CHAPTER 2 LITERATURE SURVEY

The flotation of sulphide minerals is a multiphase, chemically reactive hydrodynamic system. It is generally recognised that most sulphide minerals are readily floated though the reasons may differ. Some sulphide minerals can be floated without collectors, while others require small quantities of collectors.

Chander (1999) reported the various reactions in sulphide mineral flotation such as the oxidation of the minerals, hydrolysis of metal ions, decomposition of metal salts and collector by oxidation and metal/depressant compound formation. Hydrophobic and hydrophilic species occur simultaneously at the surface of minerals and the relative amounts and distribution of such species determine the overall flotation response.

2.1 Mechanism and reactions of sulphide mineral flotation

2.1.1 The effect of grinding on collector oxidation

The galvanic interaction among various sulphide minerals and grinding media change surface properties and influence the floatabilities of sulphide minerals (Cheng and Iwasaki, 1992). The more direct role of ferrous ions in obstructing collector oxidation and their hydrolysis has gone neglected by previous researchers and the ferrous ions act as oxygen scavengers which is needed for collectors to oxidise (Chander, 1999). Flotation is observed near the potentials at which sulphur would be expected to form and the minerals which produce sulphur seem to float the most strongly (Cheng and Iwasaki, 1992).

Woods (1984) reported that oxygen is not essential for the flotation sulphide minerals with thiol collectors. However, a species which undergoes a cathodic reduction reaction in the potential region in which collector oxidation occurs is required. Usually, oxygen is that species, but other oxidants which drive the anodic process will also be effective.

2.1.2 Self-induced or natural flotation

Many sulphide minerals exhibit self-induced or collectorless flotation in specific pulp potential ranges. Gardner and Woods (1979) reported that some of these minerals having such a tendency include chalcopyrite, molybdenite, pentlandite and bornite. This natural floatability result from electrochemical reactions that occur on these minerals after fresh surface area is created, which lead to the formation of sulphur-rich species, which are very hydrophobic, on the mineral surfaces. The pulp potential is reported to be a critical factor in the success of self-induced flotation of sulphide minerals (Yoon, 1981; Trahar, 1984; Luttrell and Yoon, 1984).

Klimpel (1999) reported that plant testing has increasingly shown that uncharged water-insoluble collectors are preferred for electrochemically enhanced sulphide minerals. Collector species such as thionocarbamates, mercaptans, dialkyl disulphides, trithiocarbonates and dialkyl sulphides have some operational advantages with minerals having some natural flotation tendency.

2.1.3 Specific cases of collector-induced flotation

2.1.3.1 Xanthate

Metal sulphides are floated effectively in the presence of oxygen with short chain sulphydryl collectors. Xanthate collectors are most commonly used in sulphide flotation (Klimpel, 1999). Woods (1984) reviewed the mechanism of collector-induced flotation in detail from a viewpoint of mixed potentials. The cathodic reaction is oxygen reduction, while the anodic processes are one or all of the following reactions in a xanthate-induced flotation of sulphide minerals,

a) chemisorption (Woods, 1976)

$$X^- = X_{ads} + e^- \quad [1]$$

b) formation of metal xanthate (Taggart, 1954)

$$MS + 2X^- + 4H_2O = MX_2 + SO_4^{2-} + 8H^+ + 8e^- \quad [2]$$

And/or

c) formation of dixanthogen (Haung and Miller, 1978)

$$\text{Anodic :} \quad 2X^- = X_2 + 2e^- \quad [3]$$

$$\text{Cathodic:} \quad \tfrac{1}{2}O_2 + 2H^+ + 2e^- = H_2O(l) \quad [4]$$

$$\text{Overall reaction:} \quad \tfrac{1}{2}O_2 + 2H^+ + 2X = X_2 + H_2O(l) \quad [5]$$

where X^- represents xanthate ion, X_2 represents dixanthogen and MS represents metal xanthate. In the presence of xanthate any of the above reactions may be responsible for sulphide mineral flotation with adsorbed xanthate, metal xanthate and/or dixanthogen. Xanthates and dithiophosphates are known to form metal-collector complexes and in some cases to form sulphur-sulphur bonded compounds such as dixanthogen (Walker et

Xanthates and dithiophosphates are known to form metal-collector complexes and in some cases to form sulphur-sulphur bonded compounds such as dixanthogen (Walker et al., 1984). Allison et al. (1972) concluded that both chalcopyrite and pyrrhotite belong to the dixanthogen group. Xanthate adsorption by pyrite or marcasite involves the formation of dixanthogen (Haung and Miller, 1978, Gaudin et al., 1956) by electrochemical reaction at the solid surface which support the conclusions of other authors. Salamy and Nixon (1953) reported that xanthate could be oxidised to dixanthogen on mercury electrodes and suggested that a similar reaction may produce hydrophobic disulphide layers on sulphide minerals. Xanthate ions appear to be chemisorbing on pyrite when oxygen is excluded (Fuerstenau and Mishra, 1980).

The existence of the two maxima is a further unexplained phenomenon of the complex pH effect on flotation (Haung and Miller, 1978; Fuerstenau and Mishra, 1980). Flotation ceases at low pH values because of the formation and decomposition of xanthic acid; at high pH values(> pH 11) flotation ceases because the amount dixanthogen that can form is exceedingly small. Flotation depression around neutral pH is also reported (Fuerstenau et al., 1968).

2.1.3.2 DTP

Thiol collectors like mercaptobenzthoazole (MBT) and diethyldithiophosphate (DTP) have to be used at low pH levels, because of the instability of xanthates at such pH levels (Sutherland and Wark, 1955). Although DTP collectors have replaced chemically dissimilar collectors, the greatest usage of dithiophosphates lies in combination with another collector type to enhance the collecting properties of each (Mingione, 1984).

$$2DTP^- = (DTP)_2 + 2e^- \quad [6]$$

$$\frac{1}{2}O_2 + 2H^+ + 2e^- = H_2O(l) \quad [7]$$

Two other mechanisms that also merit attention are the adsorption of thiol ions (Zadkin and Diog, 1960; Fuerstenau and Mishra, 1980), and the formation of a metal-collector salt (Taggart et al., 1934). The standard reduction potentials for

$$(Th)_2 + 2e^- = 2Th^- \quad [8]$$

are given E^0 = 0.252 V for DTP and E^0 = -0.049 V for MBT (Finkelstein and Polling, 1977). Chander and Fuerstenau (1974) reported that Kakovski et al. (1959) measured the oxidation potential of a series of DTP's by chemical equilibrium and potentiometric titration methods. They obtained the following relations for alkyldithiophosphates

$$E^0 = 0.40 + 0.074n \quad [9]$$

Where 2n is the number of carbon atoms in the DTP radical. Chander and Fuerstenau (1974) reported the same relation for diethyldithiophosphoric acid. The study of three electrodes, platinum, copper and coppersulphide with KDTP showed that there is a two-step process consisting of the discharge of the DTP^- ion to form a free $DTP^{\cdot}$ radical ($DTP^- = DTP^{\cdot} + 2e^-$) followed by the subsequent reaction of $DTP^{\cdot}$ to form $(DTP)_2$. Fuerstenau et al. (1971) concluded that $(DTP)_2$ is responsible for the floatation of pyrite with DTP as collector. A linear trend was reported by Groot (1982) between flotation recovery and electrode potential for pyrite floated with diethyldithiophosphate (DTP). DTP ions can also be adsorbed at potentials below the redox value, making the surface hydrophobic and the pyrite floatable. Groot (1982) also concluded that if the surface

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2.2 Electrochemistry of sulphide flotation

2.2.1 Mixed and rest potentials

A mixed potential is the steady-state, open circuit potential observed with an electrode when more than one reactions are occurring at the surface. If two redox couples are present in a system, and they are not in equilibrium, the redox condition in a solution is not characterised by a unique potential value defined by the Nernst equation. It is represented by a potential lying between two equilibrium potentials of the couples where the component anodic and cathodic processes proceed at equal and opposite rates (Cheng and Iwasaki, 1992).

The mixed potential model introduced a new significance to the electrode potential measurements in flotation systems. Gardner and Woods (1977) reported that the anodic oxidation of xanthate and the cathodic reduction of oxygen are responsible for the action of the collector on galena and pyrite from voltammetric measurements. Gardner and Woods (1973, 1977) studied it with particulate beds of galena and pyrite, and showed that flotation conditions for sulphide minerals could be simulated by controlling the potential. The behaviours of single sulphide minerals may be monitored by pulp

potentials as displayed in figure 2.1 (Richardson and Walker, 1985). Flotation separation of mineral mixtures by controlling pulp potentials, cannot be predicted from the flotation behaviours of single minerals.

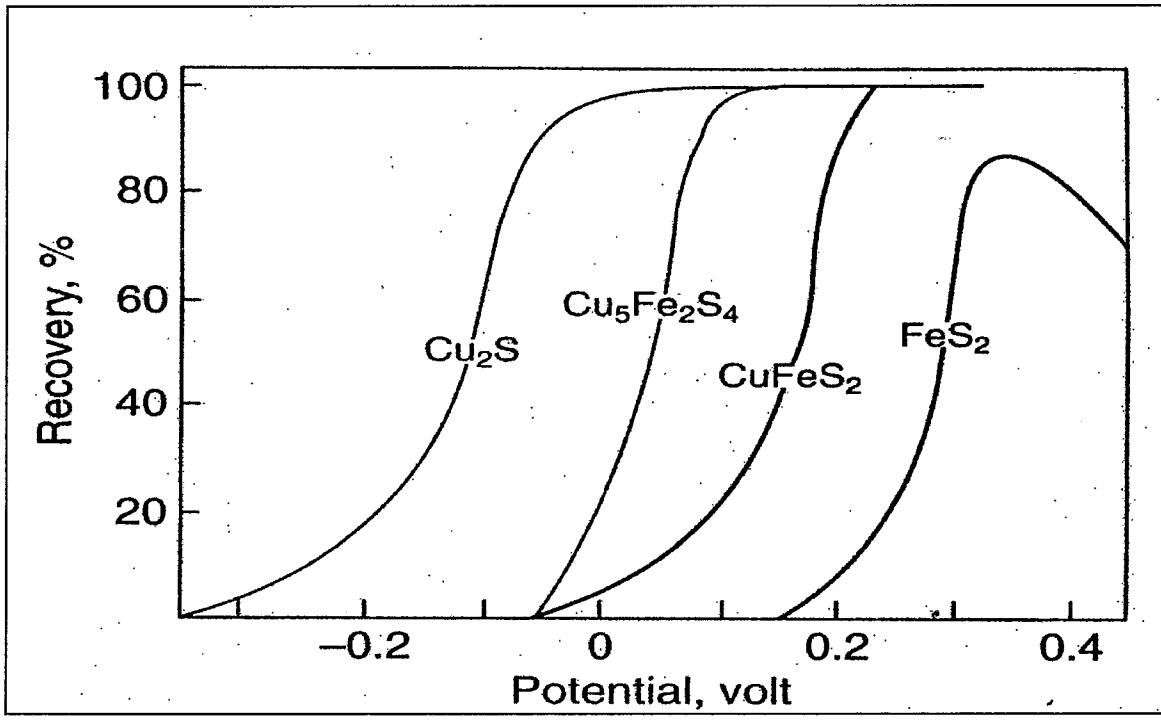

Figure 2.1 Flotation recovery of sulphide minerals as a function of potential (Richardson and Walker, 1985)

The rest potential is also referred to as a mixed potential which has equal anodic and cathodic currents (Chander, 1999). The rest potential of an electrode provides information on the identity of reactions occurring at the electrode/solution interface (Woods, 1984). The rest potential must be above the equilibrium potential for that process for an anodic reaction to take place. The reverse situation should give rise to cathodic processes. From reactions 1-3 it is possible to distinguish between the reactions from measurements of the rest potential of sulphide electrodes (Allison et al., 1972; Goold and Finkelstein, 1972). They reported products of reaction extracted from the mineral surfaces from rest potentials. Oxidation of the collector to its disulphide

(Reaction 3 : rest potential = 0.13V) occurred when the mineral displayed a rest potential above that of the potential of this reaction. A rest potential below this criterion resulted in the metal collector compound as the oxidation product. The limitations of this method is reported in Woods (1984).

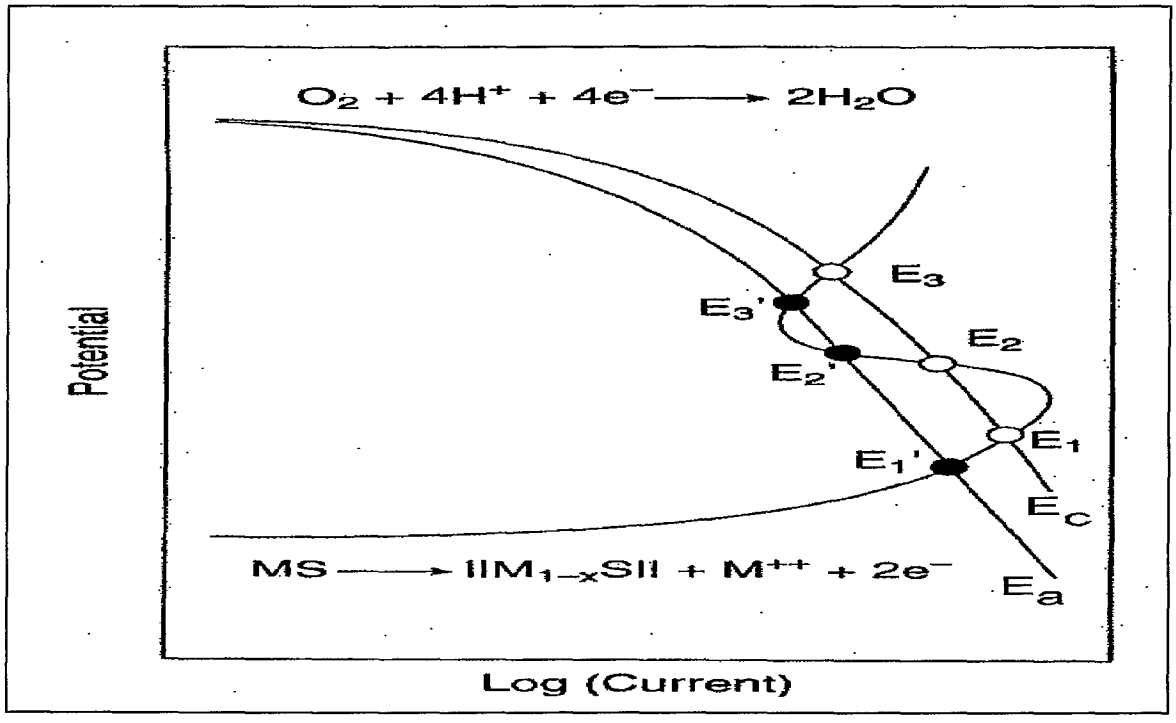

Figure 2.2 A schematic diagram showing currents for anodic and cathodic reactions (Chander 1999)

In the presence of collectors and self-oxidation products, principally sulphur and metal-deficient sulphides, the determination of rest potentials can become complex considering sulphide minerals are known to passivate (Chander, 1999). Figure 2.2 is known as an Evans diagram and shows the reversible potentials for the anodic and cathodic reactions as E_a and E_c respectively (Chander, 1999). The rest potential for the nonpassivating condition is E_1 and passivate upon oxidation to E_2 and E_3. This situation shows chemical instability as three rest potentials is present. The passive film from the anodic reaction further complicate the cathodic reaction and then the mineral might take values E_1', E_2'

and E_3' depending on the degree of passivation. This makes it difficult to use rest potential in practice as a successful control parameter.

Potentials measured in pulps respond to both ions and impinging mineral particles present in the slurry and may be referred to as pulp potentials in the presence of mineral slurry.

2.2.2 Measurement of pulp potential

An electrode pair consisting of an inert electrode and a reference electrode, most commonly a saturated calomel electrode (SCE), is used widely for measuring redox or pulp potentials. These potentials are converted to the standard hydrogen electrode (SHE) scale by adding 0.245 V and are reported in volts (Trahar, 1984).

Pulp potentials are reported to be closely related to sulphide flotation. Platinum electrodes are most widely used as an indicator for the measurement of pulp potentials in sulphide mineral flotation. Gold, chalcopyrite and galena electrodes were also used (Rand and Woods, 1984; Labonte and Finch, 1988). Woods (1984) suggested that an electrode constructed from the mineral being concentrated should make the most appropriate electrode for Eh measurements because the relevant Eh is established at the mineral/solution interface. Cheng (1991) reported that platinum was a better indicator electrode in flotation pulps than mineral electrodes. It is still not clear whether the noble metal electrode or sulphide mineral electrode is more suitable for controlling pulp potential.

According to Trahar (1984) there are five criteria which pulp flotation should meet for the measurements to have any meaning.

- Experiments should be conducted in air and should include some provision for the measurement of pulp potential if conducted in nitrogen. The reagents will give rise to the potential if any.

- It is not possible to determine the influence of a collector on floatability if the collector is not the sole cause of flotation. The oxidation reactions that lead to self-induced flotation also promote interaction with the collector and it is not always possible to separate the one from the other.

- The use of sodium sulphide solution in the preparation of minerals for research could interfere with the results of pyrite compared to other minerals. This may generate a high level of floatability which, for pyrite, cannot be prevented by washing the mineral between sulphidising and aeration. The preparation of sulphide electrodes should not include prolonged periods at potentials low enough to produce hydro-sulphide ions from the mineral itself.

- The potential measurement should be preserved until the solid is separated from the liquor. The pulp potential in a steel ball mill is in the reducing region. Once the pulp is exposed to air the potential will rise and promote uptake of the collector.

- A close relationship exists between pulp potential and pH. About the only method by which the potential can be permanently altered is the control of pH in the presence of air.

The electrode response may deteriorate with time presumably due to adsorption of impurities. Investigations of the effects of several inorganic and organic surfactants and reported that sulphide ions caused poisoning of platinum electrodes leading to sluggish

response and often erroneous readings (Natarajan and Iwasaki, 1970; Labonte and Finch, 1988). Woods (1984) also pointed out that the formation of oxidised surface layers on mineral electrodes through reaction with dissolved species in flotation pulps affected the responses of mineral electrodes. Proper cleaning of electrodes is important for obtaining rapid and reproducible potential readings.

2.2.3 Eh-pH diagrams

The metal ion concentration in solution depict the oxidation characteristics of the mineral and is a function of pH. Pourbaix diagrams is used to represent the role of potential (Eh) and pH on generalised thermodynamic equations.

Eh-pH diagrams can be useful for interpreting many metallurgical reactions. They cannot tell what will happen, but they can tell what will not happen, because the thermodynamic data are used (Cheng and Iwasaki, 1992). The Eh-pH diagrams also show only the stable phases. The stability regions of metal-thiol salt and routes by which it can decompose is displayed in these diagrams. The stability regions represent the thermodynamic conditions in which a mineral might float (Chander, 1999). Kinetic limitations may allow the development of some meta-stable phases because of the relatively short time scales in mineral processing plants. Eh-pH diagrams are despite all of the above widely applied to flotation, such as predicting the stable species for activation/depression mechanisms (Elgillani and Fuerstenau, 1968; Chander, 1985), monitoring the degree of aeration for flotation(Woodcock and Jones, 1970; Natarajan and Iwasaki, 1973b), and controlling the floatabilities of sulphide minerals for separation (Trahar, 1984; Heimala et al., 1988; Johnson and Munro, 1988).

Cheng and Iwasaki (1992) reported that a traditional model for the mechanism of sulphide mineral flotation is chemical adsorption. The development of an electrochemical theory resulted in a model combining mixed potential along with chemical adsorption. Sulphide minerals in general are semi-conductors and they can act as electron donors or acceptors. Surface phenomena in flotation may be interpreted to consist of anodic and cathodic reactions, but usually they involve more complex interaction of chemical and electrochemical processes. An electrochemical reaction may be presented by an oxidation or a reduction reaction accompanying loss or gain of electrons. The half reaction may be expressed by

$$xOx + mH^+ + ne^- = yRed + zH_2O \qquad [10]$$

When a solution containing both the oxidised and reduced species in Reaction [10] is brought into contact with an electrode and an equilibrium is established, a potential develops at the electrode so that the electrochemical potential is the same throughout the systems. Choosing the SHE as the reference, for which the potential in its standard state is taken as zero, potential for reaction [10] on the hydrogen scale, Eh, is then expressed by the Nernst equation at 25°C (Cheng and Iwasaki, 1992):

$$E_h = E^0 - \frac{m}{n}0.059\,pH + \frac{0.059}{n}\log\left(\frac{a^{x_{Ox}}}{a^{y_{Red}}}\right) \qquad [11]$$

where E^0 is the standard electrode potential, n is the number of electrochemical equivalents per mole, and a is the activities of the oxidised and reduced species participating in the electrode reaction.

Chander (1999) reported that the standard electrode potential depends upon collector type and the number of carbon atoms in the hydrocarbon chain. A lower value of E^0 indicates that the collector oxidises more readily and the ability of thiol collectors to oxidise in aqueous solutions increases with chain length. The Nernst equation defines the potential of the oxidised/reduced electrode vs. SHE as a function of the activities or concentrations of oxidised and reduced forms of the system.

There are two special cases:

(1) m = 0, z = 0 (pH independent)

Reaction [10] can be rewritten as

$$xOx + ne^- = yRed \qquad [12]$$

$$E_h = E^0 + \frac{0.059}{n}\log\left(\frac{a^{x_{Ox}}}{a^{y_{Red}}}\right) \qquad [13]$$

(2) n = 0 (Eh independent)

Reaction [10] can be rewritten as

$$pA + mH^+ = qB + zH_2O \qquad [14]$$

$$pH = -\frac{\Delta G^0}{5706m} - \left(\frac{1}{m}\right)\log\left(\frac{a^{q_B}}{a^{p_A}}\right) \qquad [15]$$

A close relationship exists between pH and potential because hydrogen ions are always present in aqueous solutions (Cheng and Iwasaki, 1992). Reaction 11 shows that generally potentials decrease with increasing pH and this affects the flotation of sulphide

minerals. The floatabilities of sulphide minerals are strongly depressed in alkaline solutions. This is due to a number of phenomena.

- Hydroxyl ions make the surfaces of sulphide minerals hydrophilic.
- Pulp potentials become more cathodic when pH is made more alkaline and this shift retards the oxidation of xanthate ion to dixanthogen.
- Minerals may undergo decomposition at cathodic potentials, and their surface properties are changed.

2.3 The basic TTC molecule

The difference between TTC and DTC (xanthate) molecules are that the sulphur atom in position 2 in Figure 2.3 is an oxygen for the DTC molecules and nitrogen for a dithiocarbamate (DTCB). The basic molecule for TTC's is displayed in Figure 2.3.

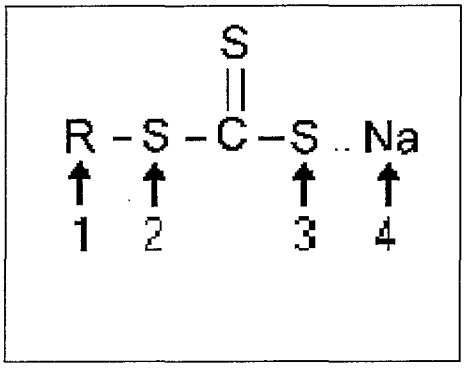

Figure 2.3 The basic TTC molecule

All previous research can be described with this figure. Slabbert (1985) varied the hydrocarbon chain of position 1 and the sulphur molecule in position 2 with nitrogen and

oxygen. The carbon molecule in the structure was also replaced with hydrogen, and the resultant mercaptans tested.

Coetzer (1987) synthesised 35 collectors with variations in positions 1,2,3 and 4 of Figure 2.3. In Slabbert's (1985) work the hydrocarbon chain lengths tested were ethyl, propyl, butyl and pentyl in position 1.

Janse van Rensburg (1988) tested the effect of the longer chain length collector with R>10 and compared the results with the pure mercaptan and ionic TTC's.

Steyn (1997) evaluated ionic and covalent TTC's and dithiocarbamate collectors on Merensky ore form Impala Platinum. One has to bear in mind that dithiocarbamate collectors are the replacement of the sulphur atom in position 2 by nitrogen.

2.3.1 Copper collection

Copper flotation generally becomes problematic when chalcopyrite is present (Davidtz, 1998a). In the recalculated work of Ackerman *et al.* (1984) by Davidtz (1998b) the conclusion has been that due to partial oxidation of this iron containing mineral, there is reduced surface coverage by collector molecules that has been quantified by G^{ex} calculations.

Slabbert (1985) evaluated the role of the number of sulphur atoms on rates and recoveries of flotation to quantify the effect of the combined role of the polar group and the hydrophobic function on the different flotation variables. In Figure 2.4 and Figure 2.5 the recoveries and rates are plotted as a function of hydrocarbon chain length.

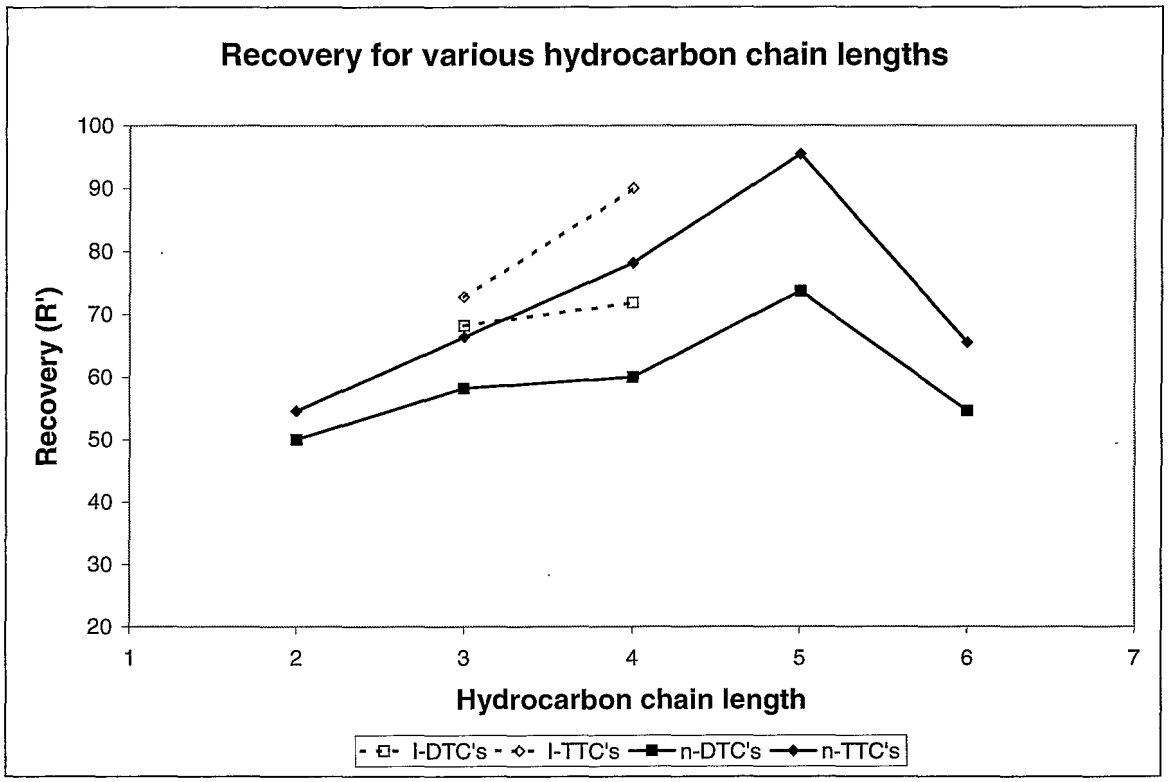

Figure 2.4 Recovery as a function of the hydrocarbon chain length at PMC (Slabbert, 1985)

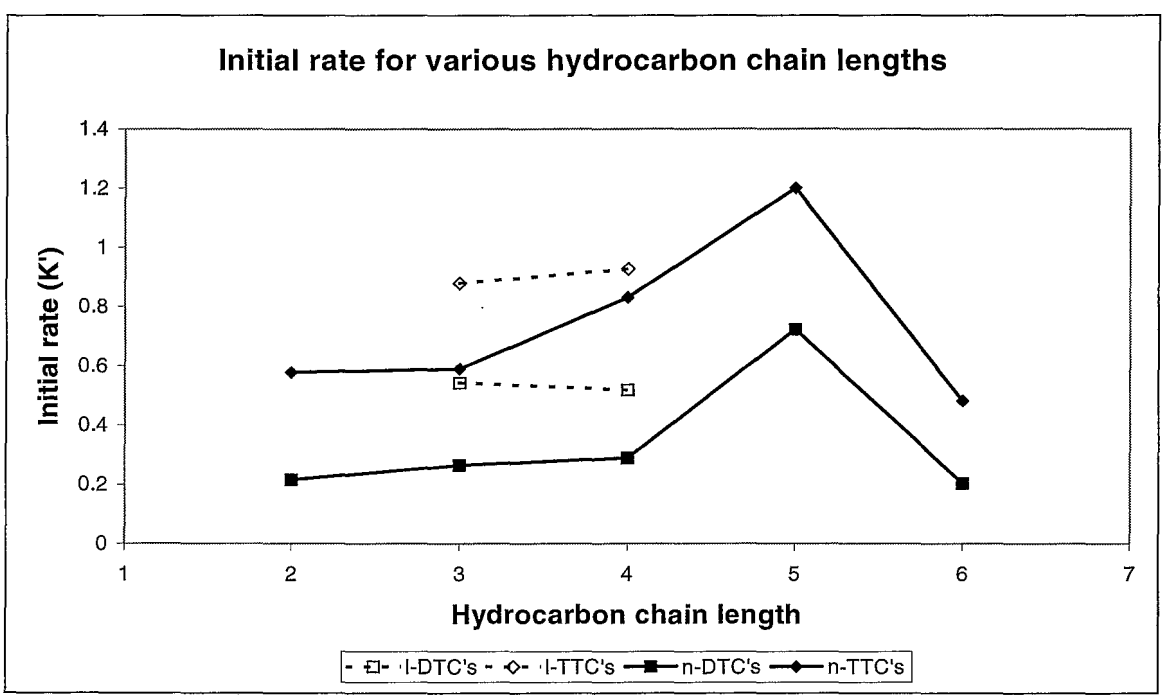

Figure 2.5 Initial rate as a function of the hydrocarbon chain length at PMC (Slabbert, 1985)

2.3.1.1 The effects of chain length on recoveries and rates

Slabbert (1985) found that the general trend for increasing chain length from C_2 to C_5 is upwards. A value of 1.1 RT is commonly reported as the free energy of expulsion per CH_2- group from the aqueous phase. This free energy gain of the particle by exclusion from the water is the driving force for the exclusion of coated particles from the water phase. The influence of the increase of carbon atoms on the hydrophobic function enhances the free energy of exclusion. Franks and Reid (1973) reported a linear increase in the enthalpy of solution of alkenes and the most negative value belonging to CH_4. The longer the chain the less soluble the collector in water and it gives a greater driving force for the adsorbed molecules to remove itself from the water and terminate in the bubble.

2.3.1.2 The effect of sulphur content of collector molecules on rates and recoveries

To explain the upward trend in floatability with an increase in the number of sulphur atoms per collector molecule, one needs to relate the collector's polar structure to effectiveness of flotation. The sulphide component of the surface is less polar and has a weaker interaction with water than oxygen and nitrogen (Yoon, 1981). The mechanism reported was the adsorption of sulphur on the exposed copper, and dehydration of the surface. The sulphide surface is indeed less polar.

Thiols contain only one , dithiocarbonate two and trithiocarbonates three sulphur atoms. These collectors can only attach to one, two or three metal cations on the surface. DTC's and TTC's have the same functional groups, except for the oxygen atom, and the oxygen cannot displace water molecules on surface metal ions (Slabbert, 1985).

2.3.1.3 Isomers

Linear hydrocarbons contain considerably more rotational and bending freedom than branched ones. The isomers that are directionally bonded away from the surface, impart greater interaction with water, and exclusion from the aqueous phase. Ackerman *et al.* (1984) reported that thionocarbamates with iso-alkyl substitutions in die O-position gave higher rates and recoveries.

Slabbert (1985) reported iC_4-TTC as the best collector tested on copper sulphide ore. TTC's gave a higher grade than the corresponding DTC's. The iC_3 and iC_4 returned higher recoveries for the TTC's and DTC's than the normal collectors.

Janse van Rensburg (1988) tested some long chain collectors on the PMC ore with SIBX as the standard collector suite. The phenomenon that branched collectors perform better than normal chain collectors is widely accepted for collectors with chain lengths less than five. The placement of the reactive group is crucial in flotation (Ackerman *et al.*, 1987). According to Janse van Rensburg (1988) 2-methyl-2-butane TTC has steric hindrance which impedes the adsorption of other collector molecules on the surface. This could have an effect on the hydrophobicity of the mineral particle and has a negative effect on recoveries.

Janse van Rensburg (1988) reported that the iC_5-TTC performed slightly better than the nC_5-TTC, but the nC_5-TTC was better than the iC_4-TTC, which is the same as Slabbert's (1985) results. The long chain TTC's mixed with iC_4-TTC performed better than the standard and iC_4-TTC alone. The improvement is 2.72% and 0.5% respectively.

2.3.1.4 Valleriite-rich copper sulphide ore

Valleriite contributes only between 3 and 12 percent of the copper entering in the PMC flotation plant and the losses of 50 to 80 percent of the copper in the tailings is associated with this mineral. The two reasons that stand out are sliming and the occurrence of intergrowths. The occurrence of valleriite intergrowths is known to be harmful to flotation of the copper sulphides. Slabbert (1985) tested thiols as collectors with varying chain lengths and found that the longer the chain the more effective the collector was.

Slabbert (1985) explained the effect of intergrowths on flotation: The surface of the mineral has both hydrophobic and hydrophilic zones, and a certain critical hydrophobicity is necessary for flotation. The intergrowths which are hydrophilic take up some of the mineral surface. With the induced hydrophobicity of the short chain collector this minimum value must be exceeded for the minerals to be able to float. The longer chains were suggested to have sufficient hydrophobicity to float valleriite. Furthermore, the basal planes are Al-oxides and collectors attach only to the tetrahedral metal sulphide portion on the edges.

Coetzer and Davidtz (1989a) reported that there is good collector-particle and particle-bubble attachment with the iC_3 and iC_4-covalent TTC esters which resulted in the extraordinary high bulk collecting and copper recovery. The allyl and benzyl derivatives both had high copper selectivities.

2.3.1.5 Long chain collectors

Long chain (C_{12}-mercaptan) was commercially used by PMC in the early part of 1980 with good effect (Davidtz, 1998). The C_{12} and C_{10}-TTC's performed almost alike and mixtures of the short and long chain collectors improved on the standard collector with 4.5% on copper recovery (Janse van Rensburg , 1988).

2.3.2 Platinum containing ores

2.3.2.1 PGM collecting with short chain collectors

Slabbert (1985) found that iC_3-TTC, pure and industrial, recovered two percent more PGM's than the standard at 30 and 45 g/t dosage levels. In figure 2.6 the grade-recovery relationship is shown. The higher recovery with the TTC's was associated with low mass recoveries, suggesting improved grades. The two percent increase in PGM recovery was obtained at a dosage of 30 and 45 g/t, where normal or standard dosage is 140 g/t (SiPX and di-iC_4-DTP) at Impala Platinum on Merensky ore. The iC_4-TTC also had higher PGM grades and recovery than the standard collector. It was suggested that the third sulphur atom also binds on the sulphide surface and that the critical hydrophobicity is reached at a lower dosage. The lower dosage meant lower consumption of chemicals and reduced costs. Higher grades implied significant savings in smelter costs.

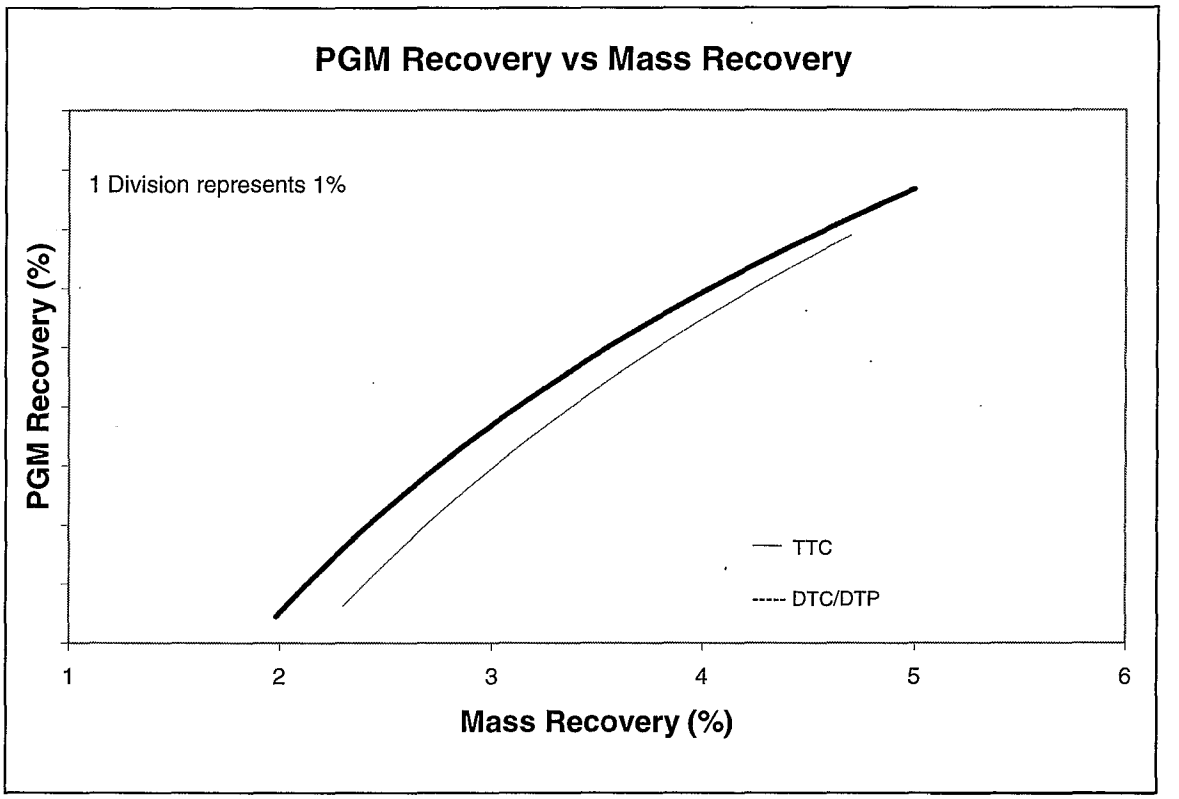

Figure 2.6 PGM recovery of the standard and iC_3-TTC at 45g/t (Slabbert, 1985)

From these results iC_3-TTC were synthesised at Philips Petroleum in America for a plant trial at Impala Platinum in 1985. The chemicals were stored in water and after weeks of storage the 40% solution had decomposed considerably. A drum of this decomposed TTC was spilled on the plant and the plant trial was cancelled.

The pure nC_5-TTC and Bz-TTC at all the dosage levels had the same or less recovery of PGM's. nC_4-TTC (industrial form) recovered inferior amounts of PGM at low dosage levels of 10 and 20 g/t. With higher dosage levels there was nothing to choose between this and the standard.

Steyn (1997) reported that TTC's outperformed the molecules containing oxygen, such as DTCB and DTP's on PGM recovery. The increase in recovery implies the recovery of a mineral, which normally would be lost, such as iron-containing minerals (De Villiers, et al., 1978). The less floatable minerals such as pyrrhotite and troilite could have been recovered by the TTC's.

Slabbert (1985) reported that less talc, an oxide, was recovered as well. This would improve the grade. It was suggested that oxide minerals could also have interacted with the oxygen in DTC collectors, leading to lower grades. The oxygen in xanthates would then reduce the grade of PGM should oxides be recovered. The third sulphur in TTC had a consistently positive effect on flotation grade.

2.3.2.2 PGM flotation with long chain collectors

Janse van Rensburg (1988) evaluated long chain collectors, ionic and covalent C_{10}-iC_3-TTC's, on Merensky Reef. The ionic C_{10}-TTC/3477 combination was superior to the recovery of the standard for both the PGM's and nickel. The improvement was 5% on PGM and 16.5% on nickel recoveries. The higher recovery was obtained with the same mass recovery as the standard due to higher grades. Strong synergism existed between the C_{10}-TTC and 3477-DTP because the long chain ionic collector did not perform as well as the standard.

The covalent ester showed good nickel grades and recoveries, but did not perform as well as the standard on PGM's. The ionic compounds performed better than the covalent long chain collectors for PGM and nickel.

2.3.2.3 TTC's and DTCB's on Merensky and UG2 ore

2.3.2.3.1 Nitrogen gas flotation

The oxidation of platinum containing base metal sulphides after milling and exposure to air reduced the recovery of the PGM's (Linge, 1995; Deng, 1995). Steyn (1997) reported that the standard ionic collectors (SIBX/DTP) performed better with air than nitrogen. The opposite was true for the remaining covalent collectors tested. It was suggested that the ionic collectors need oxygen to form dixanthogen at the mineral surface. The already oxidised covalent collectors do not need oxygen for adsorption on the mineral surface. Steyn (1997) reported that oxygen had a detrimental effect on flotation.

Yoon et al. (1995) found that oxidation rendered the mineral hydrophilic. This was more pronounced with pyrrhotite, less with pentlandite and least with chalcopyrite.

2.3.2.3.2 TTC odour

Harris (1984) reported that the rate-controlling step for the decomposition in the acid region for xanthates is the decomposition of xanthic acid to the corresponding alcohol and carbon disulphide. The iso-compounds generally had the longest half-lives in the acid range.

Xanthic acid $\rightarrow$ $OH^- + CS_2$

It was also reported that in the alkaline region the decomposition is more complex and the rate-controlling step is the hydrolysis of xanthate ion. The final products of the hydrolysis are CO_3^{2-}, S^{2-} and CS_3^{2-} (Philipp and Fichte, 1960). Finkelstein (1967)

reported CS_2 and $ROCOS^-$ as products of reaction. The following reactions of the unstable intermediate would occur:

$$RO(HO)C(SH)S^- + OH^- \leftrightarrow (RO)(HO)C(OH)S^- + SH^-$$
$$\rightarrow ROC(=O)S^- + H_2O$$

The method to reduce the odour of the TTC's is based on the elimination of water in synthesis and storage of the chemicals. Hydrolysis products such as mercaptans, which are responsible for the bad odour are reduced only by elimination of "free" water. Steyn (1997) synthesised the trithiocarbonates in hexane instead of water and determined the effect on flotation. The TTC's again performed better than the standard collector (SIBX/DTP). The same PGM recovery was reported for the water and hexane based TTC's.

Steyn (1997) added 15% of 13X zeolite to the TTC's. The free mercaptans that might be present would be adsorbed by the zeolites. The presence of zeolites did improve the odour of the TTC's but had no effect on flotation efficiency. Higher zeolite dosage had a detrimental effect on flotation.

The hydrolysis of iC_3-TTC has been evaluated to improve the odour of the decomposition products (Viljoen, 1996). It was reported that TTC's hydrolysed for about two hours, before the odour started to irritate. Low dosages of isopropyl and iso-butyl mercaptans were dosed in water to determine the solubility of the mercaptans in water. The fraction of mercaptans in the air was analysed by a gaschromotograph. The amount of mercaptans in the air increased with increasing dosage in water. With dosage levels of 10% of the normal dosage levels in plants, the mercaptan or secondary products odour started to irritate. It was concluded that only a fraction of the TTC's need to

hydrolyse to start an odour problem. Copper sulphate was used to control the odour making use of the high affinity of copper to sulphide, then binding with the free mercaptans.

2.3.2.3.3 Metal and mineral recovery with short chain collectors

Steyn (1997) reported that iC_3-TTC had better PGM rates and recoveries than the standard collector (SIBX/DTP) on Merensky ore (Figure 2.7). It was reported by Steyn (1997) that a practical implication of faster rates is that shorter flotation banks are needed and the valuables spend less time in the flotation circuit and more PGM are recovered every day. The selectivity of PGM over chromite was better with iC_3-TTC than the standard collector and is good for smelter performance (Steyn, 1997).

Most of the copper present in Merensky ore is situated in chalcopyrite, the nickel in pentlandite (Hamilton & Nölle, 1995). Steyn (1997) reported that the increase in nickel recovery was most significant as a result of recovering more pentlandite. The nickel showed far better rates compared to the standard collector.

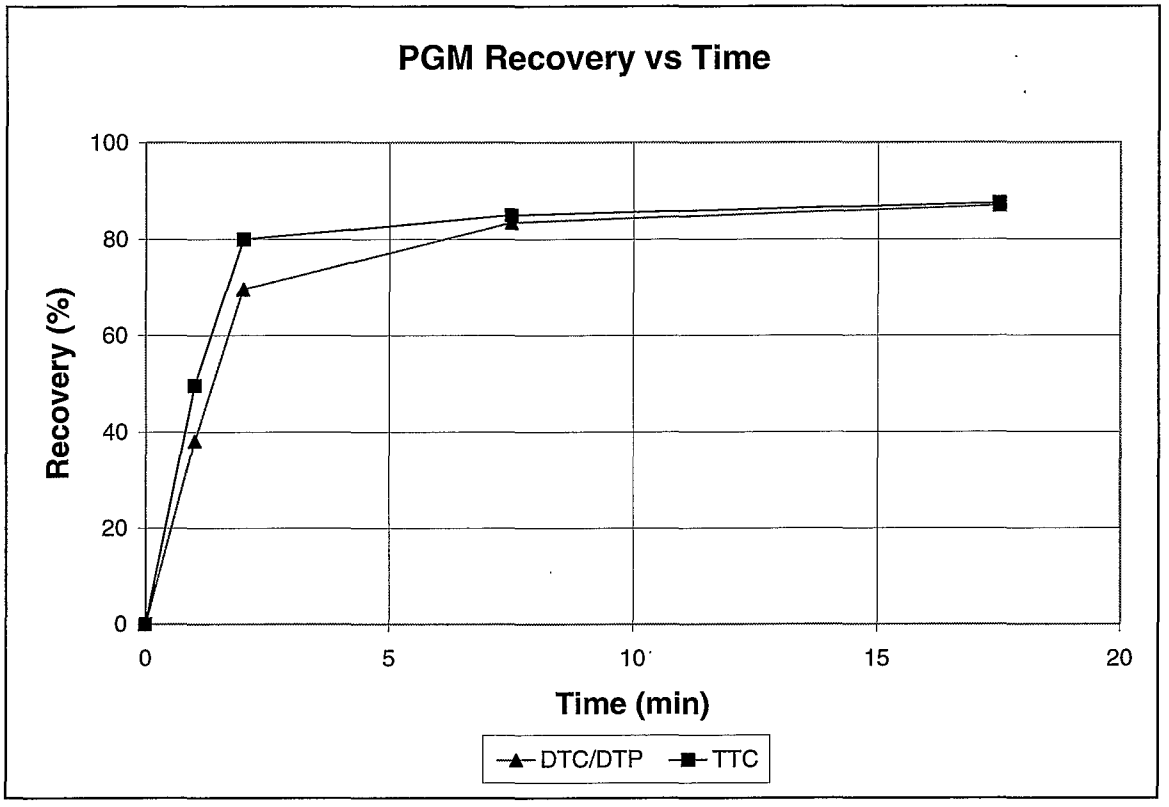

Figure 2.7 Recovery vs time for PGM (Steyn, 1997)

QEM*SEM analyses showed that the base metal sulphides in the tailings of the TTC's are less than that of the standard collector and the pyrrhotite recovery was better with TTC's (Steyn, 1997). This was interpreted as an increase in ΔG^{ex} with TTC's at the same dosage (Davidtz, 1995). The better recoveries were attributed to the higher recoveries of iron containing minerals. The recoveries of the larger size fraction recoveries were generally better than of the smaller sizes, where increased hydrophobicity is necessary to float the marginal floatable minerals.

Steyn (1997) reported that PGM's recovery on UG2 ore was better with 0.69% with iC_3-TTC. The increase was not as significant as with Merensky and the base metal recoveries also not as high.

The iC_3-TTC was compared to its covalent ester and iC_4-TTC. iC_4-TTC improved marginally on iC_3-TTC on PGM and base metal recoveries and rates. The iC_4-TTC has a lower vapour pressure. The covalent TTC had lower recoveries on PGM than the ionic collectors, but improved much on mass pull (Steyn, 1997).

2.3.3 Pyrite

2.3.3.1 Low pH flotation

2.3.3.1.1 Short chain collectors

Slabbert (1985) reported no significant difference between the final recovery of the collectors with low dosage levels (Table 2.1). Mercaptobenzothiazole (MBT) had the best recovery at 100μ moles per kg dosage and nC_4-TTC with dosage of 150μ moles collector.

Table 2.1 Recoveries and initial rate values (Slabbert, 1985)

	Recovery			Initial rate		
Collector	50μmoles	100μmoles	150μmoles	50μmoles	100μmoles	150μmoles
MBT	0.707	0.751	0.798	0.692	0.761	0.688
nC_4-TTC	0.721	0.734	0.831	0.487	0.603	0.680
Bz TTC	0.696	0.709	0.726	0.574	0.685	0.751
iC_3-TTC	0.680	0.682	0.685	0.811	0.815	0.817

Recovery was associated with sulphur recovery, which was correlated to pyrite. According to Slabbert (1985) Montan Laboratories (1984) found MBT to be a better collector for gold than TTC's. This means that gold and pyrite recovery are not synonymous, and that the gold collected by MBT are not associated with sulphides.

According to Slabbert (1985) the nitrogen atom in MBT could be operative in recovering gold in a pyrite ore.

The TTC's were superior to MBT in all of the collector dosages for the grades. At dosage levels of 50 and 100μ moles per kilogram the iC_3-TTC had the highest recoveries. The shorter the chain, the more selective the collector, the higher the grade (Slabbert, 1985).

2.3.3.1.2 Long chain collectors on gold

Low pH flotation tests (pH 3.5) were conducted with sodium-mercaptobenzothiazole (SMBT) as the standard collector. Janse van Rensburg (1988) reported that the only collectors that improved on the standard was the mixtures of long chain TTC's in SMBT. The C_{10}-TTC and C_{12}-TTC behaved similarly and showed an optimum between 10 and 15% TTC in SMBT. The mixtures of TTC's in SMBT showed improvements of up to 2% in gold recovery and this synergism was optimal between 10 and 15% mixtures.

The long chain TTC's alone in water did not improve on recovery of gold and sulphur, but had a marked improvement on rate of flotation of gold and sulphur. Janse van Rensburg (1988) reported this could be because of TTC breakdown at low pH values. A strong synergism exists between long chain TTC's and SMBT which gave excellent recoveries and rates for both gold and sulphur. The C_{10}-TTC has an optimum recovery for gold and sulphur at 10% TTC in SMBT.

Janse van Rensburg (1988) found that sodium salt of TTC's performed better than the potassium salt in mass recovery, sulphur and gold grade and recoveries at Simmergo. The sulphur recoveries showed improvement of at 5-10% TTC in SMBT for both the C_{10}

and C_{12}-TTC's. These collectors have low rates but high recoveries for gold and sulphur which means high grade. The gold grade reduced with increasing CH_2 groups.

The high grade of SMBT also has the lowest mass recovery of all the collectors tested. This low mass recoveries indicate a specific interaction of the TTC's with pyrite. The C_{10}-mercaptide in SMBT performed the best with sulphur (Janse van Rensburg, 1988) .

2.3.3.2 High pH flotation

The difference between the high and low pH flotation is that 3477 aeropromotor (DTP) was used instead of SMBT. This collector was used as solvent for the different collectors evaluated (Janse van Rensburg, 1988).

According to Janse van Rensburg (1988) the TTC grades were better than the corresponding xanthates and the long chain TTC's in water performed better on gold and silver recoveries. Very high gold grades were seen at low concentrations of C_{10}-TTC's in 3477. The best recovery was obtained from the 5% C_{10}-TTC in 3477.

2.3.4 Copper-lead-zinc-iron ore

2.3.4.1 Ionic compounds

According to Coetzer (1987) the least selective class of collector for copper was the DTC's with increasing selectivity for TTC's and the most selective the DTCB's. The general decrease in selectivity for copper for a particular group occurred as the hydrocarbon increases from C_2 to iC_4 (Coetzer, 1987). This is in agreement with previous findings (Hamilton & Woods, 1986; Davidtz, 1995).

Coetzer (1987) found that the selectivity for copper over lead and zinc with DTCB's followed the trend of decreasing with increasing chain length. The critical hydrophobicity was already reached with C_2 substitution. The opposite was true for lead selectivity. This is consistent with the specific gravity difference between chalcopyrite (4.1) and galena (7.5). The selectivity was closely related to the recovery. The selectivity of benzyl derivatives for copper was no different to that of the aliphatic substituted compounds.

2.3.4.2 Covalent TTC's

2.3.4.2.1 Aliphatic derivatives

It was found by Coetzer (1987) that the recovery of copper was high for iC_3 and iC_4-TTC derivatives and the selectivity not high because of high lead recovery. The aliphatic molecules are water soluble, indicating a high polarity. This polarity induced better bonding to metal sulphides in general and then reduced the selectivity when compared to allyl and benzyl derivatives. The recovery of zinc by the S-iC_3-S'-iC_4 TTC ester was high and this molecule was one of the best bulk collectors.

2.3.4.2.2 Allyl and benzyl derivatives

According to Coetzer (1987) the copper selectivity did not vary much for the allyl TTC's with change in hydrocarbon substituents. This trend was the same for the benzyl derivatives, and the selectivity of the allyl TTC's was higher than the benzyl derivatives. The benzyl derivatives reduced the froth stability. This could lead to better selectivity, because not all the collector molecules was adsorbed onto the sulphides. The minerals with the greatest affinity (low solubility product) for sulphur would attach to the collector

and increase copper selectivity over lead. The selectivity for lead was reversed with the benzyl and allyl derivatives, the higher the copper the lower the lead selectivity. This could be a result of critical hydrophobicity.

2.4 Development of a new flotation theory

Davidtz (1995) has proposed a method of relating flotation activity to a thermodynamic property, G^{ex}. This property was tested on the Merensky ore, and no depressants were added to maximise the adsorbed molecules and water interactions.

The different collectors were tested individually and as mixtures and compared to the standard mixture of iso-butyl-xanthate (SIBX) and di-isobutyl DTP (Steyn, 1997). Another objective of his study was to determine if there is any synergism between TTC's and DTCB with DTP..

2.4.1 Energy calculations

In the calculations used by Davidtz (1995) the general expression for Excess Gibbs Free Energy is:

$$\frac{G^{ex}}{RT} = \sum x_i \ln \gamma_i \qquad [16]$$

where x_i is the mole fraction of different components and γ_i is the activity coefficient for interacting species.

If only one collector is used the only components are water and the collector. The mole fraction of the water was chosen as 0.5. The rest of the fraction must be divided between

If only one collector is used the only components are water and the collector. The mole fraction of the water was chosen as 0.5. The rest of the fraction must be divided between the remaining collector molecules. ΔG^{ex} is calculated with UNIFAC for single components and plotted against PGM recovery obtained. The activity coefficients for mixtures were determined by UNIFAC for the two collectors and water. ΔG^{ex} was then calculated with this equation above and the two values were compared.

The ΔG^{ex} values can be used to describe the better recovery of different collectors. ΔG^{ex} is the energy change in the water environment when a collector is added to the system. The higher the ΔG^{ex} the more difficult it is for the mineral with collector attached to mix with water, and mineral recovery should improve. The ΔG^{ex} values for DTCB was considerably less than the TTC molecules, and implies the lower recoveries in PGM's. The only difference in these collectors is the nitrogen and sulphur atoms and these atoms influence the activity values calculated by UNIFAC. Nitrogen is smaller than sulphur and its attractive interactions with water is stronger. The sulphur atoms do not interact with the water - it is attached to the mineral. The iC_4-TTC performed better than the iC_3-TTC because of the extra CH_2-group (Steyn, 1997).

According to Steyn (1997) the same trend was observed with the mixtures of collectors tested. The higher the ΔG^{ex} values the better the recovery. A linear relation was also found with the collectors with the calculated values of ΔG^{ex} and PGM recoveries. The predicted recoveries are within 0.4% of the experimental recovery for all three mixtures (Figure 2.10). Previous attempts to predict flotation activity did not give quantitative values for the recoveries or synergism (Wakamatsu et al., 1979).

The correlation coefficient for the linear relationship between ΔG^{ex} and recovery for all collectors was 0.97 (Figure 2.6). The mixtures could be predicted as well, but no

synergism was observed. The theory by Davidtz (1995) and Steyn and Davidtz (1996) is well supported with these results.

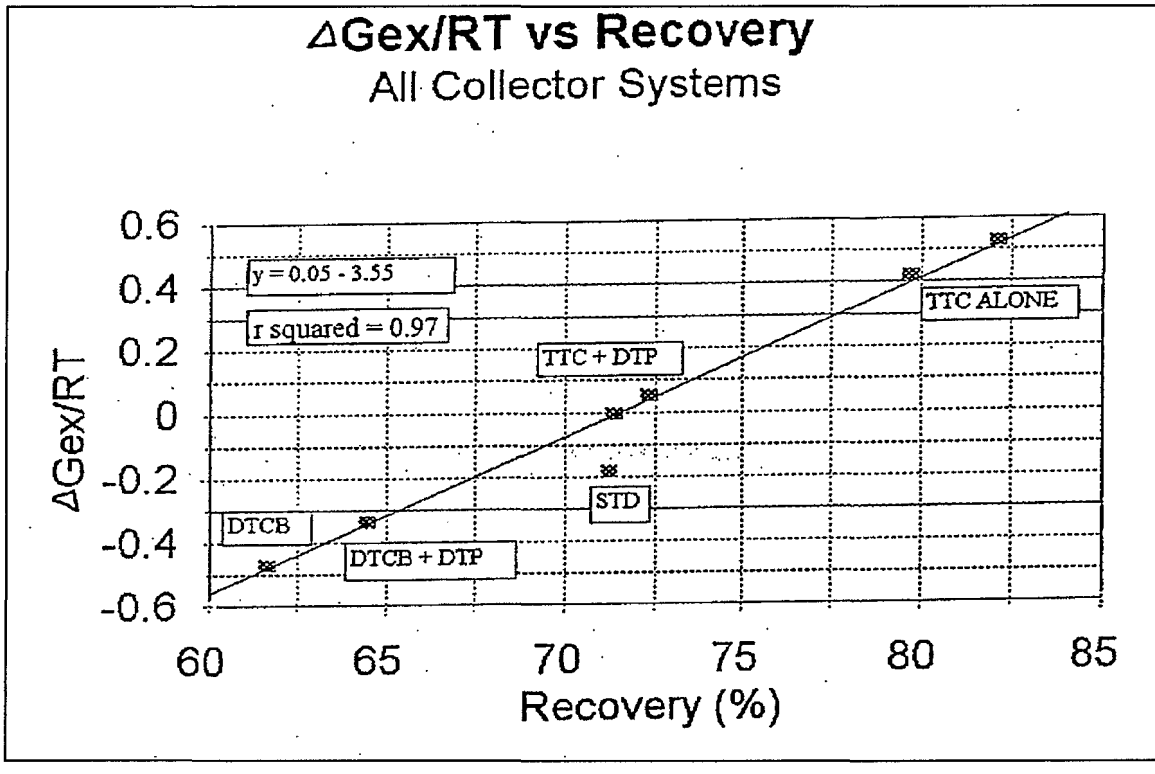

Figure 2.8 $\Delta G^{ex}/RT$ vs Recovery for singular collectors (Steyn, 1997)

According to Steyn (1997) the simplicity of this theory is a great advantage. The complex mechanism of flotation was not included in this and only a few assumptions were made. One is the irreversible adsorption, which is if the collector is attached to the mineral, it will not be displaced. Fornasiero et al. (1995) and Crozier (1991) who found a strong bond between mineral and collector, support this and under normal flotation conditions and standard agitation could not be broken.

Another assumption was that only the sulphur atoms are bonded to the mineral surface, while the other molecules (oxygen and nitrogen) could interact with water. The

interactions of the group containing sulphur, nitrogen and oxygen with water is illustrated in figure 2.7.

2.4.2 Rate/Recovery relationship

The rate and recovery values were obtained from Slabbert (1985) to determine if a relationship exists (Steyn, 1997). There is a linear correlation between the rate and recovery of the different collectors. Aleksandrova et al. (1992) found the same trend. It was found that either of these variables can be used to compare different collectors (Steyn, 1997).

2.4.3 Effect of mole fraction

Steyn (1997) reported that recovery versus dosage curves for iC_3 and iC_4-TTC molecules were used to calculate the ΔG^{ex} at different dosage levels. The dosage with the highest recovery was assumed to have full surface coverage. The recovery dosage curve was obtained from Slabbert (1985) for iC_3 and iC_4-TTC.

According to Steyn (1997) the maximum surface coverage was chosen to be $x_c = 0.5$, since the curves flatten down at this point and this value describes the theory the best (Figure 2.7).

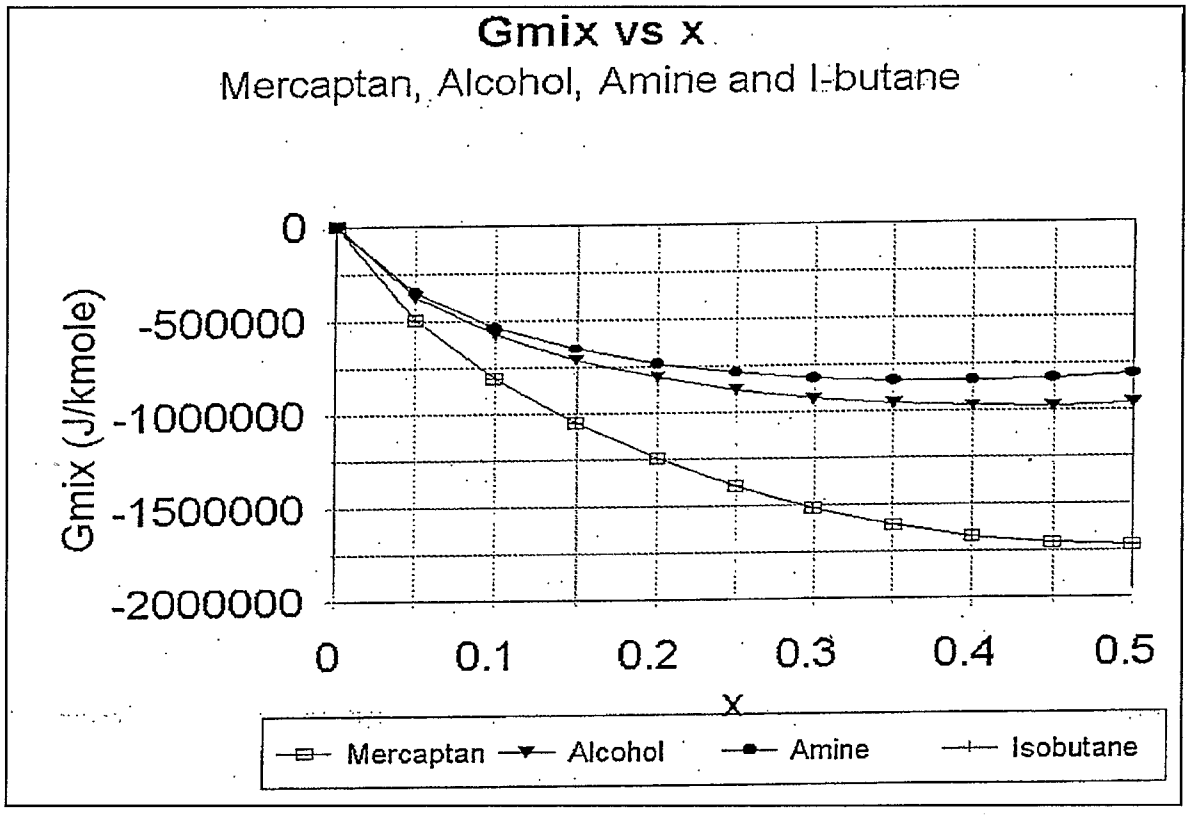

Figure 2.9 G^{mix} vs mole fraction (x) for the system organic molecule / water (Steyn, 1997)