmen}/MS_{error}$

This F value and $Df_{treatment}$ and Df_{error} are used with the F-distribution table to establish whether differences are statistically significant.

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* (Napier-Munn, 1998).

2. OKIEP COPPER COMPANY ORE

2.1 The Effect of the Functional Groups

Table D1. The results of the ANOVA comparing the copper recoveries obtained with different collectors tested at the same collector dosage.

Collectors Compared		Collector Dosage (mol/ton ore)	Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	di-C2-DTC	0.0695	1	2	139.81	Significant	99
C2-X	di-C2-DTP	0.0695	1	2	0.64	Not Significant	
di-C2-DTP	di-C2-DTC	0.0695	1	2	156.11	Significant	99
C2-X	di-C2-DTC	0.139	1	3	130.55	Significant	99
C2-X	di-C2-DTP	0.139	1	3	2.12	Not Significant	
di-C2-DTP	di-C2-DTC	0.139	1	2	73.98	Significant	99

Table D2. The results of the ANOVA comparing the copper grades obtained with different collectors tested at the same collector dosage.

Collectors Compared		Collector Dosage (mol/ton ore)	Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	di-C2-DTC	0.0695	1	2	6.05	Not Significant	
C2-X	di-C2-DTP	0.0695	1	2	8.58	Significant	90
di-C2-DTP	di-C2-DTC	0.0695	1	2	12.84	Significant	90
C2-X	di-C2-DTC	0.139	1	3	21.06	Significant	97.5
C2-X	di-C2-DTP	0.139	1	3	5.94	Significant	90
di-C2-DTP	di-C2-DTC	0.139	1	2	2.59	Not Significant	

Table D3. The results of the ANOVA comparing the sulphur recoveries obtained with different collectors tested at the same collector dosage.

Collectors Compared		Collector Dosage (mol/ton ore)	Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	di-C2-DTC	0.0695	1	2	59.26	Significant	97.5
C2-X	di-C2-DTP	0.0695	1	2	1.06	Not Significant	
di-C2-DTP	di-C2-DTC	0.0695	1	2	271.83	Significant	99
C2-X	di-C2-DTC	0.139	1	3	54.03	Significant	97.5
C2-X	di-C2-DTP	0.139	1	3	0.01	Not Significant	
di-C2-DTP	di-C2-DTC	0.139	1	2	38.64	Significant	97.5

Table D4. The results of the ANOVA comparing the sulphur grades obtained with different collectors tested at the same collector dosage.

Collectors Compared		Collector Dosage (mol/ton ore)	Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	di-C2-DTC	0.0695	1	2	4.00	Not Significant	
C2-X	di-C2-DTP	0.0695	1	2	0.03	Not Significant	
di-C2-DTP	di-C2-DTC	0.0695	1	2	6.78	Not Significant	
C2-X	di-C2-DTC	0.139	1	3	27.27	Significant	97.5
C2-X	di-C2-DTP	0.139	1	3	3.68	Not Significant	
di-C2-DTP	di-C2-DTC	0.139	1	2	1.56	Not Significant	

Table D5. The results of the ANOVA comparing the water recoveries obtained with different collectors tested at the same collector dosage.

Collectors Compared		Collector Dosage (mol/ton ore)	Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	di-C2-DTC	0.0695	1	2	2.41	Not Significant	
C2-X	di-C2-DTP	0.0695	1	2	5.89	Not Significant	
di-C2-DTP	di-C2-DTC	0.0695	1	2	2.27	Not Significant	
C2-X	di-C2-DTC	0.139	1	3	0.58	Not Significant	
C2-X	di-C2-DTP	0.139	1	3	4.48	Not Significant	
di-C2-DTP	di-C2-DTC	0.139	1	2	1.66	Not Significant	

Table D6. The results of the ANOVA comparing the mass obtained with different collectors tested at the same collector dosage.

Collectors Compared		Collector Dosage (mol/ton ore)	Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	di-C2-DTC	0.0695	1	2	18.08	Significant	95
C2-X	di-C2-DTP	0.0695	1	2	1.82	Not Significant	
di-C2-DTP	di-C2-DTC	0.0695	1	2	93.46	Significant	97.5
C2-X	di-C2-DTC	0.139	1	3	46.52	Significant	99
C2-X	di-C2-DTP	0.139	1	3	36.88	Significant	99
di-C2-DTP	di-C2-DTC	0.139	1	2	76.89	Significant	97.5

Table D7. The results of the ANOVA comparing the Klimpel rate constants obtained with different collectors tested at the same collector dosage.

Collectors Compared		Collector Dosage (mol/ton ore)	Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	di-C2-DTC	0.0695	1	2	76.18	Significant	97.5
C2-X	di-C2-DTP	0.0695	1	2	0.96	Not Significant	
di-C2-DTP	di-C2-DTC	0.0695	1	2	246.02	Significant	99
C2-X	di-C2-DTC	0.139	1	3	19.99	Significant	97.5
C2-X	di-C2-DTP	0.139	1	3	0.22	Not Significant	
di-C2-DTP	di-C2-DTC	0.139	1	2	26.39	Significant	95

2.2 The Effect of the Collector Dosage

Table D8. The results of the ANOVA comparing the copper recoveries obtained with each of the collectors tested at different collector dosages.

Collector	Collector Dosages Compared (mol/ton ore)		Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.0695	0.139	1	3	0.01	Not Significant	
di-C2-DTC	0.0695	0.139	1	2	4.24	Not Significant	
di-C2-DTP	0.0348	0.0695	1	2	1.39	Not Significant	
di-C2-DTP	0.0348	0.139	1	2	1.90	Not Significant	
di-C2-DTP	0.0695	0.139	1	2	0.08	Not Significant	

Table D9. The results of the ANOVA comparing the copper grades obtained with each of the collectors tested at different collector dosages.

Collector	Collector Dosages Compared (mol/ton ore)		Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.0695	0.139	1	3	20.44	Significant	97.5
di-C2-DTC	0.0695	0.139	1	2	0.81	Not Significant	
di-C2-DTP	0.0348	0.0695	1	2	3.61	Not Significant	
di-C2-DTP	0.0348	0.139	1	2	0.12	Not Significant	
di-C2-DTP	0.0695	0.139	1	2	0.79	Not Significant	

Table D10. The results of the ANOVA comparing the sulphur recoveries obtained with each of the collectors tested at different collector dosages.

Collector	Collector Dosages Compared (mol/ton ore)		Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.0695	0.139	1	3	0.55	Not Significant	
di-C2-DTC	0.0695	0.139	1	2	7.16	Not Significant	
di-C2-DTP	0.0348	0.0695	1	2	0.75	Not Significant	
di-C2-DTP	0.0348	0.139	1	2	0.00	Not Significant	
di-C2-DTP	0.0695	0.139	1	2	0.77	Not Significant	

Table D11. The results of the ANOVA comparing the sulphur grades obtained with each of the collectors tested at different collector dosages.

Collector	Collector Dosages Compared (mol/ton ore)		Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.0695	0.139	1	3	7.06	Significant	90
di-C2-DTC	0.0695	0.139	1	2	2.22	Not Significant	
di-C2-DTP	0.0348	0.0695	1	2	50.00	Significant	97.5
di-C2-DTP	0.0348	0.139	1	2	0.30	Not Significant	
di-C2-DTP	0.0695	0.139	1	2	0.13	Not Significant	

Table D12. The results of the ANOVA comparing the water recoveries obtained with each of the collectors tested at different collector dosages.

Collector	Collector Dosages Compared (mol/ton ore)		Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.0695	0.139	1	3	59.94	Significant	99
di-C2-DTC	0.0695	0.139	1	2	18.70	Significant	95
di-C2-DTP	0.0348	0.0695	1	2	18.68	Significant	95
di-C2-DTP	0.0348	0.139	1	2	4.26	Not Significant	
di-C2-DTP	0.0695	0.139	1	2	0.09	Not Significant	

Table D13. The results of the ANOVA comparing the mass recoveries obtained with each of the collectors tested at different collector dosages.

Collector	Collector Dosages Compared (mol/ton ore)		Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.0695	0.139	1	3	7.13	Significant	90
di-C2-DTC	0.0695	0.139	1	2	0.48	Not Significant	
di-C2-DTP	0.0348	0.0695	1	2	512.47	Significant	99
di-C2-DTP	0.0348	0.139	1	2	0.01	Not Significant	
di-C2-DTP	0.0695	0.139	1	2	4.26	Not Significant	

Table D14. The results of the ANOVA comparing the Klimpel rate constants obtained with each of the collectors tested at different collector dosages.

Collector	Collector Dosages Compared (mol/ton ore)		Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.0695	0.139	1	3	0.67	Significant	
di-C2-DTC	0.0695	0.139	1	2	0.19	Not Significant	
di-C2-DTP	0.0348	0.0695	1	2	6.85	Not Significant	
di-C2-DTP	0.0348	0.139	1	2	1.21	Not Significant	
di-C2-DTP	0.0695	0.139	1	2	0.04	Not Significant	

2.3 The Effect of the Collector Mixtures

Table D15. The results of the ANOVA comparing the copper recoveries obtained with C2-X and the collector mixtures each tested at the same equivalent collector dosage.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.0695	C2-X:di-C2-DTC	0.0695	1	2	0.65	Not Significant	
C2-X	0.0695	C2-X:di-C2-DTP	0.0695	1	2	4.07	Not Significant	
C2-X	0.139	C2-X:di-C2-DTC	0.139	1	3	9.72	Significant	90
C2-X	0.139	C2-X:di-C2-DTP	0.139	1	3	12.24	Significant	95

Table D16. The results of the ANOVA comparing the copper grades obtained with C2-X and the collector mixtures each tested at the same equivalent collector dosage

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.0695	C2-X:di-C2-DTC	0.0695	1	2	14.41	Significant	90
C2-X	0.0695	C2-X:di-C2-DTP	0.0695	1	2	1.91	Not Significant	
C2-X	0.139	C2-X:di-C2-DTC	0.139	1	3	8.64	Significant	90
C2-X	0.139	C2-X:di-C2-DTP	0.139	1	3	22.08	Significant	97.5

Table D17. The results of the ANOVA comparing the sulphur recoveries obtained with C2-X and the collector mixtures each tested at the same equivalent collector dosage.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.0695	C2-X:di-C2-DTC	0.0695	1	2	0.00	Not Significant	
C2-X	0.0695	C2-X:di-C2-DTP	0.0695	1	2	1.15	Not Significant	
C2-X	0.139	C2-X:di-C2-DTC	0.139	1	3	0.38	Not Significant	
C2-X	0.139	C2-X:di-C2-DTP	0.139	1	3	0.43	Not Significant	

Table D18. The results of the ANOVA comparing the sulphur grades obtained with C2-X and the collector mixtures each tested at the same equivalent collector dosage.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.0695	C2-X:di-C2-DTC	0.0695	1	2	3.60	Not Significant	
C2-X	0.0695	C2-X:di-C2-DTP	0.0695	1	2	0.50	Not Significant	
C2-X	0.139	C2-X:di-C2-DTC	0.139	1	3	3.27	Not Significant	
C2-X	0.139	C2-X:di-C2-DTP	0.139	1	3	26.50	Significant	97.5

Table D19. The results of the ANOVA comparing the water recoveries obtained with C2-X and the collector mixtures each tested at the same equivalent collector dosage.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.0695	C2-X:di-C2-DTC	0.0695	1	2	0.87	Not Significant	
C2-X	0.0695	C2-X:di-C2-DTP	0.0695	1	2	0.72	Not Significant	
C2-X	0.139	C2-X:di-C2-DTC	0.139	1	3	68.02	Significant	99
C2-X	0.139	C2-X:di-C2-DTP	0.139	1	3	113.55	Significant	99

Table D20. The results of the ANOVA comparing the mass recoveries obtained with C2-X and the collector mixtures each tested at the same equivalent collector dosage.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.0695	C2-X:di-C2-DTC	0.0695	1	2	5.56	Not Significant	
C2-X	0.0695	C2-X:di-C2-DTP	0.0695	1	2	0.01	Not Significant	
C2-X	0.139	C2-X:di-C2-DTC	0.139	1	3	2.51	Not Significant	
C2-X	0.139	C2-X:di-C2-DTP	0.139	1	3	39.93	Significant	99

Table D21. The results of the ANOVA comparing the Klimpel rate constants obtained with C2-X and the collector mixtures each tested at the same equivalent collector dosage.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.0695	C2-X:di-C2-DTC	0.0695	1	2	0.66	Not Significant	
C2-X	0.0695	C2-X:di-C2-DTP	0.0695	1	2	1.43	Not Significant	
C2-X	0.139	C2-X:di-C2-DTC	0.139	1	3	0.21	Not Significant	
C2-X	0.139	C2-X:di-C2-DTP	0.139	1	3	0.01	Not Significant	

Table D22. The results of the ANOVA comparing the copper recoveries obtained with different collector mixtures each at the same equivalent collector dosage.

Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X:di-C2-DTP	0.0695	C2-X:di-C2-DTC	0.0695	1	2	16.36	Significant	90
C2-X:di-C2-DTP	0.139	C2-X:di-C2-DTC	0.139	1	2	0.90	Not Significant	

Table D23. The results of the ANOVA comparing the copper grades obtained with different collector mixtures each at the same equivalent collector dosage.

Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X:di-C2-DTP	0.0695	C2-X:di-C2-DTC	0.0695	1	2	0.72	Not Significant	
C2-X:di-C2-DTP	0.139	C2-X:di-C2-DTC	0.139	1	2	0.78	Not Significant	

Table D24. The results of the ANOVA comparing the sulphur recoveries obtained with different collector mixtures each at the same equivalent collector dosage.

Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X:di-C2-DTP	0.0695	C2-X:di-C2-DTC	0.0695	1	2	2.06	Not Significant	
C2-X:di-C2-DTP	0.139	C2-X:di-C2-DTC	0.139	1	2	0.01	Not Significant	

Table D25. The results of the ANOVA comparing the sulphur grades obtained with different collector mixtures each at the same equivalent collector dosage.

Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X:di-C2-DTP	0.0695	C2-X:di-C2-DTC	0.0695	1	2	0.90	Not Significant	
C2-X:di-C2-DTP	0.139	C2-X:di-C2-DTC	0.139	1	2	32.00	Significant	95

Table D26. The results of the ANOVA comparing the water recoveries obtained with different collector mixtures each at the same equivalent collector dosage.

Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X:di-C2-DTP	0.0695	C2-X:di-C2-DTC	0.0695	1	2	0.00	Not Significant	
C2-X:di-C2-DTP	0.139	C2-X:di-C2-DTC	0.139	1	2	0.88	Not Significant	

Table D27. The results of the ANOVA comparing the mass recoveries obtained with different collector mixtures each at the same equivalent collector dosage.

Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X:di-C2-DTP	0.0695	C2-X:di-C2-DTC	0.0695	1	2	2.20	Not Significant	
C2-X:di-C2-DTP	0.139	C2-X:di-C2-DTC	0.139	1	2	83.6	Significant	97.5

Table D28. The results of the ANOVA comparing the Klimpel rate constants obtained with different collector mixtures each at the same equivalent collector dosage.

Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X:di-C2-DTP	0.0695	C2-X:di-C2-DTC	0.0695	1	2	3.75	Not Significant	
C2-X:di-C2-DTP	0.139	C2-X:di-C2-DTC	0.139	1	2	0.54	Not Significant	

Table D29. The results of the ANOVA comparing the copper recoveries obtained with each of the collector mixtures at different equivalent collector dosages.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X:di-C2-DTC	0.0695	C2-X:di-C2-DTC	0.139	1	2	12.96	Significant	90
C2-X:di-C2-DTP	0.0695	C2-X:di-C2-DTP	0.139	1	2	0.02	Not Significant	

Table D30. The results of the ANOVA comparing the copper grades obtained with each of the collector mixtures at different equivalent collector dosages.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X:di-C2-DTC	0.0695	C2-X:di-C2-DTC	0.139	1	2	3.06	Not Significant	
C2-X:di-C2-DTP	0.0695	C2-X:di-C2-DTP	0.139	1	2	2.26	Not Significant	

Table D31. The results of the ANOVA comparing the sulphur recoveries obtained with each of the collector mixtures at different equivalent collector dosages.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X:di-C2-DTC	0.0695	C2-X:di-C2-DTC	0.139	1	2	1.72	Not Significant	
C2-X:di-C2-DTP	0.0695	C2-X:di-C2-DTP	0.139	1	2	5.00	Not Significant	

Table D32. The results of the ANOVA comparing the sulphur grades obtained with each of the collector mixtures at different equivalent collector dosages.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X:di-C2-DTC	0.0695	C2-X:di-C2-DTC	0.139	1	2	1.80	Not Significant	
C2-X:di-C2-DTP	0.0695	C2-X:di-C2-DTP	0.139	1	2	0.68	Not Significant	

Table D33. The results of the ANOVA comparing the water recoveries obtained with each of the collector mixtures at different equivalent collector dosages.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X:di-C2-DTC	0.0695	C2-X:di-C2-DTC	0.139	1	2	0.50	Not Significant	
C2-X:di-C2-DTP	0.0695	C2-X:di-C2-DTP	0.139	1	2	0.12	Not Significant	

Table D34. The results of the ANOVA comparing the mass recoveries obtained with each of the collector mixtures at different equivalent collector dosages.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X:di-C2-DTC	0.0695	C2-X:di-C2-DTC	0.139	1	2	3.63	Not Significant	
C2-X:di-C2-DTP	0.0695	C2-X:di-C2-DTP	0.139	1	2	1.03	Not Significant	

Table D35. The results of the ANOVA comparing the Klimpel rate constants obtained with each of the collector mixtures at different equivalent collector dosages.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X:di-C2-DTC	0.0695	C2-X:di-C2-DTC	0.139	1	2	1.70	Not Significant	
C2-X:di-C2-DTP	0.0695	C2-X:di-C2-DTP	0.139	1	2	3.03	Not Significant	

3. PHALABORWA COPPER COMPANY ORE

3.1 The Effect of the Collector Mixtures

Table D36 The results of the ANOVA comparing the copper recoveries obtained with C2-X and the collector mixtures each tested at the same equivalent collector dosage.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.139	C2-X:di-C2-DTC	0.139	1	3	0.35	Not Significant	
C2-X	0.139	C2-X:di-C2-DTP	0.139	1	3	0.12	Not Significant	
C2-X:di-C2-DTP	0.139	C2-X:di-C2-DTC	0.139	1	2	0.50	Not Significant	

Table D37. The results of the ANOVA comparing the copper grades obtained with C2-X and the collector mixtures each tested at the same equivalent collector dosage

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.139	C2-X:di-C2-DTC	0.139	1	3	15.0	Significant	95
C2-X	0.139	C2-X:di-C2-DTP	0.139	1	3	3.02	Not Significant	
C2-X:di-C2-DTP	0.139	C2-X:di-C2-DTC	0.139	1	2	0.35	Not Significant	

Table D38. The results of the ANOVA comparing the acid soluble copper recoveries obtained with the collector mixtures each tested at the same equivalent collector dosage.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X:di-C2-DTP	0.139	C2-X:di-C2-DTC	0.139	1	2	7.71	Not Significant	

Table D39. The results of the ANOVA comparing the acid soluble copper grades obtained with C2-X and the collector mixtures each tested at the same equivalent collector dosage.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X:di-C2-DTP	0.139	C2-X:di-C2-DTC	0.139	1	2	2.00	Not Significant	

Table D40. The results of the ANOVA comparing the water recoveries obtained with C2-X and the collector mixtures each tested at the same equivalent collector dosage.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.139	C2-X:di-C2-DTC	0.139	1	3	23.9	Significant	97.5
C2-X	0.139	C2-X:di-C2-DTP	0.139	1	3	1.01	Not Significant	
C2-X:di-C2-DTP	0.139	C2-X:di-C2-DTC	0.139	1	2	54.4	Significant	97.5

Table D41. The results of the ANOVA comparing the mass recoveries obtained with C2-X and the collector mixtures each tested at the same equivalent collector dosage.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.139	C2-X:di-C2-DTC	0.139	1	3	12.8	Significant	95
C2-X	0.139	C2-X:di-C2-DTP	0.139	1	3	0.05	Not Significant	
C2-X:di-C2-DTP	0.139	C2-X:di-C2-DTC	0.139	1	2	6.9	Not Significant	

Table D42. The results of the ANOVA comparing the Klimpel rate constants obtained with C2-X and the collector mixtures each tested at the same equivalent collector dosage.

Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
C2-X	0.139	C2-X:di-C2-DTC	0.139	1	3	2.38	Not Significant	
C2-X	0.139	C2-X:di-C2-DTP	0.139	1	3	0.93	Not Significant	
C2-X:di-C2-DTP	0.139	C2-X:di-C2-DTC	0.139	1	2	0.00	Not Significant	

Table D43. The results of the ANOVA comparing the copper recoveries obtained with iC4-X and the iC4-X:di-C2-DTC collector mixture each at the same equivalent collector dosage.

Indicator of Flotation Performance	Collectors or Collector Mixtures Compared (The Equivalent Collector Dosages (mol/ton) are Included)				Degrees of Freedom		F	Statistical Significance	Level of Significance
Copper Recovery (%)	iC4-X	0.139	i-C4-X:di-C2-DTC	0.139	1	2	3.43	Not Significant	
Copper Grade (%)	iC4-X	0.139	i-C4-X:di-C2-DTC	0.139	1	2	1.11	Not Significant	
Acid-soluble Copper Recovery (%)	iC4-X	0.139	i-C4-X:di-C2-DTC	0.139	1	2	0.06	Not Significant	
Acid-soluble Copper Grade (%)	iC4-X	0.139	i-C4-X:di-C2-DTC	0.139	1	2	0.21	Not Significant	
Water Recovery (%)	iC4-X	0.139	i-C4-X:di-C2-DTC	0.139	1	2	0.19	Not Significant	
Mass Recovery (%)	iC4-X	0.139	i-C4-X:di-C2-DTC	0.139	1	2	0.16	Not Significant	
Klimpel Rate Constant (min^{-1})	iC4-X	0.139	i-C4-X:di-C2-DTC	0.139	1	2	0.02	Not Significant	

Appendix E: The chemical formulae of the minerals appearing in the mineralogies of the Okiep and Palaborwa ores

Table E1 The chemical formulae of minerals in the Okiep ore

Mineral	Chemical Formula
Ankerite	$Ca(Mg, Fe)(CO_3)_2$
Apatite	$Ca_5(F, Cl)(PO_4)_3$
Baddeleyite	ZrO_2
Biotite	$K(Mg, Fe)_3AlSi_3O_{10}(OH, F)_2$
Bornite	Cu_5FeS_4
Calcite	$CaCO_3$
Chalcocite	Cu_2S
Chalcopyrite	$CuFeS_2$
Copper Sulphide	CuS
Cubanite	$CuFe_2S_3$
Digenite	Cu_9S_5
Dolomite	$CaMg(CO_3)_2$
Enargite	Cu_3AsS_4
Galena	PbS
Hematite	Fe_2O_3
Ilmenite	$FeTiO_3$
K-Feldspar	$KAlSi_3O_8$
Magnetite	Fe_3O_4
Phlogopite	$KMg_3AlSi_3O_{10}(OH, F)_2$
Pyrite	FeS_2
Pyroxene	Fe-Mg
Quartz	SiO_2
Serpentine	$Mg_3Si_2O_5(OH)_4$
Talc	$Mg_3Si_4O_{10}(OH)_2$

Table E2 The chemical formulae of minerals in the Palaborwa ore

Mineral	Chemical Formula
Ankerite	$Ca(Mg, Fe)(CO_3)_2$
Apatite	$Ca_5(F, Cl)(PO_3)_3$
Baddeleyite	ZrO_2
Biotite	$K(Mg, Fe)_3AlSi_3O_{10}(OH, F)_2$
Bornite	Cu_5FeS_3
Calcite	$CaCO_3$
Chalcopyrite	$CuFeS_2$
Copper sulphide	CuS
Cubanite	$CuFe_2S_3$
Dolomite	$CaMg(CO_3)_2$
Galena	PbS
Ilmenite	$FeTiO_3$
Magnetite	Fe_3O_3
Phlogopite	$KMg_3AlSi_3O_{10}(OH, F)_2$
Pyrite	FeS_2
Serpentine	$Mg_3Si_2O_5(OH)_3$

Appendix F: The relationship between copper recovery and water recovery obtained in the flotation of the Palaborwa Mining Company (PMC) ore

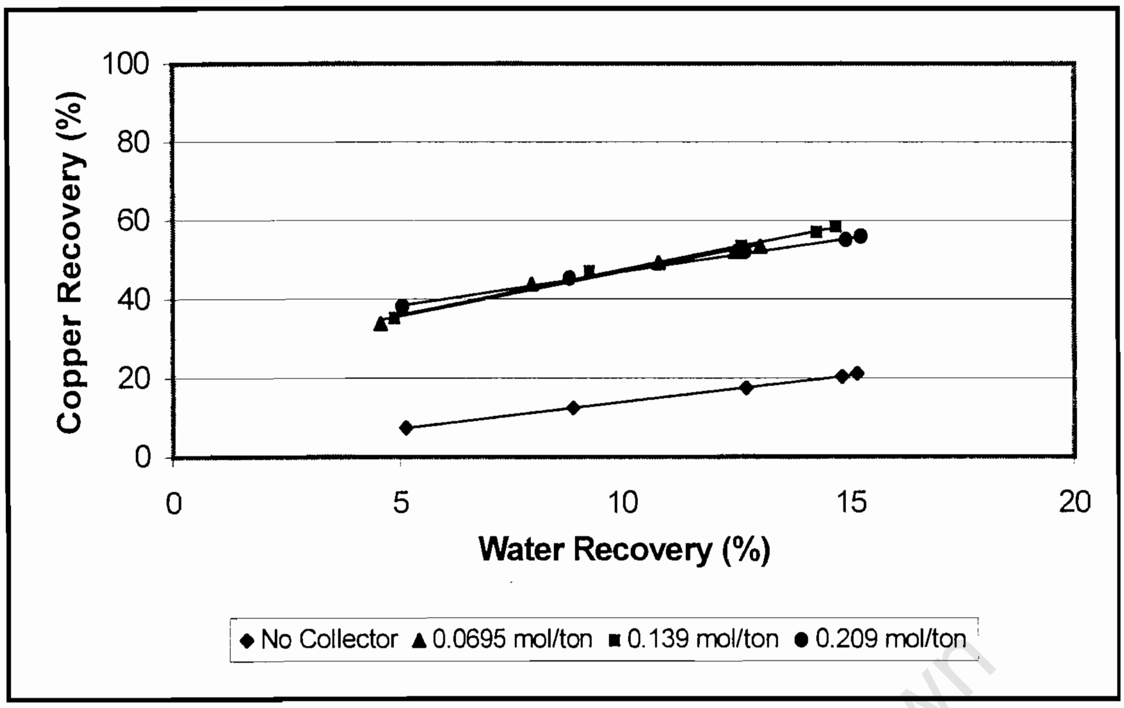

Figure F1: Copper recovery vs water recovery obtained with C2-X at collector dosages of 0.0695, 0.139 and 0.209 mol/ton ore in the flotation of the PMC ore

Table F1 Linear Regression Correlation Coefficients (R^2) for the lines in Figure F1

Collector Dosage (mol/ton ore)	No Collector	0.0695	0.139	0.209
Linear Regression Correlation Coefficient (R^2)	1.00	0.99	1.00	1.00

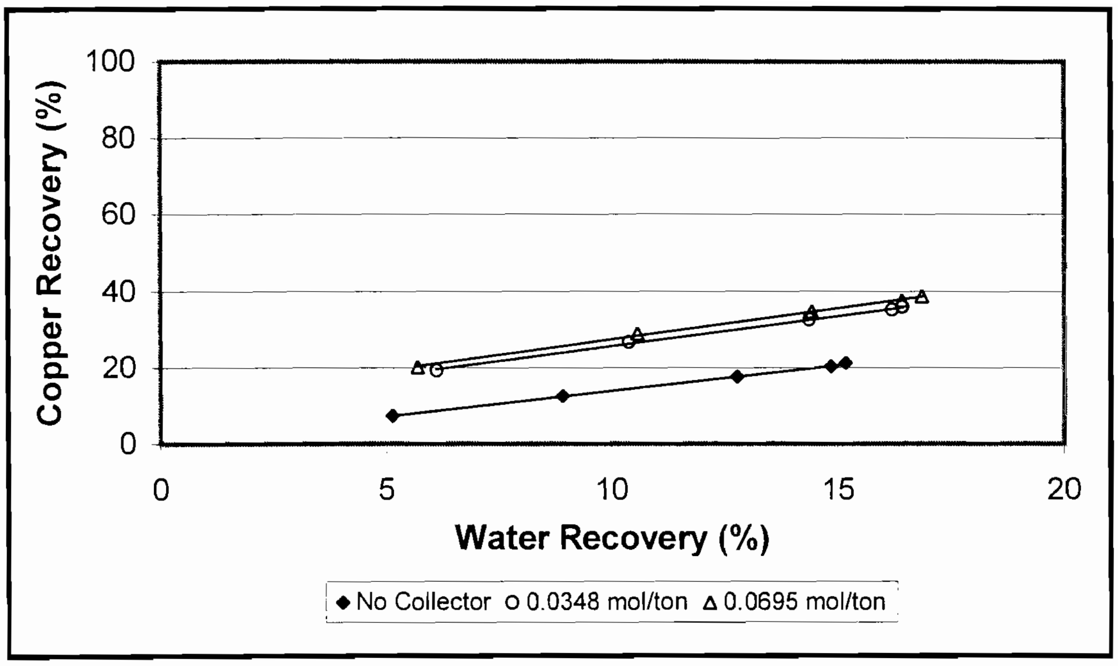

Figure F2: **Copper recovery vs water recovery obtained with di-C2-DTP at collector dosages of 0.0348 and 0.0695 mol/ton ore in the flotation of the PMC ore**

Table F2 **Linear Regression Correlation Coefficients (R^2) for the lines in Figure F2**

Collector Dosage (mol/ton ore)	No Collector	0.0348	0.0695
Linear Regression Correlation Coefficient (R^2)	1.00	1.00	1.00

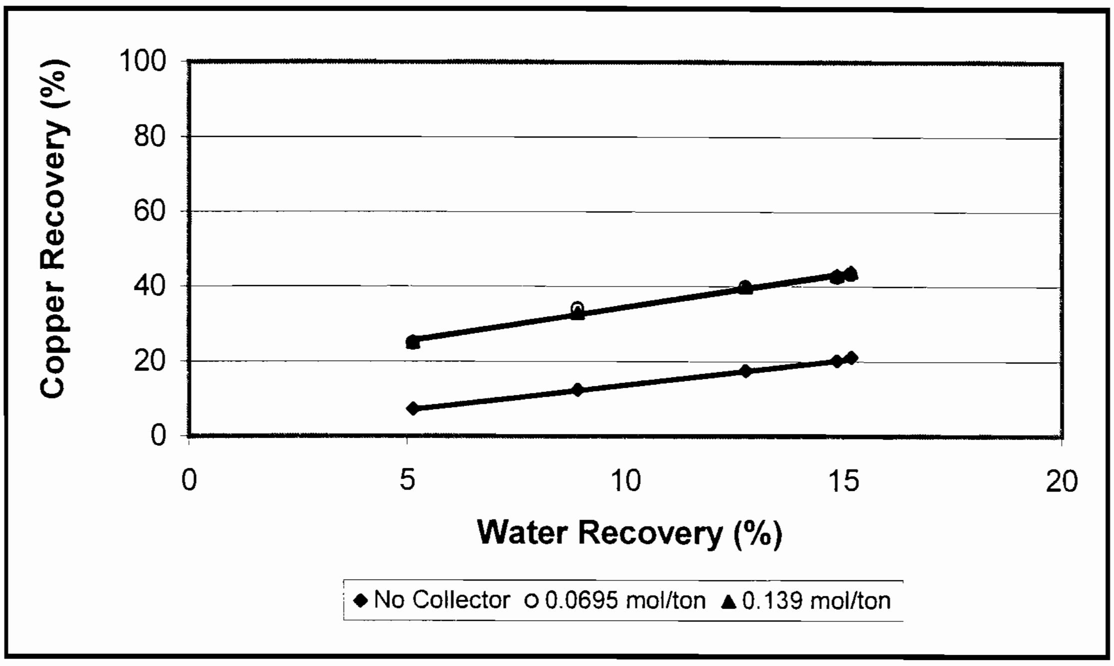

Figure F3: Copper recovery vs water recovery obtained with di-C2-DTC at collector dosages 0.0695 and 0.139 mol/ton ore in the flotation of the PMC ore

Table F3 Linear Regression Correlation Coefficients (R^2) for the lines in Figure F3

Collector Dosage (mol/ton ore)	No Collector	0.0695	0.139
Linear Regression Correlation Coefficient (R^2)	1.00	0.98	1.00

Appendix G: The relationship between acid soluble copper recovery and water recovery obtained in the flotation of the Palaborwa Mining Company (PMC) ore

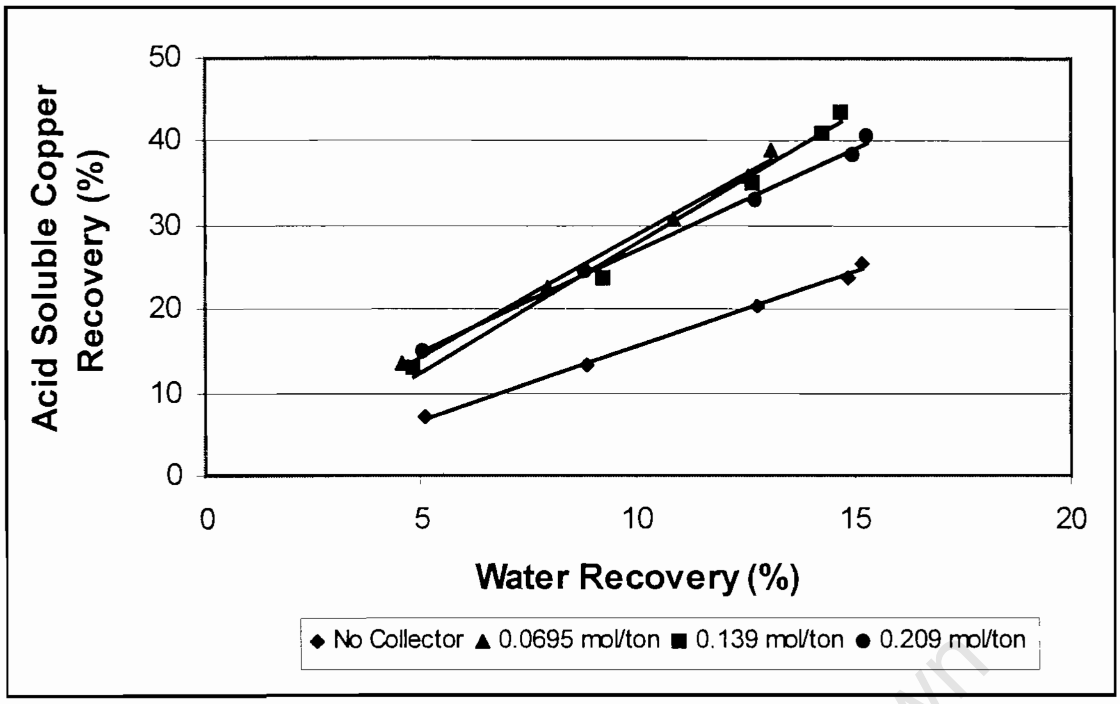

Figure G1: Acid soluble copper recovery vs water recovery obtained with C2-X at collector dosages of 0.0695, 0.139 and 0.209 mol/ton ore in the flotation of the PMC ore

Table G1 Linear Regression Correlation Coefficients (R^2) for the lines in Figure G1

Collector Dosage (mol/ton ore)	No Collector	0.0695	0.139	0.209
Linear Regression Correlation Coefficient (R^2)	0.996	0.995	0.990	0.996

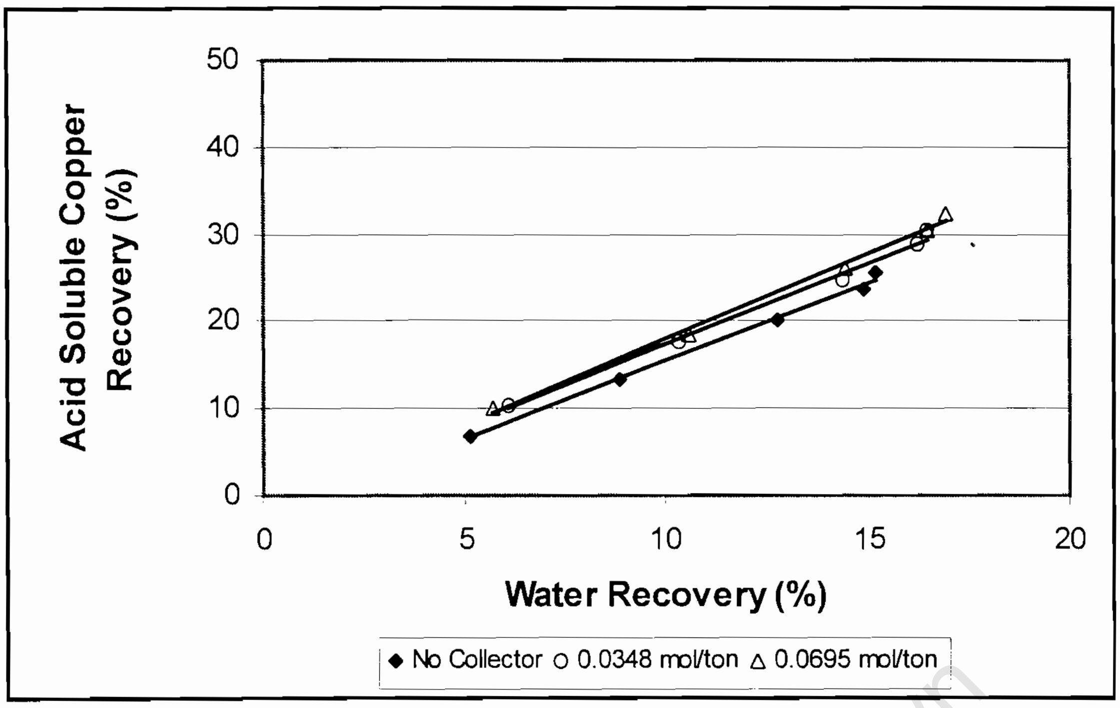

Figure G2: Acid soluble copper recovery vs water recovery obtained with di-C2-DTP at collector dosages of 0.0348 and 0.0695 mol/ton ore in the flotation of the PMC ore

Table G2 Linear Regression Correlation Coefficients (R^2) for the lines in Figure G2

Collector Dosage (mol/ton ore)	No Collector	0.0348	0.0695
Linear Regression Correlation Coefficient (R^2)	0.996	0.993	0.994

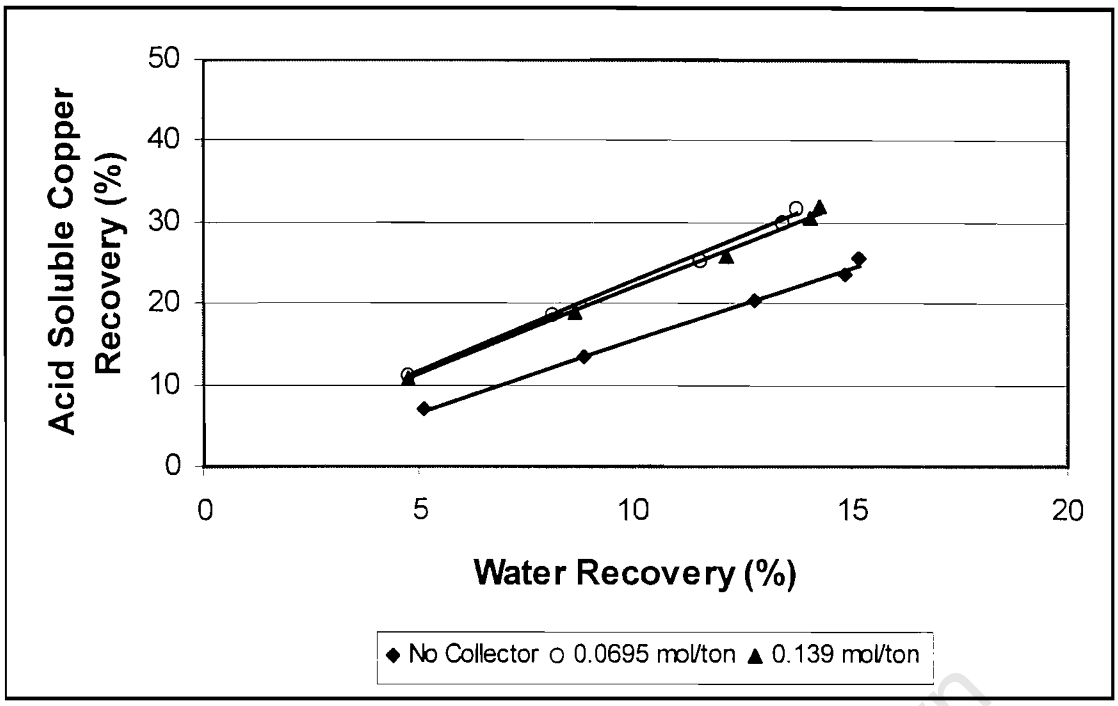

Figure G3: Acid soluble copper recovery vs water recovery obtained with di-C2-DTC at collector dosages 0.0695 and 0.139 mol/ton ore in the flotation of the PMC ore

Table G3 Linear Regression Correlation Coefficients (R^2) for the lines in Figure G3

Collector Dosage (mol/ton ore)	No Collector	0.0695	0.139
Linear Regression Correlation Coefficient (R^2)	0.996	0.996	0.996