

Investigating collector and depressant performance in the flotation of selected iron ores

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Signed

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Synopsis

As the excessive extraction of high grade iron ore reserves has led to the rapid depletion of these ore bodies, there is a growing need to extract and upgrade low grade iron ores into more economically viable products with an iron content in excess of 50%. The beneficiation of low grade iron ores through the reverse cationic flotation procedure is gradually gaining popularity as a possible processing route of the future for South Africa's iron industry. Reverse cationic flotation employs a reagent suite consisting of an amine compound which functions as a quartz collector in addition to providing the frothing effect in the flotation system, and hydrolysed starch which serves to depress hematite during flotation.

The aim of this project was to investigate the effect of using five amine collectors with different molecular structures on the flotation recovery of quartz and the entrainment of hematite in the flotation of a South African iron ore and a Brazilian iron ore. Laboratory batch flotation tests were conducted on both ore samples and the grade and recovery of hematite were recorded. The collectors were characterised through surface tension measurements and pKa value analysis. An attempt at using different polysaccharides as hematite depressants entailed the use of a CMC and a guar gum in batch flotation tests of the Brazilian iron ore.

With regards to the batch flotation of a South African iron ore, results showed that at the grind size of 80% passing 150 μm , there was no selective separation of quartz from hematite. When the most commonly employed collector, an ether monoamine (Flotigam EDA) at a dosage of 125 g/t was used in flotation, the iron grade changed from 39% to 40% whilst the quartz grade dropped from 38% to 36%. This change in grade was insignificant when experimental errors were considered. Flotation of a mill product with a grind size of 80% passing 75 μm using a hybrid flotation cell also exhibited poor flotation results when the same reagent suite was applied. The iron grade changed marginally from 39% before flotation to 41% after flotation.

The ether diamine 1 (Flotigam 3135) and a blend of the Flotigam EDA and Flotigam 3135 at a dosage of 125 g/t also failed to selectively float quartz from hematite. The remaining collectors (ether diamine 2, an imidazoline and a quaternary ammonium salt) did not yield any mass recovery to the froth zone, therefore, they were the worst performing collectors in the batch flotation tests of a South African iron ore. QEMSCAN analysis of the South African iron ore revealed that the ore was texturally complex with finely disseminated mineral phases in the sizes of $< 20 \mu\text{m}$. Poor liberation of the quartz and the hematite led to the poor flotation performance. Further milling of the ore merely produced high amounts of slimes which would lead to high losses of hematite through the entrainment of hematite during batch flotation.

Batch flotation results from the flotation of a Brazilian iron ore at the standard grind size of 80% passing 150 μm yielded good flotation results for all five collectors that were investigated.

Surprisingly, the ether diamine 2 (Flotigam 2835-2L) performed best as a collector for the Brazilian iron ore although it failed to perform in the flotation of the South African iron ore. A hematite concentrate with an iron grade of 65% and a quartz grade less of 1.5% was attained. At the same collector dosage of 125 g/t, the superiority of alky ether amines over the quaternary ammonium salt and the imidazoline was evident in the final iron grade and recovery. QEMSCAN analysis of the ore sample revealed that both quartz and hematite were above 90% liberated explaining the good response to reverse flotation using cationic collectors.

In both mineral systems, entrainment of hematite was influenced by the type of collector employed as they differed in frothing strength. The use of a collector with a strong froth stabilising effect resulted in a higher degree of entrainment as seen when ether diamine 1 (Flotigam 3135) was utilised in flotation.

The addition of an alcohol frother in systems employing the quaternary ammonium salt and the imidazoline salt as quartz collectors introduced a strong frothing effect to the system as well as an enhancement in quartz recovery to the froth zone. The presence of a neutral species in a flotation system either through the addition of an alcohol or the manipulation of chemical conditions i.e. the pH such that the alkyl ether amines generate neutral molecular species and ion-molecule complexes is necessary in order to achieve good flotation results. The neutral species and the ion-molecule complexes assist with frothing and adsorption of cationic collectors onto the quartz surface.

Batch flotation using a CMC and a guar gum as hematite depressants showed that starch remains a superior hematite depressant. At the same depressant dosage of 1500 g/t a system using starch as a depressant yielded a hematite concentrate with an iron grade and recovery of 65% and 97%, respectively. The CMC and guar gum yielded a hematite concentrate with iron grades of 51% and 66% respectively and iron recoveries of 88% and 80%, respectively. The CMC, employed at a dosage of 1500 g/t, had a dispersive effect which resulted in more hematite reporting to the froth phase hence the lower iron recovery after flotation. At lower depressant dosages i.e. 250 g/t and 500 g/t, the system using a guar gum attained a higher iron grade of 63%. The results confirmed the strong flocculation effect of a guar gum in higher concentrations which results in the agglomeration of quartz causing it to remain in the pulp zone.

In general, the study showed that the South African iron ore under investigation was not amenable to flotation. Further studies into the processing of ultrafine ore will be required if the desired iron grade is to be attained. Another key finding is that the collectors' molecular chemistry alone does not accurately determine their flotation performance as their flotation behaviour can differ depending on the mineral system.

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1. Introduction

1.1. Background to research

Iron is one of the most abundant elements in the earth's crust. The element is hosted in hematite, magnetite and goethite which are the economically significant iron bearing minerals. Sedimentary iron ore rock layers, commonly referred to as Banded Iron Formations, form the majority of the parent rock in which alternating bands of iron bearing minerals and their associated gangue minerals are synthesised (Prior, 2015). Quartz, kaolinite and gibbsite are the main gangue minerals associated with the iron ores. According to a 2013, United States Geology Survey, South Africa is the world's 7th largest producer of iron ore. Mining activities in the country are conducted in the Northern Cape and Limpopo provinces by Kumba Mineral Resources, a division of Anglo America. South African iron ores are mostly in the form of Banded Iron Formations (BIFs) (Holmes & Lu, 2015).

Worldwide, the steel industry consumes approximately 98 % of the iron that is produced annually. Currently the demand for iron has decreased, however, the past few decades had seen an ever growing demand for iron which led to a rapid depletion of the high grade iron reserves, known as "direct shipping" ores (Bruckard, Smith & Heyes, 2015). The elevated demand in iron, in turn prompted the extraction and beneficiation of low grade iron ore deposits which are characterised by iron grades of less than 45 %.

Iron upgrading through magnetic separation, froth flotation, jigging, spiralling or a combination of some of these techniques has been well established as an efficient and economically viable means of quartz rejection. The primary aim of upgrading iron bearing ores is to reduce the quartz content in the ore to less than 2.5 %, thus, meeting the furnace feed specifications. Excessive quartz in the furnace feed leads to a high consumption of limestone, as the compound neutralises the large amounts of a corrosive slag formed from quartz, thereby, preventing damage to the furnace's refractory lining (Holmes & Lu, 2015).

Flotation utilises the differences in minerals' affinity for water, thus, allowing separation of gangue material from the valuable ore. It is the intention of this project to examine the reverse cationic flotation of iron ores. Unlike conventional flotation, reverse flotation is a process that recovers the gangue minerals in the froth phase whilst the valuable material remains in the pulp zone. In order to separate the quartz from the hematite using reverse cationic flotation, a reagent suite consisting of a cationic amine collector and a depressant (starch) is added to the pulp zone. Cationic collectors attach to quartz particles rendering them hydrophobic, hence, they float to the froth zone. In excess and at the appropriate chemical conditions, cationic amine collectors act as frothers, stabilising the froth zone and reducing bubble

coalescence in the pulp zone. Polysaccharide depressants strongly adsorb on the hematite surface through interactions between the depressants' hydroxyl groups and the hydroxylated iron cations on hematite surfaces, inducing hematite hydrophilicity and depressing the hematite so it remains in the pulp zone after reverse flotation.

Previous studies on the use of various amine collectors in the cationic flotation of pure quartz and the reverse cationic flotation of Brazilian and Indian iron ores have been widely reported in literature. Investigations have focused on the flotation performance of the different collectors and the explanations of the flotation phenomena observed. The flotation performance has been explained by collector pKa values, the nature of collector species in a flotation system which is dependent on chemical conditions e.g. pH and the mineralogy of the minerals in question (Papini, Brandao & Peres, 2001; Vieira & Peres, 2007; Filippov, Filippova & Severov, 2010; Sahoo et al., 2016). Of utmost importance was the elucidation of the adsorption mechanisms of alkyl amines on quartz surfaces by Chernyshova et al. (2001) and Vidyadhar et al. (2002), as this presented a profound insight on collector adsorption mechanisms and their associated collector behaviour.

Turrer and Peres (2010) carried out investigations on alternative hematite depressants. A number of polysaccharides were tested in an attempt to depress hematite in an itabirite ore. There was minimal success as only one CMC, one guar gum and conventionally used starch delivered hematite concentrates with a low silica content and high iron recoveries. Araujo, Viana and Peres (2005) suggested that CMCs have the potential to become alternative starch depressants provided that they can be applied in very small dosages and still perform as well as starch wherein reagent costs are offset.

The current study initially intended to focus on the reagent chemistry of the collectors and depressants used in the reverse cationic flotation of iron ore. However, as the project progressed, it was observed that the mineralogy and texture of the South African iron ore under investigation was responsible for some processing complexities. The study therefore became a comparative study of the mineralogy of a South African iron ore and a Brazilian iron ore in order to ascertain how the different ore mineralogy would influence flotation.

Currently no iron ore mining operation in South Africa employs reverse flotation to upgrade iron ores. South Africa has hosted high grade iron ore reserves, hence, there was no need for upgrading the ores. With the increased mining activities, the depletion of high grade ores has necessitated the extraction and upgrading of low grade ores if South Africa is to remain a significant producer of iron ore on the world market. It is against this background that this project was conducted on the use of the collectors and depressants to ascertain whether the reverse flotation of a South African iron ore is viable. Batch flotation tests with comparison to

the Brazilian iron ore were made as the Brazilian iron ores bear mineralogical similarities to South African iron ores. The similarity lies in that both ores are composed of hematite and quartz due to their similar genesis through supergene enrichment of BIFs (Prior, 2015).

1.2. Research Objectives

In light of the previous work that has been conducted in the field of iron ore processing and with the research gaps having been identified, the main objectives of the study are therefore to:

- Characterise the ether amine collectors by determining the collectors' pKa values.
- Use batch flotation tests to establish the best amine collector by assessment of the recovery, grade and entrainment of hematite.
- Investigate the frothing characteristics of the collectors as well as determining the degree of adsorption of the amine collectors through surface tension measurements and quantification of residual concentration of amines in solution, respectively.
- Use batch flotation tests to investigate the effect of different depressants in the separation of quartz from iron oxide minerals. Carboxymethyl celluloses and guar gums are utilized either in their pure form or as blends.

1.3. Scope of thesis

The current project aims to understand the chemistry aspect of reverse cationic flotation as summarised in Figure 1-1. Interest will be channelled towards investigating the use of five cationic collectors provided by Clariant. The effect of collector chemistry on the recovery, grade and entrainment will be established and the extent of amine collector adsorption on mineral surfaces will be considered. As these collectors also behave as frothers, surface tension measurements on a supernatant from a conditioned slurry will add value to the project since a surfactant's frothing strength can be predicted from the extent to which a surfactant lowers the surface tension of water.

Polysaccharide depressants widely used on South African platinum processing plants will be employed as hematite depressants. The effectiveness of the polysaccharides in depressing hematite will be established using the differential iron and quartz recovery and grade to determine selectivity.

The operational aspect of a flotation system will also be investigated, in particular the mineralogy of the South African and the Brazilian iron ores. The Brazilian iron ore will be used as a comparison. The mineralogy is essential as it helps in explaining the flotation behaviour of the minerals under investigation.

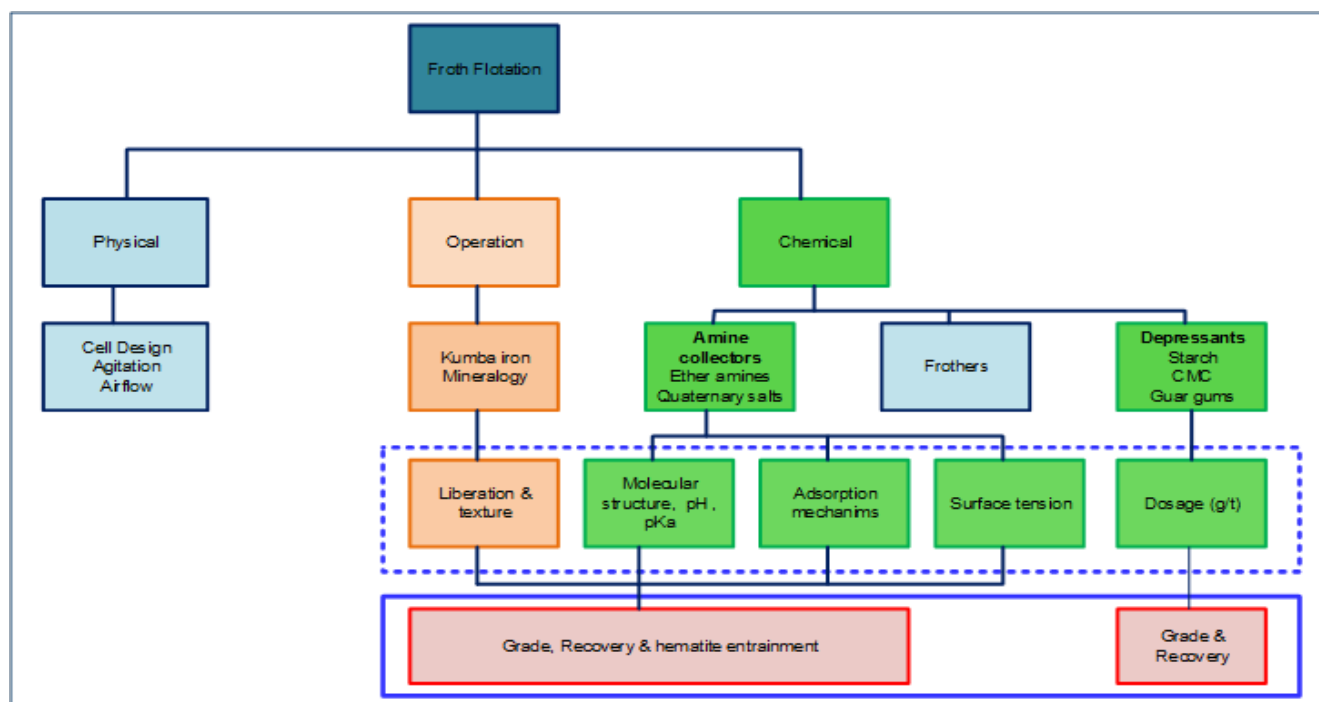


Figure 1-1: Schematic representation of the project scope. The areas highlighted by the dotted and blue solid lines show the inputs and outputs respectively

The project only focuses on the use of collectors and depressants. As previously mentioned, amine collectors simultaneously behave as frothers in the flotation system, hence, the work does not focus much on the chemistry of other frothers besides amines. As the project is only a characterisation project, no factorial design was used in the experimental stage of the research work.

1.4. Thesis Structure

This thesis is divided into 6 key sections, with each section focusing on a particular aspect of the project. The thesis structure is laid out as follows

Chapter 1: An introduction to reverse cationic froth flotation is provided. The motivation behind the study as well as the significance of the study is established.

Chapter 2: The pertinent literature focusing on froth flotation is reviewed in the first part of Chapter 2. The chapter then identifies important literature which focuses on facts and previous studies on reagents used in the reverse cationic flotation of iron ore bearing minerals.

Chapter 3: This chapter provides a detailed methodology of each experimental technique that was used in the experiential phase of the research study.

Chapter 4: The results and discussion section provides all the relevant results obtained from the test work. Included is data on the grade and recovery of iron, the extent of hematite

entrainment during flotation, surface tension analysis, as well as, a mineralogical analysis of the ores under investigation. Relevant literature which substantiates the discussion is cited

Chapter 5: The chapter gives final verdict on the work conducted and research findings synthesised from the project.

Chapter 6: Recommendations on future work to be considered in the field of iron ore beneficiation are provided in this section.

2. Literature review

2.1. Fundamentals of flotation

Flotation is a physico-chemical process that utilizes the differences in the surface chemistry of minerals in order to selectively separate gangue (waste) material from valuable minerals. Flotation follows the comminution process, where, large ore particles are mechanically broken down using crushers and mills (Wills & Napier-Munn, 2005). The ore is usually broken down to sizes below 100 μm before it can be floated. In the beneficiation of ores, flotation is usually employed after classification processes such as hydrocycloning or screening of the medium and coarse sized particles from fine and ultra-fine particles produced in the milling stage. The presence of slimes is responsible for mineral coatings through electrostatic interactions subsequently depressing material that is supposed to be recovered through flotation (Jameson, 1984).

A flotation system consists of two distinct zones, each characterised by different physical and chemical processes. The zones are namely, the pulp zone and the froth zone. In the pulp zone, the milled ore slurry mixture, conditioned with a collector, a frother and a depressant, is contacted with air bubbles allowing attachment of the floating hydrophobic particles onto the air bubbles. The collectors render some mineral particles hydrophobic. The hydrophobic particles possess an affinity for the air bubbles thus attaching to the air bubbles and floating to the froth zone. The depressants impart hydrophilicity to some minerals in the slurry. Hydrophilic material does not attach to the air bubbles, but instead, interacts with the water and remains in the bulk slurry. Consequently, collection occurs in the pulp zone with the result being a particle–bubble aggregate with a density lower than the pulp. The aggregate moves up to the froth phase against gravity whilst the hydrophilic substance remains in the pulp (Yianatos et al., 2009). In a direct flotation process, the unwanted gangue material is hydrophilic and the valuable mineral is hydrophobic, whereas in reverse flotation such as the process commonly used in iron ore beneficiation, the opposite holds true.

The froth phase serves to facilitate the upgrading of the desired mineral reporting to the froth concentrate i.e. the valuable mineral in direct flotation and the gangue mineral in reverse flotation (Bradshaw, Oostendorp & Harris, 2005). A frothing agent is vital to a flotation system as it enhances air dispersion in the flotation machine, reduces bubble coalescence and slows down the rate of bubble rise to the surface, thereby, increasing the residence time for more solids collection to occur. A good frother must produce froths that break easily during further treatment processes (Harris, 1982).

In a flotation cell, minerals reach the froth phase by two methods, viz, true flotation and entrainment. True flotation is the selective attachment of mineral particles to bubbles. It is directly affected by the chemical environment such as collector and depressant dosages (Wiese, Harris & Bradshaw, 2005). Entrainment on the other hand, is non-selective and thus results in the recovery of both the gangue and valuable minerals to the froth zone during direct flotation. Recovery by entrainment is affected by particle size and density as well as the recovery of water from the flotation cells. It has been inferred that the factors that affect the froth phase can also affect entrainment (Robertson, 2003).

The structure of the froth permits water drainage, thus, reducing the entrainment of the unwanted minerals reporting to the froth together with the desired mineral. Subsequently this increases the concentrate grade whilst limiting the reduction in recovery of the desired froth concentrate (Wills & Napier-Munn, 2005). In the froth zone, an optimum froth stability is required. If the froth phase is too stable, there will be a high degree of entrainment although there might be a low probability of losing bulk material from the froth. On the contrary, if the froth is too unstable, there is a reduction in entrainment, but the loss of bulk material is high (Bradshaw, Oostendorp & Harris, 2005).

A flotation process is an intricate blend of multiple interdependent variables. Analysing a flotation system can be difficult since changing one variable has a pronounced effect on other variables that make up the system. Flotation is an ideal example of an engineering system as it combines variables such as the chemistry, equipment and operation conditions in order for the system to function efficiently. Figure 2-1 shows the various parameters influencing a flotation system.

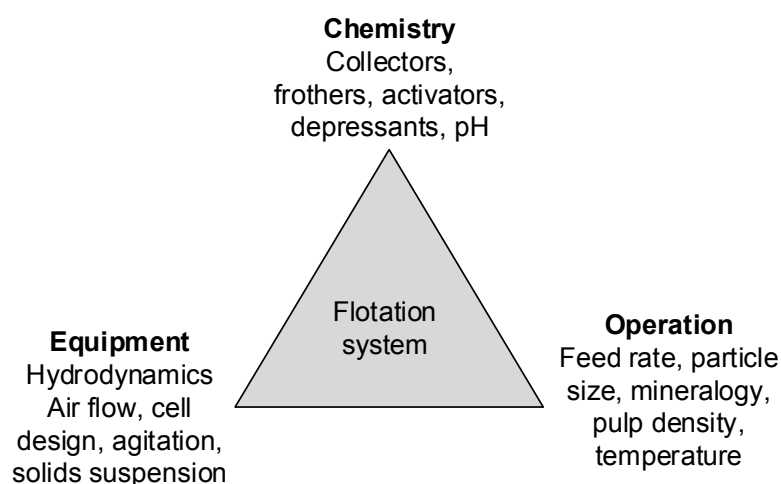


Figure 2-1: An illustration of the variables in a flotation system (Klimpel, 1995)

Pulp alkalinity is an important flotation variable. Flotation should be carried out in alkaline mediums as most collectors are stable in these conditions e.g. xanthates and amines. Furthermore, alkaline conditions reduce the effects of equipment corrosion, preventing the unnecessary replacement of equipment after only short periods of usage (Wills & Napier-Munn, 2005).

2.2. Overview of the iron ore beneficiation industry

An estimated 32.07 % of the earth's mass is in the form of iron (Clout & Manuel, 2015). The majority of iron ore deposits worldwide, consist of metamorphosed iron formations called banded iron formations (BIFs). Economically important iron bearing minerals are hematite (Fe_2O_3), magnetite (Fe_3O_4) and goethite ($\text{FeO}(\text{OH})$). Clout and Manuel (2015) reported that quartz (silica) is by far the most abundant gangue mineral within the iron oxides. Kaolinite and gibbsite clays are also present but in relatively smaller quantities. Sedimentary ore deposits associated with BIFs, such as the ones prevalent in Brazil and South Africa, are characterised by alternating layers of iron and fine and coarse grained quartz. The iron content of such deposits is within the range of 55 % - 65 % (Prior, 2015).

Traditional high grade iron ore reserves have an iron content of approximately 70 %, hence, these high grade iron ores do not require any beneficiation. However, the depletion of high grade ore reserves has led to the extraction of iron ores from low grade reserves, in an attempt to meet the ever increasing demand for iron, a principal raw material in steel manufacturing. Due to the low iron content in low grade iron ores (less than 45 %), beneficiation techniques are employed, increasing the grade of the iron concentrate by rejecting quartz.

Of paramount importance to the selection of an iron ore beneficiation route, is the mineralogy of the ore (Araujo et al., 2003). Ores present varying extents of mineral liberation from their parent rock after the comminution process. Therefore, the choice of an upgrading method relies on the degree of liberation e.g. an ore with highly liberated quartz will be amenable to reverse flotation. Popular beneficiation techniques include magnetic separation, jigging, flotation or a combination of the aforementioned techniques (Araujo et al., 2003).

As the chief aim of this project is to study the beneficiation of iron ores through flotation, it is necessary to highlight the flotation methods available to date. Three iron ore flotation methods have been widely reported in literature i.e. the direct anionic flotation of iron oxides, the reverse anionic flotation of quartz and the reverse cationic flotation of quartz, where anionic and cationic refer to the ionic nature of the collector (Filippov, Severov & Filippova, 2014; Fouchee, 2015). The direct anionic flotation was used in the 1950s, employing collectors such as petroleum sulphonates and fatty acids. In theory iron oxides must be easily separated from

quartz using direct flotation, however, the existence of hydrolysable cations in the pulp hinders the selectivity of direct flotation (Ma, 2012). In the 1960s, reverse cationic flotation of quartz employing fatty amines as the collecting agent and starch as the depressant was introduced. However, the poor water solubility of fatty amines necessitated the development of alkyl ether amines which display higher water solubility (Araujo, Viana & Peres, 2005).

Reverse anionic flotation of quartz is a much more recent technique increasingly gaining popularity with iron ore processing plants in China. Lime is used as an activating agent, inducing quartz activation by Ca^{2+} ions whilst starch remains as the hematite depressant (Ma, 2012).

Column flotation is relatively a new technique well developed for iron ore beneficiation in Brazilian mines since 1991. Samarco Mineracao S.A was the first producer in Brazil to include column flotation with mechanical flotation cells in a flotation circuit (Wyslouzil, n.d.). A column with wash water can be employed where the froth wash water reduces the loss of finely ground iron oxide material due to entrainment. The main benefits of using column flotation include improved metallurgical recovery, low capital expenditure and ease of fitting automatic controls to the flotation circuit.

2.2.1. South African Iron ore industry

South Africa hosts 1000 Mt (million tonnes) of unprocessed iron ore with an iron content of 650 Mt. The largest iron ore mining operations in South Africa are located in the Northern Cape and the Limpopo province (Holmes & Lu, 2015). Sedimentary iron ore deposits of the Paleoproterozoic Transvaal Supergroup are dominant in these regions (Prior, 2015). Laminated hematite with quartz as an impurity is the main iron bearing mineral. Three mines of economic significance are namely; Sishen mine, Kolomela mine, both located in the Northern Cape and operated by Kumba Mineral Resources and until recently, Thabazimbi mine in Limpopo province, which has since halted iron ore extraction operations.

Bore hole drill data extracted from geological tests at the Sishen mine at the time Taylort, Page and Geldenhuys (1988) published their article, showed that the average chemical composition of the mine's high grade ore was as follows : Fe content of 65 %, a SiO_2 content of 3 % and an Al content of 1.25 %. Taylort, Page & Geldenhuys (1988) further classified three iron ore grades in the processing of South African iron ores:

- High grade iron ore with an average iron content greater than 70 %.
- Medium grade ore with an iron content between 55 % and 63 %.Thabazimbi mine mainly supplied the medium grade ore.

- Low grade ore with iron contents between 20 % and 47 %. The low grade ore at Sishen and Thabazimbi is fine and predominantly made up of hematite. Interbedded impurities e.g. shale are present, hence, the need for beneficiation. Du Plessis, Jonck & Kruger, (1997) stated that beneficiation using high intensity magnetic separation, or flotation, or a combination of the two methods is necessary to obtaining a high grade concentrate.

Traditionally iron ore mined at these sites has been of a high grade and no beneficiation is employed. Only Sishen mine conducts some beneficiation work i.e. dense media separation and jigging, in order to meet their customers' specifications (Myburgh & Nortje, 2014).

2.2.2. The Brazilian iron ore industry

Outside China, Brazil is the world's largest producer of iron ore. Iron ore reserves in Brazil are situated in the amazon basin particularly in the state of Para and in the "Iron Quadrangle" in the state of Minas Gerais (Prior, 2015). The largest mines in Brazil are the Carajas mine (Para state) which is wholly owned by Vale and the Samarco Algeria mine (Minas Gerais state) which is jointly operated by Vale and BHP Billiton. Vale owns iron reserves to the amount of 14 billion tonnes making them the largest producer of iron in the world on a company basis (Clout & Manuel, 2015).

Brazilian iron ores primarily consist of hematite and goethite as a secondary iron bearing mineral. Quartz is the main gangue mineral found in the iron ore deposits. In their natural state, the ores are well liberated, hence, comminution is mainly targeted at size reduction. (Araujo et al., 2003). High grade iron ore extracted in the Minas Gerais state typically has an iron content of around 65% to 66% Fe. However, in some sections of the state, itabirite (banded hematite-quartz) with an iron content between 30% and 35% is present. The low grade iron ore is upgraded in order to meeting shipping grade ore quality (Clout & Manuel, 2015). The Brazilian iron ore industry has well established beneficiation techniques which have been developed since the 1970s. Nowadays most beneficiation is conducted through magnetic separation, flotation or gravity concentration. The choice of a concentration method is largely influenced by the mineralogy of the given ore.

2.2.3. Chemical and physical properties of Quartz

The quartz crystal structure consists of a silicon atom surrounded by four oxygen atoms, forming a networked tetrahedral structure, with an overall chemical formula of SiO_2 . The tetrahedron gives the silica mineral its physical structure. Bonds between the oxygen and silicon atoms are 40 % ionic in character and about 60 % covalent (King, 1982). The quartz mineral's physical structure represents that of a framework silicate. The framework silicate

consists of a three dimensional network of tetrahedral formed from the polymerization of the tetrahedral. Quartz has a specific gravity of 2.65 and a hardness of 7 on the Mohs scale.

Surface charge on the silica mineral can be generated by:

- Chemical interactions
- Preferential dissolution of surface ions
- Lattice substitution

During particle size reduction and cleaving of the minerals in comminution, a fracture line develops along points of weakness. The plane of fracturing allows the breakage of the silicon molecule as shown in Figure 2-2. When quartz particles are submerged in aqueous solutions, the H^+ and OH^- ions from the aqueous solution adsorb on the mineral surface's anionic and cationic sites. At equilibrium the $SiOH$ dissociates, behaving as Bronsted acid, releasing H^+ ions to the solution and subsequently leaving the mineral surface negatively charged (Fuerstenau, Graeme & Yoon, 2007).

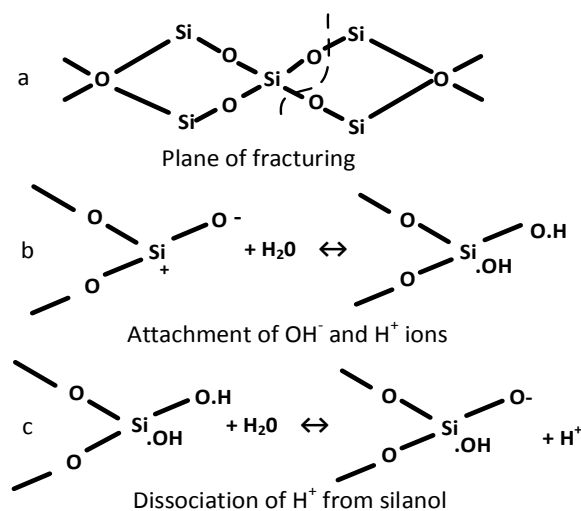


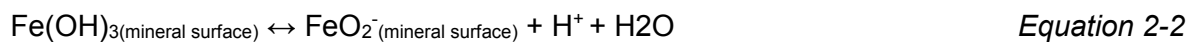
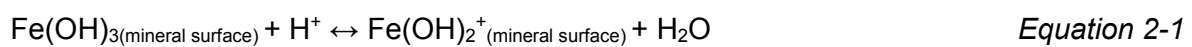
Figure 2-2: General mechanism for surface charge creation on a quartz surface (King, 1982).

2.2.4. Chemical and Physical properties of hematite

Hematite (Fe_2O_3) consists of six oxygen atoms forming an octahedral group around an Fe atom, whilst each oxygen atom is in co-ordination with 4 Fe atoms (Partridge & Smith, 1971). Salient characteristics of hematite include a specific gravity of 5.3 to 5.6, a metallic to earthy lustre and a hardness of 5-6 on the Mohs scale. The mineral is weakly magnetic, hence, it does not respond well to magnetic separation.

The surface charge on a hematite surface in aqueous conditions is strongly dependent on the type of Fe species present on the hematite surface. The surface charge creation on the

hematite surface is relatively similar to that occurring on the quartz mineral surface. After particle breakage in preparation for flotation, the particles acquire high surface to volume ratios thus exposing a number of Fe ions on the mineral surface. A two-step surface charge creation process occurs. Firstly, the OH⁻ ions and water molecules from an aqueous solution adsorb on the surface, interacting with the Fe cations on the mineral surface forming the surface hydroxide Fe(OH)₃. Hydration is followed by the dissociation of the surface hydroxide, inducing an electrical charge on the mineral surface which is dependent on the pH of the solution. The net result being a surface that is covered by a hydroxyl layer with cations buried below (Fuerstenau, Graeme & Yoon, 2007). Surface charge creation on a ferric oxide (hematite) is represented by Equation 2-1 and Equation 2-2.



Based on these equations, the binding of a hydrogen ion on a hydroxide surface results in FeOH⁺₂ groups dominating in acidic conditions, hence, the mineral surface is positively charged. When the pH is increased to alkaline conditions, the hydroxide surface takes up a hydroxyl ions forming the FeO₂⁻ groups, which dominate the mineral surface, producing a negatively charged surface (Rao, 2004).

2.3. Influence of fine grinding in reverse cationic flotation of iron ore.

The complex structures of quartz minerals in low grade banded iron ores e.g. banded hematite quartz (BHQ), has a significant impact on liberation which in turn affects iron recovery after flotation (Rath et al., 2014). The constraints in the beneficiation of BHQ and BHJ (banded hematite jaspers), arise from the complex interlocking nature of quartz and hematite at both coarse and fine particle size ranges. The inclusion of finely disseminated quartz grains in hematite and vice versa at fine sizes, also results in difficulties in attaining good liberation, making beneficiation difficult. This necessitates the design of more advanced flotation circuits that incorporate finer grinding (Das et al., 2010; Nayak, 2013). The finer the grind size, the higher the liberation, which increases chances of valuable mineral recovery.

The side effect of finer grinding is the inevitable generation of slimes. Slimes can be described as the fine material that is found in the milled ore, usually below the size of 25 µm. The presence of slimes has deleterious effects on iron recovery during the reverse cationic flotation of iron ore, hence, the need for slimes removal. On the contrary, direct anionic flotation has

been shown to be insensitive to the presence of slimes (Ma, Marques & Gontijo, 2011). This is discussed in more detail below.

A detrimental effect of slimes in the reverse flotation of hematite is the inevitable deportment of ultra-fine hematite particles to the froth zone through entrainment, thus reducing the recovery of hematite. Ultra-fine material has a froth stabilising effect which complicates froth management and rheology. Furthermore, heterocoagulation of ultrafine quartz particles with coarser hematite particles, masks the surface properties of the coarser particles and significantly reduces the selectivity of starch adsorption (Ma, Marques & Gontijo, 2011). Fine particles exhibit much higher specific surface area than coarse particles, so the collector consumption required for a certain coverage degree is much larger for fine particles in comparison to coarse particles. When a combination of coarse and fine particles are exposed to a large collector dosage, most of the collector will be consumed by the fines that require less coverage for efficient flotation. Not enough collector species are left for effective flotation of the coarse particles (Rocha, Canado & Peres, 2010).

Column flotation with wash water has previously been applied to control iron ore slimes with notable success. As mentioned before, wash water creates a counter-current flow to wash the fine entrained hematite out of the network of plateau borders back to the pulp zone, thus reducing iron losses (Kumar et al., 2010; Praes, de Albuquerque & Luz, 2013). Where batch flotation of iron slimes has been conducted, high starch dosages i.e. 1000 g/t to 1500 g/t of starch, are added to facilitate the flocculation and depression of fine hematite particles. Rocha, Canado and Peres (2010) conducted reverse column flotation tests on Brazilian iron ore slimes, yielding excellent results. Metallurgical recovery was as high as 80% and iron concentrates had silica grades below 1%. Studies on the column flotation of Indian ore slimes also showed that high concentrate grades and better recoveries can be obtained using column flotation in comparison to agitated mechanical cells (Raju & Prabhakar, 2000; Kumar et al., 2005).

2.4. Entrainment

As previously mentioned, particles report to the froth phase via two methods i.e. true flotation and entrainment. In true flotation, a particle–bubble aggregate forms and subsequently floats to the froth phase. Entrainment is the process by which particles report to the base of the froth and are transferred up and out of the flotation cell, suspended in the water between bubbles (Trahar & Warren, 1976). Entrainment is not chemically selective, hence, both the gangue and valuable minerals report to the froth phase.

Recovery by entrainment is far more common for particles with a size of less than 50 μm , because of their small particle sizes which result in them settling slowly and easily becoming

part of the fluid phase (Robertson, 2003; Wills & Napier-Munn, 2005). Particles reporting to the froth phase due to entrainment are freely moving along the Plateau borders together with the water entrapped between the bubble lamellae (Neethling & Cilliers, 2002). The process of entrainment is a two-step process. The first step is characterised by mineral particles ascension to the froth from a layer below the pulp/froth interface and the second step entails the transfer of entrained material in the froth to the concentrate launder (Wang et al., 2015).

Previous work on entrainment has revealed that the mass of entrained material is proportional to the water recovery. The correlation between the mass of particles entrained and the water is linear for most regions of interest. When extrapolated, the linear relationship has a zero intercept on the water recovery axis for fine particles. For medium and coarse sized particles, the relationship has an increasingly positive intercept (Neethling & Cilliers, 2002; Konopacka & Drzymala, 2010). It is widely accepted that increases in water recovery in the froth lead to lower ore grades. This is attributed to the presence of a wetter froth resulting in higher gangue mineral being transported from the froth to the concentrate through entrainment.

The degree of entrainment in a flotation system can be affected by the slurry density as well as the particle size of the solids in the mineral slurry. Wiese (2009) states that entrainment is also indirectly affected by changes in froth stability initiated by chemical changes in the pulp zone such as depressant addition.

To date literature has widely discussed three common entrainment methods i.e.:

- The boundary layer theory, where entrained material is carried up to the froth zone in a bubble lamella i.e. the water surrounding the air bubble (Gaudin, 1957; Hemmings, 1981).
- The bubble wake theory, where water and the entrained material are transported in the wake of an air bubble (Yianatos, Finch & Laplante, 1988)
- The bubble Swarm theory, where entrained material is carried between layers of bubbles (Smith & Warren, 1989)

2.4.1. Entrainment Measurement methods

Various entrainment measurement methods have been summarised in literature. Trahar (1981) used two batch flotation tests, one with a collector and the other collectorless, recording recoveries of solid matter and water in each test. The method assumed that the amount of matter recovered by entrainment was similar in both tests and that true flotation only occurred in the presence of a collector, hence, the difference in solids recoveries indicated that amount of matter recovered by true flotation. This method assumes that there is no naturally floatable

material present. Warren (1985) and Ross (1989) also investigated entrainment with different assumptions made to aid in measuring the extent of entrainment in a flotation system.

More recently, tracer tests have been employed in studies to estimate the amount of gangue material recovered by entrainment. An entrainment tracer is a gangue mineral that is fully liberated and non-floatable. Due to its non-floatability, the only means of reporting to the froth phase is due to entrainment (Wang et al., 2015). Yianatos et al. (2009) used a radioactive tracer technique to investigate entrainment and Robertson (2003) investigated entrainment using MnO_2 as the tracer element, both yielding scientifically sound results. Chromite is widely used as a naturally occurring tracer in determining entrainment in platinum-bearing UG2 ores. The advantage of using the tracer method is that it is applicable to both batch flotation cells and continuous flotation cells. Furthermore, entrainment can be measured without changing the operation conditions of the cell (Wang et al., 2015).

A practical method developed by Wiese (2009), was used to estimate the amount of entrained gangue reporting to the froth when floating a platinum-bearing Merensky ore. The principle is that, if high enough depressant dosages are added to the pulp zone, any unwanted material reporting to the froth zone does so as a result of entrainment only. The advantage of the practical UCT method over the tracer method lies in the fact that no foreign matter is introduced in the system to attain the amount of entrained material. Wiese (2009) calculated the entrainment function from the practical method and its value was similar to the empirical function suggested by Robertson (2003) for the Merensky ore that was under investigation. The method, however, has only been tested on sulphide minerals. Literature on studies that review hematite entrainment during the reverse flotation of iron ore is scarce.

2.5. Reagents in flotation

In a typical flotation cell a reagent suite is introduced in order to alter the surface wettability of the minerals, allowing the selective separation of gangue from valuable minerals. A reagent suite usually consists of a collector, a depressant and a frother. Some collectors are also frothing e.g. the collectors used in the reverse cationic flotation of iron ore have a dual function, acting as a cationic collector and, in their neutral molecular form (undissociated amine form), as a frother (Pearse, 2005). Collectors adsorb on to a mineral surface promoting hydrophobicity, resulting in the mineral particles attaching to air bubbles and floating to the froth phase. As frothing agents, they stabilise the air bubbles such that they maintain a well dispersed arrangement in the slurry. They also enable a stable froth layer to form, which can be recovered before the bubbles burst (Kawatra, 1995).

Depressants are modifiers that influence the attachment of collectors to the mineral surface. In the reverse flotation of iron oxide minerals, depressants essentially prevent collectors from attaching on to the iron oxide mineral surfaces, thus, they act to oppose the function of collectors. Frothers are neutral medium chain hydrocarbon molecules with a polar group (King, 1982). The chemical structure of the frother allows the molecule to have an affinity for both air and water. Due to its neutral nature, a frother can co-adsorb with a collector at the mineral surface reducing electrostatic repulsion between polar ionised heads, allowing more collector coverage on a mineral surface (Pearse, 2005). pH control chemicals are modifiers since a change in the pH of a system affects the surface chemistry of the mineral in the flotation cell.

2.6. Collectors in flotation of iron ore

Collectors are heteropolar compounds which consist of an active polar group and a non-polar hydrocarbon chain. The polar group adsorbs on the mineral surface and the hydrocarbon chain, projected into the bulk solution, induces the hydrophobicity of the mineral particles due to the incompatibility of the non-polar chain and the polar water molecules (King, 1982). The two main classes of collectors utilized in the direct and reverse flotation of iron ores are the anionic collectors and the cationic collectors.

Anionic collectors utilise a negatively charged solidophilic group to attach onto a mineral surface. They are subdivided into two groups i.e. oxyhydrils, when the solidophilic site is based on organic or sulfoacidic ions and sulfhydryl collectors when the solidophilic group contains sulphur. Anionic flotation of iron ores utilises the oxyhydril anionic collectors in the form of fatty acids (Bulatovic, 2007). Fatty acids are derived from vegetable or animal fats in alkaline conditions. Their hydrocarbon chain is hydrophobic whilst the carboxylic (COO^-) end is hydrophilic.

Reverse anionic flotation used in China entails quartz activation using limestone followed by floating the activated quartz using anionic collectors. The procedure has shown good recoveries even in the presence of slimes thus eliminating the desliming stage prior to flotation (Ma, Marques & Gontijo, 2011). Direct flotation using anions has also been reported in literature although it is not a popular beneficiation route. Pearse (2005) reported that the process of direct anionic flotation may be attractive for low grade iron ores. However, results from some studies in literature have shown that on a laboratory scale, the flotation of iron oxides with anionic fatty acids yields iron concentrates with a higher silica content than required. The sodium silicate depressant is not effective in depressing the silica mineral.

Cationic collectors can be fatty amines derived from fatty acids and rosin acids, ether amines derived from alcohols and acrylonitrile or ammonium salts that utilize the positively charged amine

group to attach to a mineral surface (Yang, 1988; Papini, Brandao & Peres, 2001). They are typically employed as salts and neutralised acetic acids in the flotation of silicates from metal oxides and in some cases, the flotation of calcites and dolomite from phosphate bearing minerals (Kou, Tao & Xu, 2010). The neutralisation improves water dispersibility of the collector. Cationic collector mixtures and mixtures of cationic collectors and neutral molecules, e.g. alcohols, have also been employed in iron ore concentrators on mineral processing plants. Such collector mixtures have been noted to yield iron concentrates with a low silica (quartz) content (Vidyadhar et al., 2002; Araujo, Viana & Peres, 2005; Filippov, Filippova & Severov, 2010). The current study compared different reverse cationic flotation collectors and, therefore, this review will focus on these compounds.

2.6.1. Alkyl Ether Amine Compounds

Early industrial applications of reverse cationic flotation made use of aliphatic amines and their acetates as collecting reagents. Due to technological advancements and a profound understanding of amine adsorption mechanisms in flotation, aliphatic amines have been modified through the insertion of an ether $(\text{O}-\text{CH}_2)_3$ group, subsequently forming alkyl ether amines (Filippov, Severov & Filippova, 2014). Alkyl ether monoamines are the product of a reaction between alcohols and acrylonitrile acid. The general molecular formula of alkyl ether monoamines is $\text{R}-\text{O}-(\text{CH}_2)_3-\text{NH}_2$. Where R is the alkyl chain. Alkyl chain lengths vary from depending on the compound chemistry.

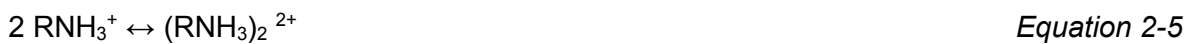
The presence of the $-\text{NH}_2$ group allows the ether amine compounds to adsorb on the mineral surface through hydrogen bonding, in addition to electrostatic bonding via NH_3^+ cations present when the ether amines dissociate in aqueous solutions. The alkyl ether amine reagents are characterised by a covalent C-O bond within the amine molecular structure. Flotation is more effective and selective due to the addition of the polar $\text{O}-(\text{CH}_2)_3$ group in the amine structure. There is an enhanced adsorption of the collector on the minerals surface via $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds between the hydroxyl groups on the mineral surface and the oxygen atom in the amine molecule. The $\text{O}-(\text{CH}_2)_3$ group enhances water solubility and adsorption at the liquid-gas interface and it enhances the elasticity of the liquid film around bubbles (Araujo, Viana & Peres, 2005).

A secondary reaction between the alcohol and acrylonitrile acid forms an alkyl ether diamine. Alkyl ether diamines are characterised by the formula $\text{R}-\text{O}-(\text{CH}_2)_3-\text{NH}-(\text{CH}_2)_3-\text{NH}_2$, where R is the alkyl chain. The distinct difference between the monoamines and diamines is the presence of the extra $\text{NH}-$ group which possesses an extra lone pair of electrons. The extra pair of electrons enhances the probability of hydrogen bond formations as the electrons are readily available for hydrogen bonding.

The ionisation of alkyl amines and diamines in water occurs according to Equation 2-3 and Equation 2-4 represents a saturated system where precipitation of the amine molecule occurs:



The equilibrium reactions and basicity of alkyl amines are pH dependent. At high pH values, the ionisation of the RNH_3^+ is suppressed and the molecular RNH_2 is abundant, whereas at lower pH values, the ionised amine is prevalent as seen in the speciation diagram of dodecylamine hydrochloride in Figure 2-3 (Fuerstenau, Graeme & Yoon, 2007). Alkyl amines may undergo intramolecular reactions whilst in the aqueous medium. Rao (2004) mentions the formation of ion-molecular complexes through the reaction between the aminium ion and the neutral molecular amine as well as the dimerization of aminium ions represented by Equation 2-5 and Equation 2-6 respectively. The ion-molecular complex is surface active, improving flotation.



Alkyl amines perform best as collectors at slightly alkaline pH values in the range of pH 8 to pH 10. In this pH range, there is a co-existence of the neutral molecular amine and its cationic species. The presence of the neutral molecules reduces electrostatic repulsion between cationic amine groups on the mineral surface, hence, more collector cations can adsorb on the mineral surface. Such conditions ensure maximum collector coverage resulting in improved quartz collection and subsequent flotation (Vieira & Peres, 2007). The co-adsorption phenomenon is best attained when there is 50% dissociation of the amine molecule, hence, at pH values equivalent to the collectors' pKa value, maximum flotation is possible (Gaudin, 1957).

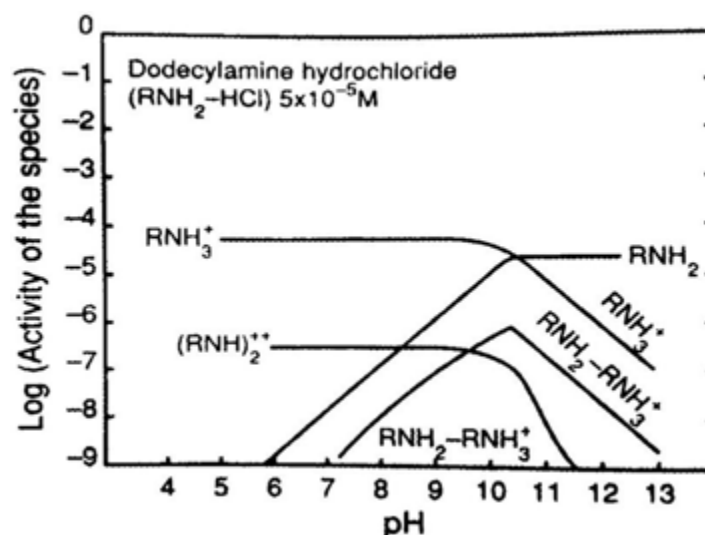


Figure 2-3: Speciation diagram for dodecyl amine as a function of the system's pH (Rao, 2004)

The effect of collector chain length was investigated by Scott and Smith (1991). For set amine concentrations, diamine collectors with longer chain lengths yielded better quartz flotation. This phenomena has been attributed to the influence of the chain length on surfactant adsorption at the solid liquid interface. At the critical hemi micelle concentration, where there is enough alkyl amine collector to form micelles and collector patches on a mineral surface through van der Waals interactions, there are increases in contact angles and flotation recovery. Longer chain alkyl amines attaching through stronger van der Waals forces, easily form long hydrophobic aggregates of collector on the mineral surface in comparison to short chain alkyl amines. The result is the lowering of the critical hemi micelle concentration, thereby, improving the flotation recovery and recovery rate (King, 1982; Rao, 2004).

2.6.2. Imidazolines

Imidazoline compounds are products of the reaction between fatty acids and diethylenetriamine (DETA). The products are condensed resulting in ring closure. Reacting the imidazoline ring with a dimethyl sulphate produces the quaternary ammonium salt of the imidazoline (Bajpai & Tyagi, 2006; Tyagi, Tyagi & Pandey, 2007).

Imidazoline compounds are quaternary nitrogen salts with 5 membered heterocyclic rings containing two nitrogen atoms. One of the nitrogen atoms represents a pyrrole type nitrogen with the other resembling a pyridine type nitrogen (Xi, Huang & Liu, 2008). Only one of the nitrogen atoms in the ring is basic with a lone pair of electrons. The most common representation of imidazolines is a tallow alkyl derivative shown in Figure 2-4.

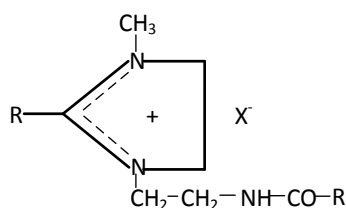


Figure 2-4: Structural representation of an imidazoline in the form of a tallow alkyl derivate. The cyclic ring can be substituted at the first position by a fatty acid chain, a hydrogenated tallow fatty acid or an oleic acid. A long alkyl substituent (C16-C17) is present at position 2 and a methyl group at position 3 (Bajpai & Tyagi, 2008).

Tallow alky derivatives with long chain lengths of 16 or more carbon atoms have low activity at the liquid /air interface hence they may need to be used in conjunction with a frother (Papini, Brandao & Peres, 2001). Imidazolines are strongly cationic, thus, they can adsorb on negatively charged mineral surfaces inducing hydrophobic properties in the mineral. The positive charge on the molecule is unaffected by changes in pH, hence, adsorption occurs in both alkaline and acidic conditions. Imidazoline compounds have traditionally been used in the flotation of dolomite, an impurity in phosphate ores (Sis & Chander, 2003). Material information sheets from Clariant suggest that imidazoline salts can be used in quartz flotation with the addition of a frother to the system for froth generation.

2.6.3. Quaternary ammonium salts

Quaternary ammonium compounds consist of a nitrogen atom, covalently bonded to four substituent groups thereby obtaining a positive charge on the nitrogen atom as shown in Figure 2-5. These compounds are synthesized from the reaction between a tertiary amine and a halocarbon compound (Svensson, Gustafsson & Klingberg, 2003). The chemical structure of quaternary ammonium salts does not allow for a lone pair of electrons, hence, they are not basic.

In each of the four covalent bonds in a quaternary salt, both atoms in a bond contribute one electron to the covalent bond. The compound, therefore, is stable in alkaline media, fully dissociated and possessing a positive charge at all pH values (Rao, 2004). Adsorption of these compounds on a mineral surface is thus due to physisorption i.e. electrostatic interactions with a negatively charged mineral surface whilst the R-groups are non-polar, supplying the hydrophobic ends (Yuhua & Jianwei, 2005). Studies on quartz flotation using quaternary ammonium compounds yielded high quartz recoveries. Furthermore, there was a high selectivity when floating quartz from magnetite (Svensson, Gustafsson & Klingberg, 2003; Yuhua & Jianwei, 2005)

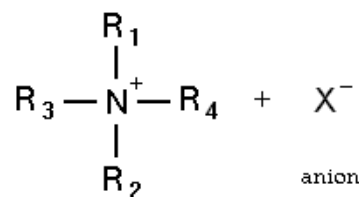


Figure 2-5: Structure representation of a quaternary ammonium compound

2.6.4. Cationic collector adsorption mechanisms

2.6.4.1. Electrical Double Layer

Adsorption of collectors on to mineral surfaces is strongly dependant on the mineral's surface charge. The electrical double layer is an interface which constitutes of a layer of positive charge adjacent to a layer of negative charge with the net result being a system that is electrically neutral (King, 1982). The presence of potential determining ions in the electrical double layer influences the charge created on the mineral surface. The interface is typically between the mineral surface and the thin layer of liquid surrounding the mineral surface (Partridge & Smith, 1971). When surface charge develops, the surface charge is compensated for by an equal and opposite charge distribution in the aqueous phase. The mineral surface contains potential determining ions, which are usually OH⁻ and H⁺ ions in the case of mineral oxides and silicates (Fuerstenau & Pradip, 2005).

Region 2 in Figure 2-6 shows the mineral surface including the potential determining ions which induce counter ions in the surrounding solution. Region 3, the Stern layer, consists of immobile counter ions some hydrated and others dehydrated. The Stern layer's thickness is no more than the diameter of one hydrated ion. Chemisorption of collectors on a mineral surface has been reported to prevail in the inner Stern layer, whereas, physisorption is more likely to occur in the outer Stern layer. Beyond the Stern layer are regions 4 and 5, where counter ions are mobile and their concentrations decrease exponentially into the bulk solution (Partridge & Smith, 1971).

An important characteristic of the double layer is the zeta potential (ζ), essential in assessing flotation behaviour. The zeta potential is an experimentally determined thermodynamic potential at the stern layer/diffuse layer interface. A value of zero is assigned to the zeta potential when the charge density of potential determining ions is equal i.e. at the point of zero charge. At pH values above the point of zero potential the mineral surface is positively charged and below this point the mineral surface is negatively charged (Fuerstenau & Pradip, 2005). Adsorption of collectors onto oxide mineral surfaces is dependent on the surface charge created on the mineral surface hence the point of zero charge (PZC) plays a significant role in the flotation response of oxide minerals.

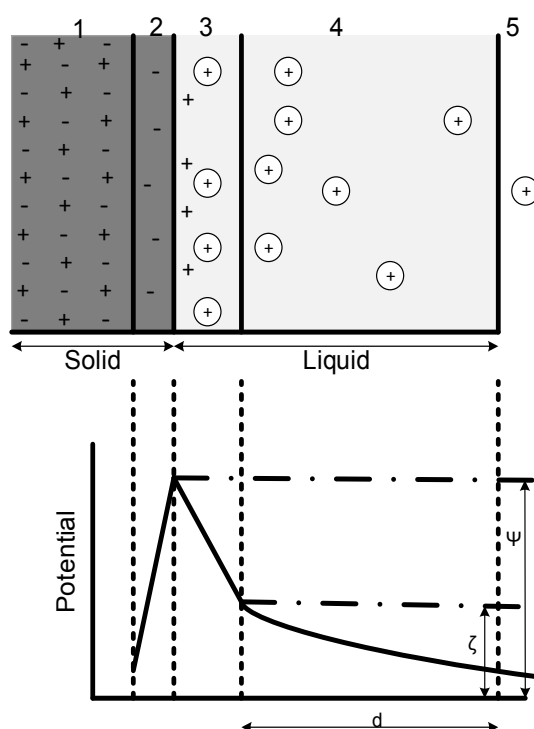


Figure 2-6: An illustration of the electrical double layer and its associated regions. Adapted from (Partridge & Smith, 1971)

2.6.4.2. Chemisorption

Chemisorption occurs in the inner Stern layer of the electrical double layer. It involves the complete or partial transfer of electrons. The extent of a chemisorption reaction is affected by the size and charge of the adsorbate ions (Partridge & Smith, 1971). Adsorption through chemisorption involves the chemical interactions between the cations and the mineral surfaces through the formation of ion complexes. In addition to the chemical bonds, hydrogen bonds can be formed when the mineral surface and collectors contain hydroxyl and amine groups (weak chemisorption) (Bulatovic, 2007).

2.6.4.3. Physical adsorption (electrostatic interactions)

Physical adsorption occurs in the outer Stern layer of the electrical double layer. The most common interactions present in physical adsorption are ions or molecules held in the outer stern layer through electrostatic or dispersion forces or a combination of both (Partridge & Smith, 1971). In physical adsorption no true bonds are formed and the process is reversible. FTIR results obtained by Yuhua and Jianwei (2005) on a quartz sample, conditioned with a quaternary ammonium compound, revealed that there was no shift in spectrum bands before and after collector adsorption on a quartz surface. The lack of a shift in spectrum bands suggested that no new chemical bond had been formed during adsorption, therefore, the author proposed that adsorption of quaternary ammonium compounds had occurred through physisorption.

2.6.4.4. Adsorption of ether alkyl amines on quartz minerals

Until recently, the adsorption of alkyl amines and alkyl ether amines on silicate mineral surfaces has been widely reported to follow the hemi-micelle theory suggested by Gaudin, Fuerstenau-Somasundaran in 1957 (Vieira & Peres, 2007). The general agreement from literature was that, the adsorption of amine cations is a result of physisorption at the silicate-water interface where the silicate surface potential is negative in alkaline pH conditions. Amines adsorb on the mineral surface as a result of electrostatic and hydrophobic interaction forces at concentrations lower than the critical micelle concentration. When the amine concentration is high enough in the electrical double layer (critical hemi micelle concentration-CHC), weak van der Waals forces between the hydrocarbon tails of the amines result in the formation of 2D aggregates of collector ions. This point has been associated with a sharp increase in flotation recovery (Smith, Haddenham & Schroeder, 1973; Vidyadhar et al., 2002; Filippov, Severov & Filippova, 2014).

However, the theory has no consideration for specific bonding between the surfactant and the mineral surface and, there is no possibility of surfactant precipitation (Rao, 2004). Chernyshova et al. (2001) and Vidyadhar et al. (2002) in their studies of alkyl amine collector adsorption on quartz surfaces, noted hydrogen bonding between the ammonium ions and silanol groups on the quartz mineral surface which the hemi micelle theory fails to substantiate.

Fourier Transform Infrared Spectroscopic studies carried out by Vidyadhar et al. (2002) in PhD studies, showed that the adsorbed layer in higher pH ranges consisted of a molecular alkyl amine and the alkyl ammonium ions. The authors proposed that the adsorption of the molecular amines on the silanol groups is achieved by charge transfer in the strong hydrogen bond between the nitrogen atom and the silanol group. The adsorption was described as taking place in three stages. At stage 1, ammonium cations are hydrogen bonded with the silanol groups according to Equation 2-7, where the dashed line represents a hydrogen bond.



In stage 2, the molecular amine species begins to appear, hydrogen bonded to the silanol group together with the ammonium cation hydrogen bonded to the deprotonated silanol group, thus producing monolayer patches of a closely packed amine molecules, rendering the surface hydrophobic. This process occurs when the CHC is reached and is two dimensional. The equilibrium established between the amine molecules and cations is represented by Equation 2-8. .



Equation 2-8

By attenuating the electrostatic repulsion forces of the cationic heads in the hemimicelles, in stage 3, the neutral molecules alter the adsorption layer, increasing the density of adsorbed material in the monolayer resulting in a bilayer. This process has been reported to represent three dimensional precipitation. Similar results were observed by Fuerstenau and Jia (2004) and Kou, Tao and Xu (2010). The authors summarised that at low amine concentrations, amine adsorption is characterised by physisorption through electrostatic interactions, at medium amine concentrations, hemimicelles form and there is co-adsorption of cationic species with their molecular species. At high enough concentrations above the CHC, surface precipitation of the neutral molecule occurs on the mineral surface. Figure 2-7 illustrates the adsorption mechanisms in the different stages.

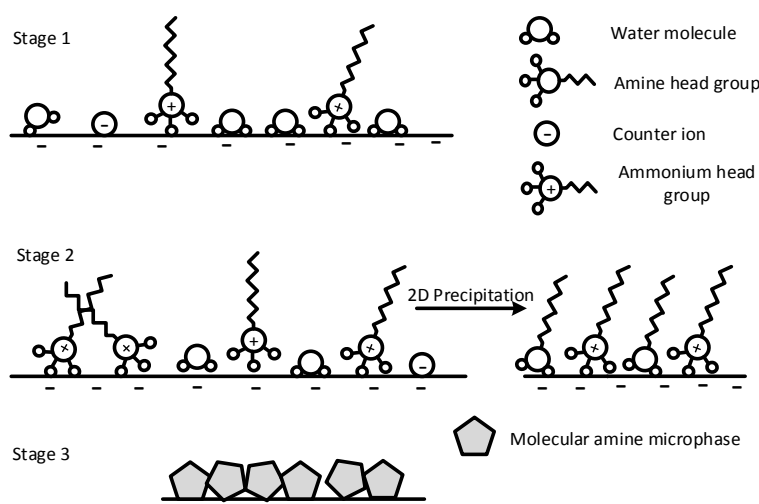


Figure 2-7: Adsorption of alkyl amines on a quartz surface through physisorption and co-adsorption of amine cations and their neutral molecular species (Vidyadhar et al., 2002)

2.6.5. Summary of collector flotation performance in previously studied systems

Papini, Brandao and Peres (2001) conducted batch flotation tests using a range of collectors on an itabirite iron ore with a grind size of 80% passing 149 μm . Results from the study showed that alkyl ether amines were the best quartz collectors in comparison to condensate amines and fatty amines. It was also reported that iron concentrates with lower silica contents were achieved using alkyl ether monoamines in comparison to alkyl ether diamines, suggesting that alkyl ether amines were superior in quartz flotation for the ore under investigation.

These results differ from observations made by (Vieira & Peres, 2007), who observed that the collector performance was also dependant on the particles sizes of the quartz mineral. In their studies on pure quartz flotation, fine quartz responded well to flotation using an alkyl ether

monoamine Flotigam EDA, whereas, medium and coarse sized particles were better floated when using the alkyl ether diamine collector Flotigam 2835, for all pH conditions that were investigated.

Filippov, Filippova and Severov (2010) reported that the alkyl ether diamine collectors used in their studies exhibited better collecting strengths than the alkyl ether monoamine collectors. However, flotation was only conducted on a single particle size range i.e. -53 μm to + 10 μm . The paper did not consider the collectors' performance in the flotation of coarser material.

The differences in quartz recoveries and subsequently the collector performances reported by the authors could stem from the variations in test conditions that were applied in the studies e.g. variations in pH which subsequently affect the nature of the collector species in solution and its effect on quartz recovery. Although the collectors are of the same nature i.e. alkyl ether amines, they were supplied by different manufacturers. Hence, different collecting strengths are expected depending on their proprietary molecular structures. Differences in conditioning time, agitation rate and flotation cell sizes also influence the recovery of the quartz particles. Furthermore, mineral interactions could make the difference in quartz recoveries obtained when floating quartz from a binary mineral system (iron oxide mineral and quartz) in comparison to floating pure quartz.

Vidyadhar et al. (2002) reported on synergistic collector adsorption in the presence of alcohols. Co-adsorption of neutral alcohol molecules with amine cations results in a densely packed surface which is more hydrophobic. Filippov, Filippova and Severov (2010) and (Liu et al., 2015) made similar observations, reaching a similar conclusion.

Vieira and Peres (2007) observed that at pH 9.5 and pH 10, higher quartz recoveries were prevalent than at pH 9. High quartz recoveries at pH 9, equivalent to recoveries at pH 9.5 and pH 10, were mostly achieved at high collector dosages. The high quartz recoveries obtained in this pH range were attributed to the presence of the cationic amine species and their neutral molecular amine species in the system, which reduces electrostatic repulsion between the cationic heads, promoting a densely packed collector coverage on the mineral surface. Work carried out by Chernyshova et al. (2001); Vidyadhar et al. (2002) and Kou, Tao and Xu (2010), revealed the presence of alkyl amine cations and their neutral alkyl amine molecules on mineral surfaces. The phenomena has been well established as the driving force behind the enhanced flotation performance of such collector types.

Yuhua and Jianwei (2005) and Vieira and Peres (2007) studied the effect of pH on the flotation recovery of quartz. Results from both authors agree that the highest quartz flotation recovery is achieved when the system is operated in alkaline conditions. The results corroborated previous findings frequently reported in literature.

Work carried out by Yuhua and Jianwei (2005), also showed that quaternary ammonium salts can yield a sizeable recovery of quartz over a wide pH range i.e. pH 6 to pH 12. The results were of significance as they indicated that quaternary ammonium compounds can be used over a wider pH range in comparison to ether amine collectors which exhibit high collecting strength over a narrower pH range. Work conducted by Vieira and Peres (2007) corroborates results established by Fuerstenau (1957), where high flotation recovery with an alkyl amine collector dodecyl ammonium acetate was observed to occur over a narrow pH range of pH 9 - 9.5

2.7. Polysaccharide Depressants

Polysaccharides are condensation polymers, synthesized from simple monosaccharide sugars (repeat units), forming macromolecules with high molecular weights. Their ability to behave as depressants is attributed to the presence of the glucopyranose ring which hosts OH groups that interact with hydroxylated metal atoms on a mineral surface, rendering the mineral hydrophilic (Turrer & Peres, 2010).

Polysaccharides are potentially sustainable modifiers in the flotation process as they are biodegradable, naturally occurring organic polymers that are nontoxic and oxidation resistant in comparison to inorganic depressants (Liu, Zhang & Laskowski, 2000). The adsorption of the polysaccharides results in the formation of a protective layer around the mineral particles. The layers being hydrophilic, readily interact with the water molecules through hydrogen bonding (Laskowski, Liu & O'Connor, 2007).

Plant practice in South African platinum ore processing plants is to use polysaccharides, namely, carboxymethyl celluloses and guar gums to control the flotation of talc, a naturally floating silicate gangue (Mhlanga, O'Connor & Mcfadzean, 2012). Iron ore beneficiation plants makes use of starch as a hematite depressant in the reverse anionic/cationic flotation of iron ore. The average consumption of corn starches in Brazil around the period of 1996 was 40,000 metric tonnes/year with iron ore processing accounting for 80% of the total usage (Peres & Correa, 1996). A secondary effect of starch is its action as a flocculant in a flotation system (Ravishankar, Pradip & Khosla, 1995).

Amylopectin and amylose present in a starch molecule are responsible for the depression effect imparted to iron oxides by starch. The ratio of the amylopectin to amylose varies depending on the hybrid of corn, however, the most common ratio in corn starch is 3:1 respectively (Pavlovic & Brandao, 2003). Corn starch can be modified through thermal means or via acidic hydrolysis resulting in the conversion of the corn starch to dextrin. Dextrins have the same amylopectin/amylose ratio as corn starch, but lowered molecular weights. They do not bridge into the solution and aggregate mineral particles, hence, dextrins cannot behave as flocculants (Kar et al., 2013).

Guar gums and carboxymethyl celluloses have been proposed as alternative iron oxide depressants. As mentioned before, the performance of these polysaccharides as depressants of hematite could be attributed to the presence of the glucopyranose ring which is equally present in starch molecules (Turrer & Peres, 2010). In the reverse flotation of iron oxide minerals, blending of starches by partially substituting the starch with another molecular species up to one third has also been reported to produce depressant mixtures that are equally as active as a pure starch depressant.

2.7.1. Starch

Starch ($C_6H_{10}O_5$)_n, is a polysaccharide produced from the synthesis of glucose monomers generated via the photosynthesis process (Peres & Correa, 1996). Starch is made up of D-glucose monomers which are cyclic in nature. The monomer rings consist of five carbon atoms and an oxygen atom. Hydroxyl groups within the cyclic rings are located on the C-1 (anomeric hydroxyl group) and C-2, C-3 carbon atoms (secondary hydroxyl groups) as seen in Figure 2-8. The hydroxyl groups are responsible for the polysaccharide's interaction with the mineral surface and the water molecules rendering them hydrophilic.

As has been mentioned, starch consists of two major components i.e. amylopectin and amylose. The amylose, a linear α -D-glucose molecule, is linked via C-1 to C-4 carbon linkage of adjacent glucopyranose units and connected to the branched amylopectin molecule through C-1 to C-6 carbon atoms (Liu, Zhang & Laskowski, 2000). Conformational effects have been shown to influence the water affinity and attachment of starch and modified starches such as dextrin to hematite surfaces (Laskowski, Liu & O'Connor, 2007).

Starches with an oil content greater than 1.5% have been reported to yield lower flotation recoveries. The oils have an inhibiting effect on the depressing of hematite hence the ideal maximum limit of oil in starch should be approximately 1.5% (Peres & Correa, 1996).

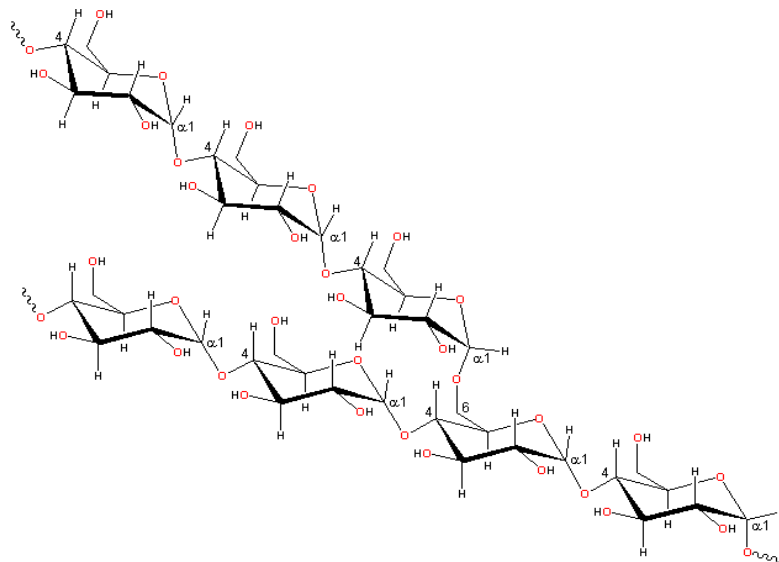


Figure 2-8: The conformational structure of a starch repeat unit (Chaplin, 2015)

2.7.2. Guar

Guar gums are branched polysaccharide molecule classified under the group of galactomannans. Guar gum is made up of a straight chain molecule of β -D-mannoses connected via the C1-C4 linkage and they are connected to the α -D-galactose units through C1-C6 linkage after every two β -D-mannose units (Liu et al., 2000). Guar gums are characterised by activity contents around 90% and low charges because of low degrees of substitution (Wiese, 2009). Guar gums are effective depressants of talc in the flotation of sulphide minerals in platinum ore processing.

Little work has been done on the depressant effect of guar gums on iron oxides. Notable investigations by Turrer and Peres (2010) reported that the guar gum tested in the reverse flotation of a hematite rich ore, yielded a significant recovery of iron in the iron concentrate. Figure 2-9 shows the structure of a typical guar gum monomer unit.

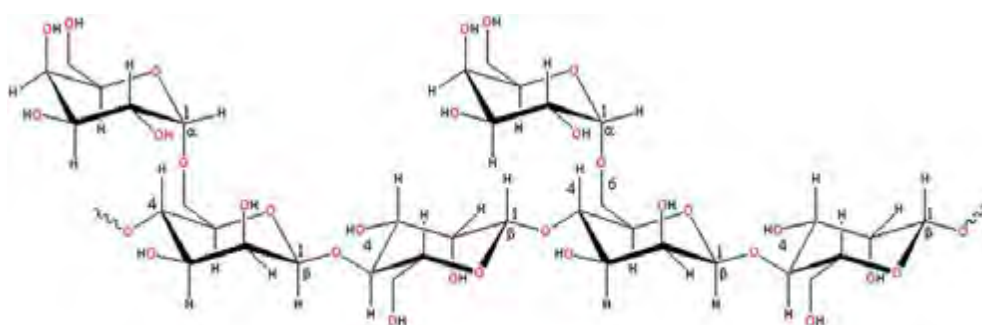


Figure 2-9: The conformational structure of guar gum repeat unit (Chaplin, 2015)

2.7.3. Carboxymethyl cellulose (CMC)

Carboxymethyl celluloses are modified polysaccharides, produced as a result of the etherification of the plant polysaccharide, cellulose. Their base unit is a D-glucose monomer. Etherification introduces new functional groups, carboxylates (COO^-), substituting the OH groups that are attached to the C-2, C-3 and C-6 carbon atoms in the glucose ring. The OH groups vary in their reactivity, with the reactivity following the order of C-6 > C-2 > C-3 (Laskowski, Liu & O'Connor, 2007). Carboxymethyl cellulose molecules possess a strong negative charge due to the presence of carboxylates and they have activity ranging around 70% (Wiese, 2009). The degree of substitution, DS is essentially the number of substituted functional groups in a monomer. Theoretically the maximum degree of substitution for CMC is 3, where all the hydroxyl groups are exchanged for carboxymethyl groups. Practically, the DS is less than 1 or around the value of 1. CMCs with lower DS values are less negatively charged (Liu, Zhang & Laskowski, 2000; Wiese, 2009). In iron ore reverse flotation, CMCs have promising iron oxide depressant capabilities. High recoveries of iron with a low silica content have been noted after employing CMCs as depressant, however, the economic viability of using CMCs is substantiated only if the depressant dosages are 1/5 to 1/10 of the starch dosage (Araujo, Viana & Peres, 2005). Figure 2-10 shows the conformational structure of CMC.

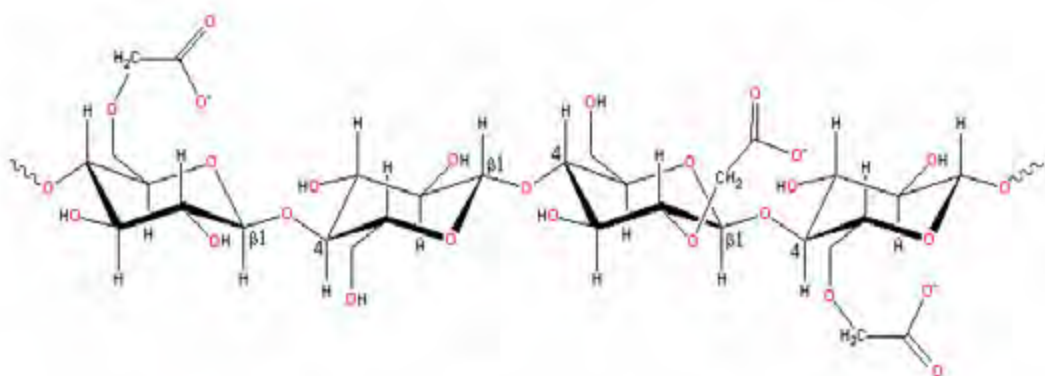


Figure 2-10: Conformational structure of carboxymethyl cellulose repeat unit (Chaplin, 2015)

2.7.4. Adsorption mechanisms of polysaccharides

Earlier literature proposed that hydrogen bonding and hydrophobic interactions were responsible for polysaccharide adsorption on to the mineral surface (Weissenborn, Warren & Dunn, 1996; Wiese, 2009). However, results by Liu, Zhang and Laskowski (2000) showed that the adsorption density increased on quartz surfaces doped with lead ionic species and the adsorption was dependent on the pH of the system. The authors inferred that the strong dependence of adsorption on pH was from the interaction of natural polysaccharides with metal-hydroxylated species which themselves are dependent on pH. Weissenborn, Warren and Dunn (1996) studied complexing reactions between amylopectin and iron (III) solution. The results

also showed a strong interaction between the amylopectin and the iron (III) solution. From these results, it was suggested that a similar interaction between amylopectin and hematite was possible since the mineral also possesses hydroxylated iron cations when in aqueous solution at the right pH.

The mineral surface behaves as a Bronsted base, giving away an –OH group whilst the two OH groups on the C-2 and C-3 carbon atoms of the polysaccharide behave as Bronsted acids giving away a proton. The strength of the acid /base interaction determines whether the bonding on the mineral surface is due to hydrogen bonding or due to chemical complexation. Strong acid/base interactions have been linked to chemical complexation whereas weak acid/base interactions infer that the bonding is based on hydrogen bonds (Liu, Zhang & Laskowski, 2000).

2.7.5. Depressant flotation performance in previously studied mineral systems

From experimental results collated by Filippov, Filippova and Severov (2010), the flotation recovery of quartz and pargasite was decreased by the introduction of starch into the system. The authors suggested that silicates imbedded with hematite atoms interact with starch in a similar manner to iron oxides. These observations were supported by Sahoo et al. (2016).

Kar et al. (2013) reported that in reverse cationic flotation, the grade of the iron concentrate decreased after a certain depressant dosage. High depressant dosages resulted in the depression of quartz, subsequently reducing the iron concentrate's grade. The flocculation effect from starch results in the agglomeration of quartz particles, rendering them too heavy to report the froth zone through bubble transportation.

On the contrary, Lima, Valadão and Peres (2013) observed that high starch dosages had little to no effect on the flotation of quartz. Upon increasing the amine dosage from 150 g/tonne to 250 g/tonne, when floating a coarse itabirite ore sample (-150+45 μm), the percentage of SiO_2 in the hematite concentrate increased from 1.18% to 3.81%. Increase in starch dosage from 500 g/tonne to 1000 g/tonne had an insignificant change in SiO_2 content in the hematite concentrate. Instead, increasing the collector dosage at a constant starch dosage resulted in the depression of some quartz in the coarse particle size range. The interaction between the ionic amine species and the unabsorbed residue starch molecules was reported to be responsible for depressing quartz material. The authors, therefore, failed to agree on the extent of the flocculation effect on quartz particles as well as whether the quartz was getting depressed by starch or it was rather composite particles being depressed.

Limited research has been carried out with regards to investigating the use of alternative hematite depressants in reverse iron ore flotation. Turrer and Peres (2010), investigated reverse cationic iron ore

flotation using starch, six carboxymethyl celluloses, three lignosulphonates, one guar gum and four humic acids. The experimental results showed that most of the depressants were not selective and there was a high silica content in the iron oxide concentrate. Only one carboxymethyl cellulose (CMC5), one guar gum and starch yielded iron concentrates with quartz contents less than 2.5 % and the iron recoveries in the concentrates above 40%.

Essentially CMCs have been proved to be alternative starch depressants. Araujo, Viana and Peres (2005) investigated CMCs with different degrees of substitution on ore from the Iron Quadrangle, Brazil. All CMCs under investigation yielded concentrates with lower quartz concentrations than starch, however, the froth product had slightly more Fe. These authors suggested that, at the prevailing prices at the time, in order to consider using CMCs and guar gums as alternatives to starch, their dosage should be reduced by a factor of 5-10 and still achieve the same separation efficiency as starch.

Pavlovic and Brandao (2003) also investigated the adsorption of starch, amylose, amylopectin and a glucose monomer on hematite as well as their effect on the flotation of quartz from hematite. All the carbohydrates were successful at depressing the hematite. However in the presence of amines, there was a mild flocculation effect on quartz, decreasing the flotation of quartz when amylopectin was used as the depressant. This flocculation effect observed with amylopectin and not the other carbohydrates could be attributed to the shear depressing strength of the amylopectin as it is a stronger depressant than all the carbohydrates that were employed.

2.8. Summary of Literature Review

Previous studies on amine collectors' behaviour and interactions of the collectors with silicate and quartz mineral surfaces have been well documented in literature. However, the continual introduction of new collectors with different molecular structures and the variations in ore mineralogy and textures from different geographical locations, prompts a recurring need to study collector performance on the removal of quartz from iron bearing minerals.

The main focus of the reviewed literature was on the adsorption mechanisms of the collectors on mineral surfaces, collector performance with regards to the selectivity of the collectors as well as the effects of collectors and depressants on the iron grade and recovery after flotation.

It can be suggested that there is still no concrete conclusion on which collectors are superior in the flotation of quartz. A conservative conclusion could be that the flotation of quartz using amine collectors is affected by the particle size, pH and interactions of the amines with the mineral surface as well as the mineralogy of the ore sample. The amine collector's molecular chemistry alone is not sufficient in predicting or explaining the flotation response of a mineral

system. The flocculation effect of starch is debatable and experimental procedures should consider that reagent interactions could promote the depression of quartz particle

2.9. Hypotheses

Based on the objectives and previous work in the field, the following hypotheses have been postulated:

- Ether amine collectors exhibit better flotation performance than quaternary amine salts because ether amines are densely adsorbed on a quartz surface, through hydrogen bonding and co-adsorption of cations with their neutral molecules, thereby, reducing electrostatic repulsion of cationic heads. Quaternary salts adsorb by physisorption resulting in electrostatic repulsion between cationic heads and a lower collector coverage on a quartz surface.
- Polymeric depressants (CMCs and guar gums) or blends of starch with these depressants can be used as depressants of hematite in the reverse flotation of iron ore because of the presence of the glucopyranose ring in the depressants which interacts with the hydroxylated iron cations on an iron oxide surface.

2.10. Key Questions

To test the aforementioned hypotheses, the following questions have to be answered:

1. Does the collector type affect the flotation recovery of quartz and the entrainment of hematite fines?
2. What are the pKa values of the three alkyl ether amine collectors under investigation?
3. Does the depressant type and dosage affect the recovery and grade of hematite recovered from the tailings, hence how efficient is the depressant in comparison to starch?
4. How does the ore mineralogy and texture influence the flotation recovery of hematite?

3. Experimental Procedure

3.1. Experimental Equipment

The standard batch flotation procedure makes use of two major pieces of equipment, viz, the mill and the batch flotation cell. These will be described in detail in this section, however, equipment used in other experiments conducted as part of this research, will be explained together with the associated experimental technique.

Rod mill: A rod mill was used to establish the milling curves and the subsequent milling of the minerals to the required grind size. A 1 Kg rod mill was charged with six (285 mm × 16 mm) rods, eight (285 mm × 20 mm) rods and six (285 mm × 25 mm) rods. The rod mill employed wet milling and allowed a capacity of 1kg of ore to be fed in at a solid concentration of 66 %.

Batch flotation cell: The flotation cell used in this study was a 3 litre Leeds flotation cell. It consists of a Perspex flotation cell making it possible to visually observe and maintain the pulp level in the cell, allowing a constant froth height to be obtained. The cell is connected to an air supply and fitted with an impeller. Air supply was controlled using the rotameter and the impeller speed was controlled using a digital tachometer.

3.2. Ore preparation

The South African iron ore used in this study was sourced from Anglo American Technical Solutions. The ore was received as a bulk mixture of fine particles, coarse sized particles and large chunks of ore. The ore was screened in order to separate the fine materials from the coarse particles. Thereafter, the coarse particles were further crushed to smaller particles using a cone crusher to a particle size of approximately 3 mm. Large rocks were broken down in a jaw crusher before being fed to a cone crusher for further particle size reduction. The ore was blended, riffled and split into 1kg bags in order to acquire a representative ore sample which reduces the degree of the standard error in repeated readings. The splitter used was manufactured by Dickie and Stockler. The Brazilian iron ore employed in the study was received from Vale Mineral Resources as a milled sample. The ore was also blended, riffled and split into 1 kg bags.

3.2.1. Milling curves and Particle size distribution curves

A feed ore (South African iron ore or pure quartz) weighing 1 Kg in mass was milled in the rod mill described in Section 3.1. Wet milling was conducted using tap water at 66 % solids density. An initial grind size of 80 % passing 150 μm was chosen as literature suggests that at this grind size, most of the quartz and hematite are liberated (Araujo et al., 2003). The required milling time for the South African iron ore and the pure quartz sample, to achieve a grind size of 80 % passing 150 μm , was obtained from the milling curve illustrated in Figure 3-1.

Fine grinding was initially not considered due to the undesired and inevitable slimes generation linked with fine grinding. As seen in Figure 3-3, the initial grind size i.e. 80 % passing 150 μm , produced a mill product constituting of 40 % fine material below 25 μm . The fine material complicates froth control as fines have a strong stabilising effect in the froth zone in addition to contributing to iron losses through entrainment. However, as will be noted in Chapter 4, there was a failure to achieve any selective separation after reverse flotation in the Leeds batch flotation cell at the initial grind of 80 % passing 150 μm . This prompted a move to finer grinding (90 % passing 75 μm), in conjunction with column flotation. Fine grinding was employed in an attempt to liberate more quartz and hematite. The milling curve shown in Figure 3-2 was required to achieve a grind size of 90 % passing 75 μm . After fine grinding the South African iron ore, the fines (-25 μm) content in the milled product had increased to 60 % as shown in Figure 3-3.

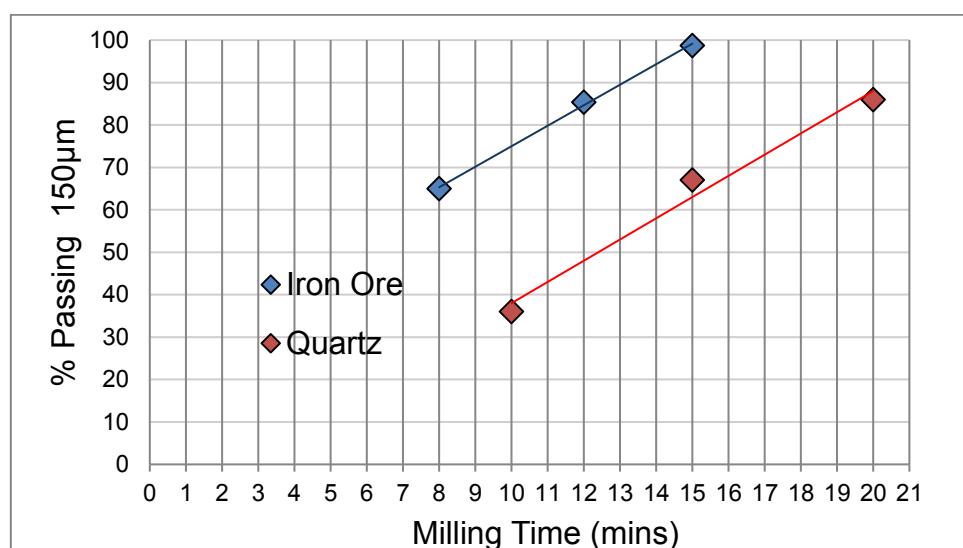


Figure 3-1: The milling curve for the South African iron ore and pure quartz mineral, achieving a grind size of 80 % passing 150 μm .

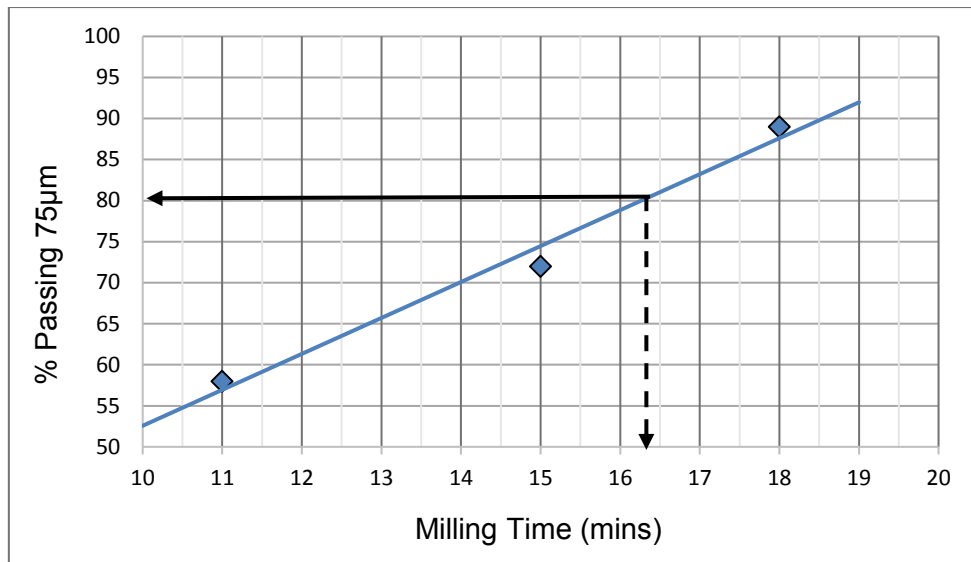


Figure 3-2: The milling cure for the South African iron ore after fine grinding to 90 % passing 75 µm

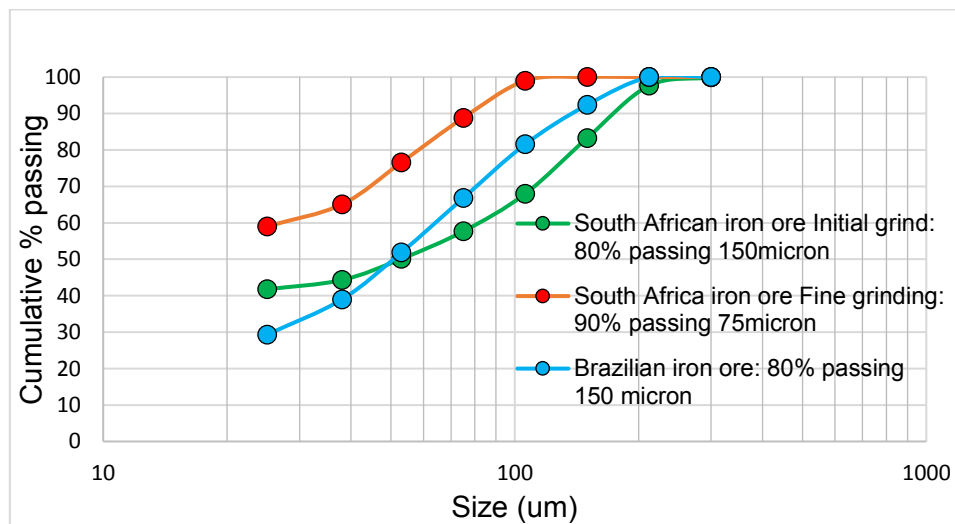


Figure 3-3: The Particle Size Distribution of the mill product. Milling times are determined by the milling curve.

A Brazilian iron ore was used in the flotation studies for comparison. As has been mentioned, the Brazilian iron ore was received as a milled and deslimed ore with a grind size of 80 % passing 150 µm. In an attempt to generate more fine material so that the ore has almost similar fine material contents to that in a South African iron ore, the Brazilian ore was wet milled at 66 % solids density using a rod mill, for a period of 3 minutes. The resultant PSD is illustrated in Figure 3-3. It can be seen that after milling, the Brazilian iron ore had a slightly lower slimes content in comparison to the South African iron ore, however, the milled Brazilian iron ore’s PSD and the South African iron ore’s PSD (grind size 80 % passing 150 µm) were almost similar, hence, their use in a comparative study.

3.3. Mineralogical Characterisation

The mineralogical characterisation of the mill product (flotation feed) was carried out using a QEMSCAN (Quantitative Evaluation of Minerals by SCANNing electron microscopy) instrument located in The Centre for Minerals Research Laboratories at UCT. QEMSCAN is a versatile analysis technique developed by CSIRO in Australia (Pascoe, Power & Simpson, 2007; Wiese, 2009). The system operates by identifying particles in an ore sample which are subsequently scanned with an electron beam. The back scattered electron signals are then compared with a library of known minerals i.e. the Species Identification Program (SIP) list, producing a mineralogical identification (Pascoe, Power & Simpson, 2007).

The SIP determines how the elemental information measured by the scanning electron microscope (SEM), is classified into a mineralogical composition or species. The SIP consists of a list of entries (SIP definitions), each with a set of user-specified criteria to match the X-ray spectra and Back Scatter Electron (BSE) data from a measurement point to a mineral species. As each point on a sample is scanned, its spectrum is converted to element information which is compared to the entries in the SIP list until one is found with parameters matching the scanned material. If the elemental information does not match any of the SIP definitions, the pixels are grouped into the “unclassified” SIP definition at the bottom of the list.

A comprehensive set of data can be extracted from the QEMSCAN machine. Relevant data includes, mineralogical liberation and association data, elemental department and mineralogical mapping of the sample ore (Becker et al., 2009). Elemental analysis of the mill product and the concentrates obtained after flotation was carried using a Panalytical Axios Wavelength dispersive XRF machine.

3.3.1. Feed ore Mineralogical Analysis

3.3.1.1. Vertical Sections preparation

A standard sample preparation procedure was used in the preparation of vertical sections for QEMSCAN analysis. A 250 g sample of milled iron ore was screened using dry and wet screening methods. The sample was split into seven particle size classes defined by the PSD as represented in Table 3-1.

Table 3-1: Representative size classes for QEMSCAN analysis

Sample No	Size class
1	+150 μm
2	-150 μm +106 μm
3	-106 μm +75 μm
4	-75 μm +53 μm
5	-53 μm +25 μm
6	-25 μm +10 μm
7	-10 μm

The split samples were used in the preparation of polished vertical section blocks. Hematite is a dense mineral which settles to the bottom of a conventional QEMSCAN block, instead of the mineral being evenly spaced throughout the block. To avoid mineral settling and improve the quality of results from analysis, vertical sections are preferred. The detailed preparation of the blocks is provided in Appendix A1.

3.3.1.2. QEMSCAN Analysis and Validation

The Field Emission Gun (FEG) QEMSCAN 650F equipped with high resolution back scattered electron (BSE) detectors, energy dispersive x-ray spectroscopy (EDS) detectors and a spectral analysis engine was used in analysing the feed iron ore samples. Figure 3-4 shows the QEMSCAN machine that was employed in the study at the University of Cape Town. The Particle Mineral analysis method (PMA) was used to analyse the samples. The method was chosen as it gives detailed particle mineralogical information. PMA aims to provide data on liberation, association and locking characteristics of a mineral sample (Solomon, 2010). Minerals stereology (particle and grain size) and touching particles were analysed using the machine.

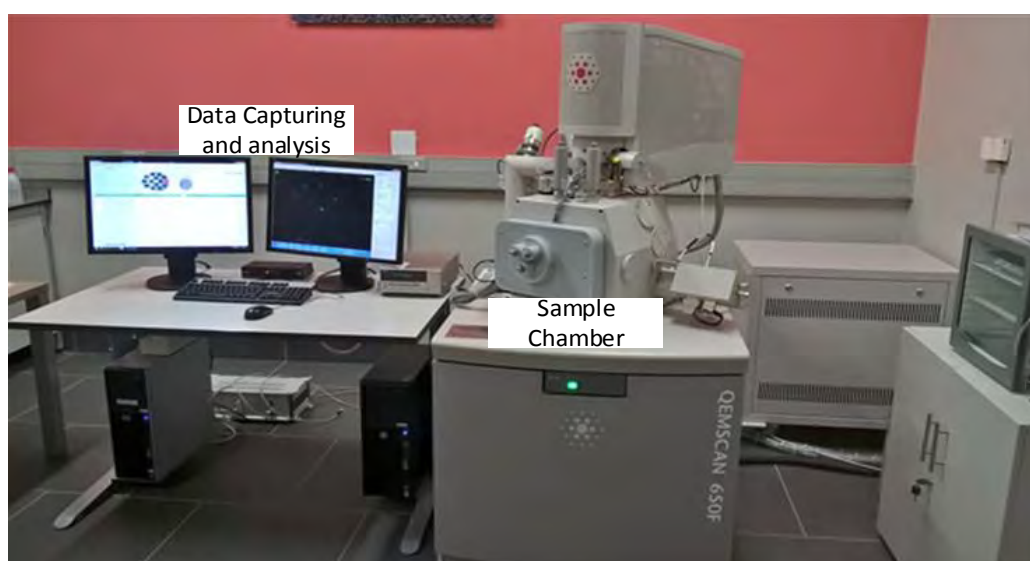


Figure 3-4: QEMSCAN 650F machine located in the Chemical Engineering Department (University of Cape Town). Data analysis can be simultaneously carried out using the i-explorer software.

Data validation was carried out as a quality control procedure for the South African iron ore and Brazilian iron ore. The calculated QEMSCAN assays were compared to the bulk chemical compositions assays obtained using X-ray fluorescence spectroscopy. A graph of QEMSCAN assays against chemical assays for the South African iron ore was plotted as illustrated in Figure 3-5. In the study of a South African iron ore, for the four size fractions that were analysed, there is a fairly satisfactory correlation between the QEMSCAN results and the chemical assays as the data points lie close to the line $y=x$. Similar observations were made for the Brazilian iron ore.

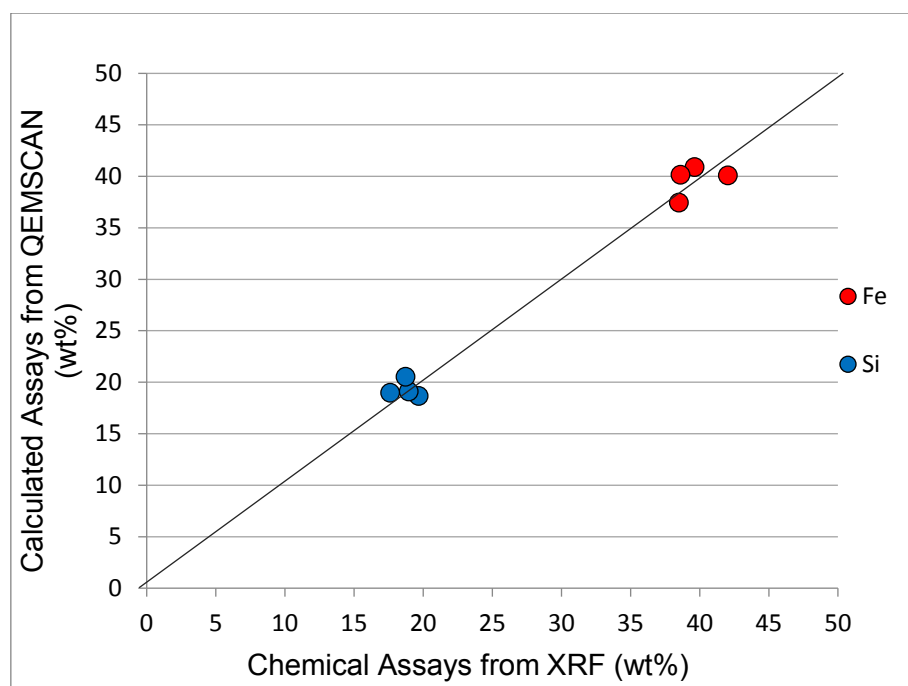


Figure 3-5: Parity chart for Data validation of QEMSCAN assays and chemical assays

3.4. Flotation reagents

Five different amine collectors from Clariant Chemicals, widely used in the reverse flotation of iron and phosphate bearing minerals, were employed in the first phase of the study, together with a standard starch depressant. A frother was used in the conjunction with the quaternary alky amine and imidazoline quaternary salt since characterisation tests in this study established that the collectors have poor frothing properties. A base case collector dosing strategy was employed following standard industrial flotation dosing procedures. A base case depressant dosage was established from previous literature studies by (Rocha, Canado & Peres, 2010), where it was reported that high slimes contents required depressant dosages between 1000 g/t and 1500g/t. Furthermore, analysing the solids mass as a function of water recovery, allowed the identification of a depressant dosage that minimises solids recovery in the froth zone due to entrainment. The reagent suite for phase one of the experimental work is shown in Table 3-2.

Table 3-2: The reagent suite used in phase one of the experimental work

Reagent name	Chemical Group	Supplier	Dosage (g/t)	Reagent Type
Flotigam EDA Ether monoamine	Alkyl ether amine, DON*: 48 % - 52 %	Clariant	125	Collector
Flotigam 3135 Ether diamine 1	Alkyl ether amine, DON*: 33 % - 37 %	Clariant	125	Collector
Flotigam 2835-2L Ether diamine2	Alkyl ether amine, DON*: 18 % - 22 %	Clariant	125	Collector
Flotigam K2C QAS	Quaternary ammonium salt	Clariant	125	Collector
Flotigam ITU Imidazoline salt	Imidazoline quaternary salt	Clariant	125	Collector
Starch	Polysaccharide	Sigma-Aldrich	1500	Depressant
Montanol 800	Alcohol	Clariant	60	Frother
MIBC	Alcohol	Akzo Nobel	60	Frother

DON* = Degree of neutralisation

Table 3-3: Detailed summary of molecular structures of collectors and frother used in the flotation studies

Compound name	Molecular name	Chain length & Chain structure	Molecular Formula
Flotigam EDA Ether monoamine	Alkyl ether monoamine	C8-C10 branched	R-O-(CH ₂) ₃ -NH ₂
Flotigam 3135 Ether diamine 1	Alkyl ether diamine	C8-C10 branched	R-O-(CH ₂) ₃ -NH-(CH ₂) ₃ -NH ₂
Flotigam 2835-2L Ether diamine 2	Alkyl ether dipropylene diamine	C12-C15 linear	R-O-(CH ₂) ₃ -NH-(CH ₂) ₃ -NH ₂
Flotigam K2C QAS	Dimethyl dicoco alkyl ammonium chloride	C8-C18 branched, linear	$\begin{array}{c} \text{CH}_3 \\ \\ \text{R} - \text{N}^+ - \text{R} + \text{Cl}^- \\ \\ \text{CH}_3 \end{array}$
Flotigam ITU Imidazoline salt	1-amino-2-alkyl imidazoline acetate	C15-C17	
Montanol 800	Hexanol & 2-ethyl hexanol	C6 linear	CH ₃ -(CH ₂) ₅ -OH & C ₈ H ₁₈ O
MIBC	4-methyl 2-pentanol	C5 branched	C ₆ H ₁₄ O

Based on the performance of the amine collectors in the flotation of quartz from hematite in phase 1 of the study, the best operating collector was chosen. The best performing collector was then applied at a constant dosage of 125 g/t whilst varying the type of hematite depressant and depressant dosage in the second phase of experiments. Three depressant dosages i.e. 250 g/t, 500 g/t and 1500 g/t were applied. Table 3-4 shows the main characteristics of the two alternative hematite depressants that were investigated.

Table 3-4: Characteristics of the polysaccharide compounds used as alternative hematite depressants

Reagent name	Chemical Group	Molecular Weight (g/mol)	Purity	Degree of Substitution
KU9	Guar gum	503 709	86.3 %	-
Depramin 267	CMC	353 759	73.3 %	0.71

3.4.1. Collectors

A 1 % collector solution was prepared by adding 1 g of collector to a previously weighed 150 ml beaker. 100 g of distilled water was added to the beaker which was set on a magnetic stirrer. The agitator was switched on to allow mixing and agitation was conducted until a homogeneous mixture was attained.

3.4.2. Depressants

A 2 % starch solution was prepared by adding 2 g of starch to a previously weighed 150 ml beaker. About 20 ml of distilled water was added to the beaker and the starch/water mixture was placed on a magnetic stirrer. 5 ml of 10 % NaOH was added to the beaker and the mixture was agitated until gelatinized. Distilled water was then added to the beaker placed on a balance, making up 100 g of solution.

1 % solutions of the CMC and guar gums were prepared by hydrating the required amount of polysaccharide powder in distilled water over a magnetic stirrer for approximately two hours.

3.5. Scoping Tests to explain the flotation behaviour of the South African ore

As will be discussed in Chapter 4, the South African iron ore was not amenable to batch flotation. Additional tests were conducted in order to establish the cause of the poor flotation behaviour. The scoping tests and their objectives are summarised in this section.

Flotation of pure quartz: This test was an attempt at decoupling the binary mineral system by focusing on the flotation of a simpler single mineral system. The successful batch flotation of pure quartz using cationic amine collectors is well documented in literature. Thus, the objective of this intervention study was to observe whether pure quartz, without possible interference from hematite, would respond well to batch flotation using the amine collectors employed in this study.

Mineralogical Characterisation of the iron ore: The bulk mineralogy and liberation of the hematite and quartz in the South African iron ore were established using the QEMSCAN instrument. The liberation data was useful in assessing whether the quartz and hematite had been liberated enough for the reagents to effectively interact with the liberated surfaces.

Fine grinding and Hybrid column flotation: Fine grinding was employed in an attempt to improve the liberation of the hematite and quartz. Reverse flotation was conducted in a hybrid cell, equipped with a batch and column section (see section 3.6.1). The aim of this tests was to recover a higher hematite grade whilst reducing iron losses through entrainment. Wash water added to the column section of the cell was required to wash the hematite fines back to the pulp zone thereby reducing the entrainment of hematite and minimising hematite losses.

3.6. Batch Flotation Procedure

All the batch float tests were conducted in the 3 litre Leeds flotation cell described earlier in Section 3.1. An illustration of the flotation cell is presented in Figure 3-6.

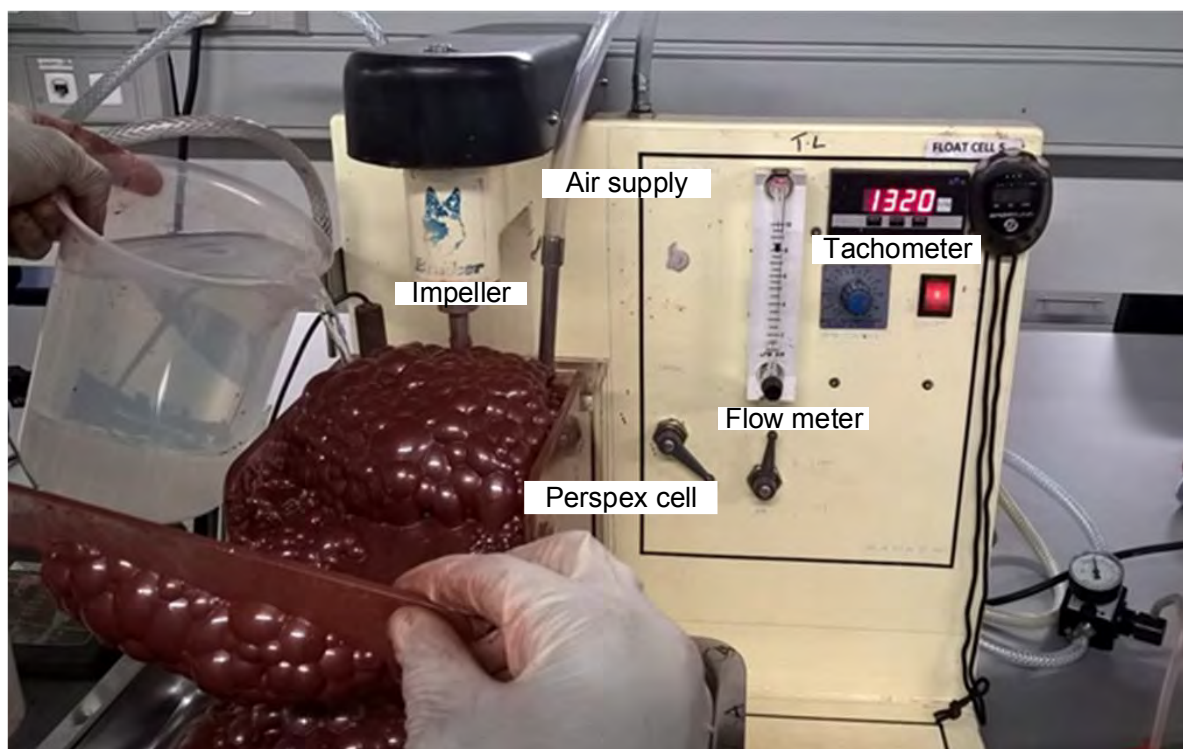


Figure 3-6: The 3 Litre Leeds flotation cell modified at UCT.

A feed ore weighing 1 Kg in mass was milled in the rod mill as described in Section 3.2. After obtaining the required grind size, determined from the milling curve, the mill product was transferred from the mill to the flotation cell. At this point, a weighed amount of City of Cape Town water was added to the flotation cell to ensure a 50 % solids density in the slurry mixture. The flotation cell's rotor was switched on and its speed was adjusted to the desired rotation speed of 1300 rpm. All conditioning with reagents took place at the above mentioned solids concentration. Before adding any reagents, the slurry was conditioned for 1 minute and the natural pH was noted to be approximately pH 7.

Freshly prepared starch, gelatinized with sodium hydroxide in a weight ratio of 4:1, starch: sodium hydroxide respectively, was added to the slurry. The slurry was then conditioned for 5 minutes and during conditioning, the pH was adjusted and maintained at pH values between 9 and 10.5, depending on the pKa values obtained for each collector used in the tests. The pH modification was carried out using a 5 % NaOH solution. This was followed by the addition of a cationic collector and pulp conditioning for 2 minutes. In the cases where a frother was required i.e. when the quaternary salts Flotigam K2C and Flotigam ITU were used as collectors, a frother was added and the slurry was conditioned for a further 2 minutes.

After conditioning, water was added to make up to the 3 litre mark indicated on the Perspex cell and subsequently this reduced the pulp density to 25 %. The air supply was opened and air was fed to the system at a flowrate of 7 L/min. As soon as the foam started to form, collecting began at a constant collecting rate. Five concentrates were collected during the reverse flotation of the South African iron ore at the following times: 30 seconds, 1, 2, 5 and 9 minutes, after air was introduced into the flotation cell. Four concentrates were collected when floating quartz from the Brazilian iron ore and during the flotation of a pure quartz mineral. The collection was at 30 seconds, 1, 2 and 5 minutes.

A constant froth height was maintained and this was achieved by water addition, maintaining a certain water level marked on the Perspex cell. In order to maintain the pH at the desired value, the water added to maintain the pulp level was also at the system's desired pH. The batch flotation tests were carried out in duplicate to account for reproducibility. After flotation, the froth concentrate and the sinks were vacuum filtered and dried at 80 °C for 12 hours. After complete drying, the masses of the floats and sinks were determined. *Table 3-5* summarises the procedure followed in the execution of batch flotation tests.

Table 3-5: Batch flotation procedure summary

Procedure	Time (minutes)	
Milling	11 (from milling curve)	
Depressant	t = 0	
Collector	t = 5	
Air switched on	t = 7	
	South African ore	Brazilian ore / quartz
C1	t = 7.5	t = 7.5
C2	t = 8	t = 8
C3	t = 9	t = 9
C4	t = 12	t = 12
C5	t = 16	

** Where a frother was required, conditioning was carried out for two minutes following the addition of a frother.

A hybrid mechanical-column cell adapted from Harris, O'Connor and Stonestreet (1992), was used in tests to assess the effectiveness of grinding the South African iron ore to finer particle sizes. It was thought that the increased froth depth would assist in drainage of the entrained fine hematite particles. The hybrid cell shown in Figure 3-7, consists of a 7 cm diameter column attached via a conical adaptor to a Leeds batch flotation cell. The column section is 20 cm in length and the batch section is equipped with an impeller and stator, an air inlet port and slurry

inlet and outlet ports. A rotameter is also fitted to regulate the air flowrate and a tachometer for monitoring the impeller's rotational speed. The agitated section serves to suspend solids in the cell and allow equal collection time of particles in the collection zone (Harris, O'Connor & Stonestreet, 1992). Wash water for froth cleaning was provided through a water dispenser which was mounted 5 cm above the top of the column.

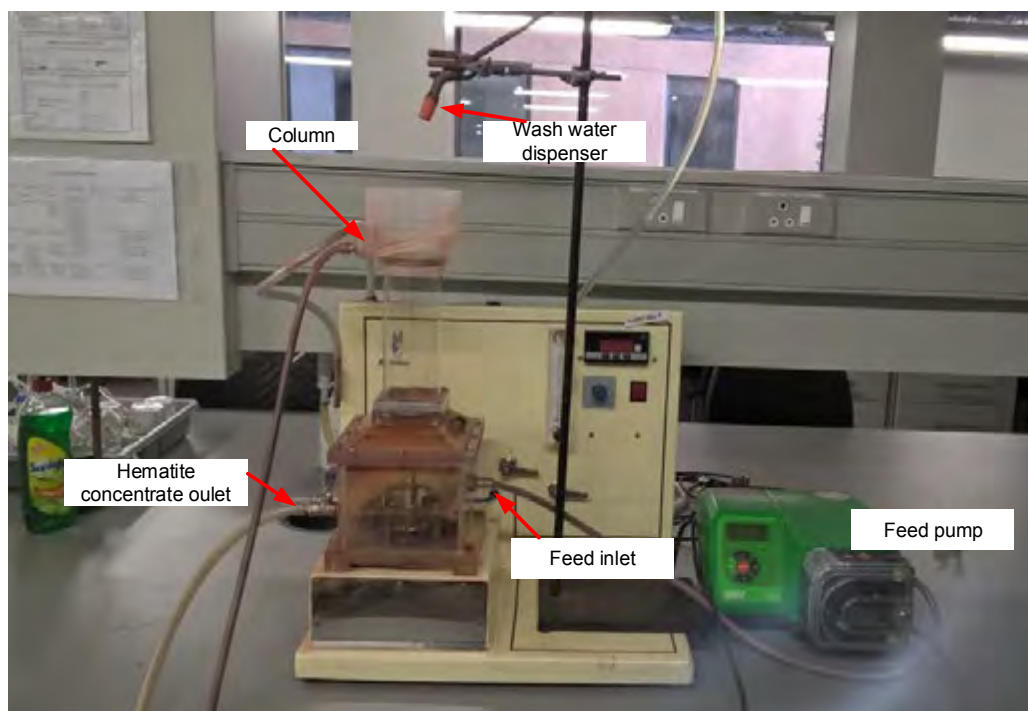


Figure 3-7: Hybrid cell equipped with a Leeds batch cell attached to a 7 cm diameter column

3.6.1. Hybrid column flotation procedure

Tests were initially conducted in order to establish feasible operating conditions for the hybrid cell. From visual observations of the column cell, at a pulp density of 25 %, a thick, viscous and immobile froth formed, possibly due to the high content of fine material which strongly stabilised the froth. The slurry density was then reduced from 25 % to 12.5 % resulting in a more controllable froth. However, this solids concentration is far from the industrially accepted pulp density of 25 % - 30 %. Wash water flowrate was also varied in order to establish a flowrate which allowed solids mass recovery in addition to maintaining a visible collection/froth zone interface.

A 1kg sample of ore was wet milled using a rod mill as described in the preceding sections. The ore was then transferred to a 20 litre bucket (feed tank) where 7 litres of water were added to make a slurry of 12.5 % solids density. An impeller was placed in the bucket to allow mixing of the slurry. As this column flotation was merely a scoping procedure, only two collectors i.e. EDA (ether monoamine) and K2C (quaternary ammonium salt) were used. The necessary

reagents [collector, depressant and (frother for K2C)] with the same dosages to those added in Section 3.5, were added to the tank and the slurry was conditioned. The slurry was then pumped from the feed tank into the batch cell section of the hybrid cell at a feed rate of 0.5 L/min, in order to achieve a residence time of 4 minutes. The Leeds cell agitation rate was set at 1300 rpm. Air at a flowrate of 4 L/min was then introduced into the system.

As the froth rose up the column, the wash water was introduced at 200 ml/min. The system was run, in closed circuit until near steady state conditions were achieved. The tails outlet was not connected to a pump, therefore, the outlet stream was manually used as a control parameter for the position of the interface throughout the experiment. After 1.5 residence times, the tails and concentrates were simultaneously collected for a period of 9 minutes at near steady state conditions. The tails and concentrates were oven dried at 80 °C overnight. XRF spectroscopy was used to analyse the Fe content in the concentrates and tails. All experiments were carried out in duplicate to account for experimental errors.

3.7. pKa measurements

Increasing the pH of a dissociated amine solution to basic conditions results in the equilibrium of Equation 3-1 shifting to the right.



pKa measurements were performed in order to obtain the pH at which the amine collectors would be 50% dissociated as per definition of the pKa. At that pH, literature suggests that a high flotation recovery is observed. A potentiometric titration curve, together with analysis by calculus i.e. the first derivative technique were used to obtain the pKa values of the alkyl ether amine collectors. It should be noted that, due to the quaternary ammonium salt and the imidazoline quaternary salts' full dissociation at all pH values, the collectors did not respond to the pKa measurement. As a result, the pKa values for these collectors could not be established.

A solution of 0.05 M HCl acid was gradually added to 25 ml of a 1 % amine collector solution until the solution's pH was at pH 1.5. At this point, 0.05 M of NaOH solution was titrated into the collector solution in aliquots of about 0.5 ml noting the new pH after the addition of each aliquot of NaOH. When the pH remained constant, 1 ml aliquots of the 0.05 M NaOH solution were added, once again checking the pH of the amine solution. As the pH began to rise, aliquots of 0.5 ml were once again added up until a pH value of 12 was reached.

A graph of pH against the volume of NaOH added was plotted as shown in Figure 3-8. The pKa lies within the buffered region. To determine the approximate value of the pKa, a graph of $\Delta\text{Volume (NaOH)} / \Delta\text{pH}$ against pH was also plotted as illustrated in Figure 3-9. The point

on the pH axis where there is a maximum slope in the curve of $\Delta\text{Volume (NaOH)} / \Delta\text{pH}$ against pH represents the pKa.

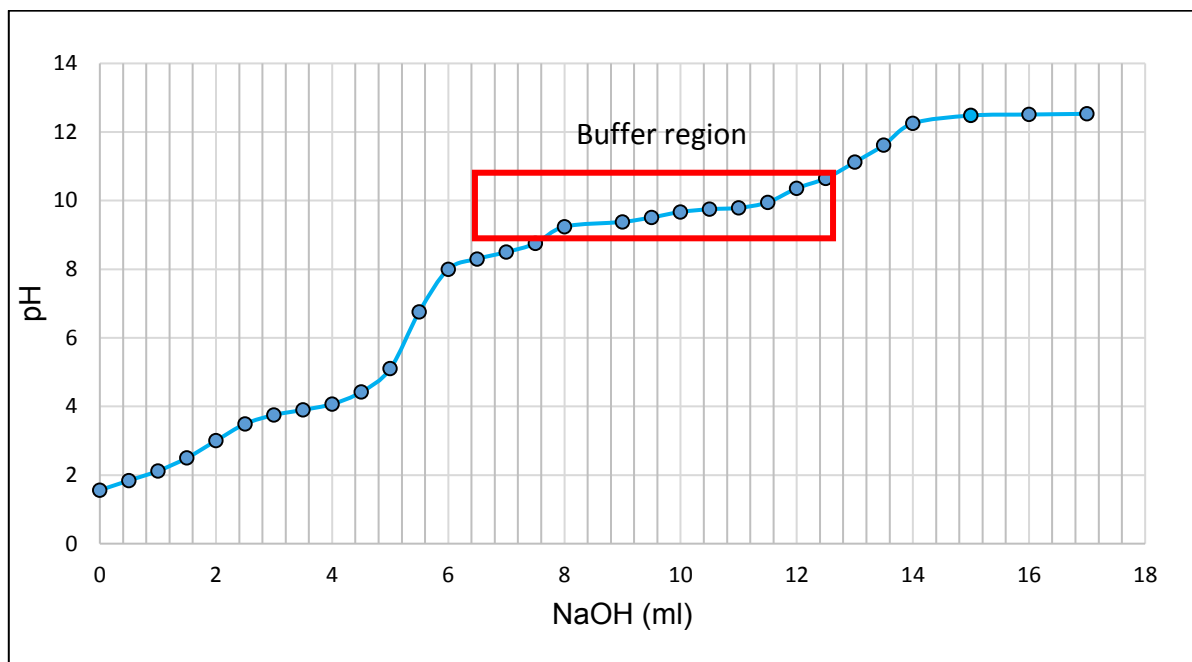


Figure 3-8: A potentiometric titration curve for the Flotigam EDA collector. The pKa value, lies within the buffer region marked by the red square.

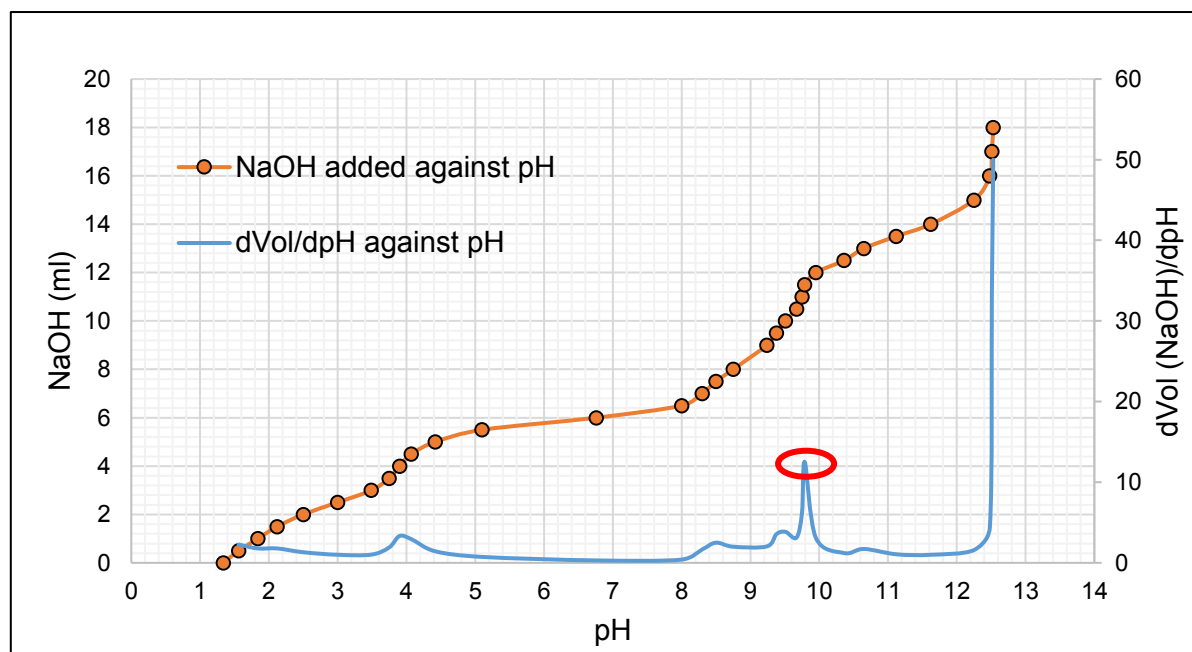


Figure 3-9: Establishing the pKa value of EDA using the first derivative method. The peak encircled in red indicates the pH equivalent to the pKa which lies in the midpoint range of the buffer region.

3.8. Surface tension measurements

Dynamic surface tension measurements were performed with the intention of assessing the surface activity of the collectors under investigation. The surface tension measurements were carried out using the Kruss K12 tensiometer which utilizes the De Nouy ring method to record surface tensions. The method is based on a force measurement exerted on a liquid surface as the ring is pulled away from the liquid surface. The apparatus used in the study is shown in Figure 3-10.

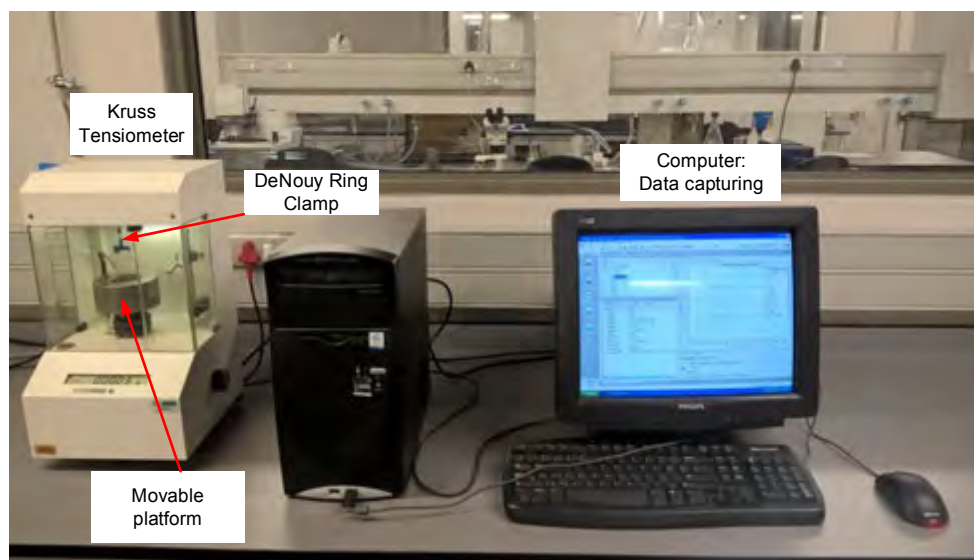


Figure 3-10: De Nouy Ring tensiometer used in determining the surface tension of conditioned pulps

The tensiometer consists of a movable platform on which a petri dish with the liquid whose surface tension is to be measured is placed. The top end of the tensiometer enclosure is fitted with a clamp which holds the De Nouy ring in place.

A sample of the pulp conditioned with a depressant and collector was drawn from the batch flotation cell using a 60 ml syringe. The pulp was centrifuged thus separating the solid material from the supernatant using a Hettich EBA 20 centrifuge. About 25 ml to 30 ml of the supernatant was placed in a glass petri dish which was mounted on the movable platform in the tensiometer. The clamped De Nouy ring was then lowered towards the liquid surface so that it just touched the liquid surface. The tensiometer was then run from a Kruss computer programme and surface tension readings were recorded as the ring pulled away from the liquid surface whilst the readings were stored in excel files.

3.9. Residual Amine analysis

Araujo, Carvalho and Yoshida (2009) developed a colorimetric method for the determination of the concentration of ether amines used in iron ore reverse flotation. The method utilizes

chloroform and the indicator bromocresol green. It is based on the synthesis of a quaternary ammonium salt when an ether amine and indicator react in a chloroform medium. Statistical results from the study by Araujo show that the method is accurate and precise with an amine detection limit below 1 mg/L. Batisteli and Peres (2008) employed the same method when analysing water from iron ore mechanical flotation cells, obtaining acceptable results that validated the usefulness of the bromocresol green method.

A buffer solution of bromocresol green was prepared by mixing bromocresol green solution with a buffer solution prepared by mixing 100 ml of freshly prepared 0.1 M potassium biphthalate solution with 45 ml of 0.1 M NaOH solution. The ratio of bromocresol green to buffer solution was 1:3 respectively. Amine quantification was carried out by adding 25 ml of chloroform and 10 ml of the bromocresol green buffer mixture to 10 ml of filtrate sample in a separation funnel. The mixture was agitated and left to settle, followed by the separation of an organic layer from an aqueous layer. The chloroform-rich organic fraction settled at the bottom of the funnel where it was decanted. Its absorbance was measured using the Ultrospec UV spectrophotometer shown in Figure 3-11, at a wavelength of 409 nm. Pure chloroform was used to reference the spectrophotometer before absorbance readings could be recorded. The chloroform fraction's absorbance reading obtained from the spectrophotometer was then used to determine the amine concentration from a previously prepared calibration curve of absorbance as a function of amine concentration.

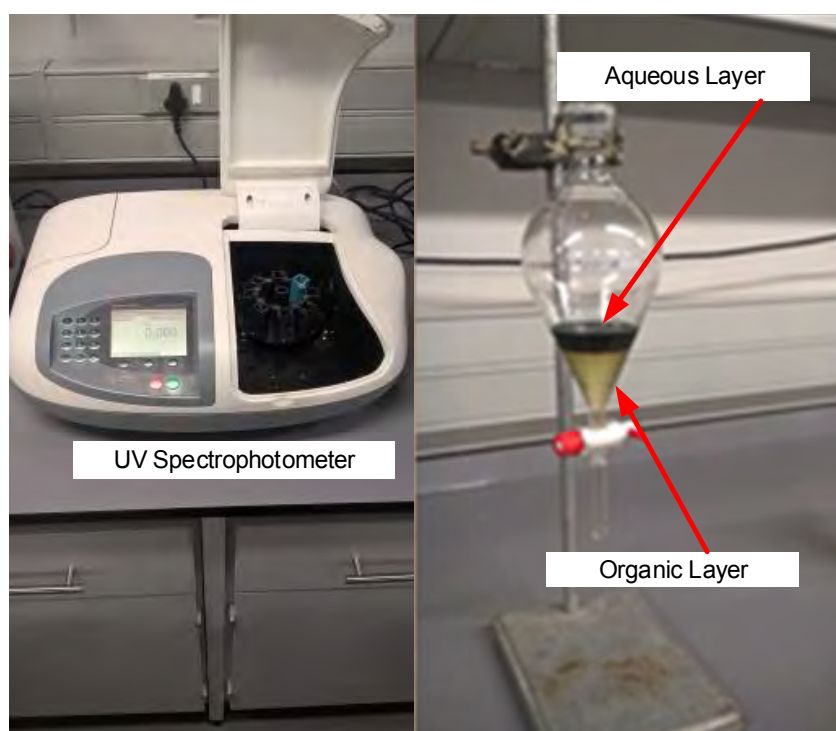


Figure 3-11: Ultrospec 2100 spectrophotometer (left) and the separation funnel used to decant the organic chloroform layer from the aqueous phase (right)

3.10. Analytical and Evaluation Techniques

3.10.1. Iron grade and Recovery

The tails and the concentrate assays were analysed for their Fe content using XRF spectroscopy. Assaying by size class was conducted in order to establish the extent of hematite entrainment when the different reagent suites were tested. The XRF results provided the Fe₂O₃ and SiO₂ contents which were used in a mass balance to determine the recovery and grade of iron after flotation.

3.10.2. Recovery Kinetic Model

From a literature search, the classical first order model and the first- order model with rectangular distribution (Klimpel model), Equation 3-2 and Equation 3-3 respectively, have been identified as good fits in most batch flotation results.

$$r=R_{\infty}\{1-e^{-Kt}\} \quad \text{Equation 3-2}$$

$$r=R_{\infty}\left\{1-\frac{1}{Kt}[1-e^{-Kt}]\right\} \quad \text{Equation 3-3}$$

Where R_{∞} is the ultimate recovery, K is the rate constant and r is the recovery at time. These constants can be established by linearizing Equation 3-2 and Equation 3-3 or by using a least squares fitting routine. The convenience of the Klimpel model is in its accountability for particle size variations and differences in degree of hydrophobicity of hydrophobic material (Kawatra, 1995).

3.10.3. Statistical Analysis

Experiments were carried out in duplicate to account for reproducibility of the results. The calculated arithmetic mean value is used as it provides a more accurate reading of the masses recovered during flotation. The arithmetic mean is calculated as shown in Equation 3-4.

$$x(\text{mean})=\frac{1}{N}\sum_{x=i}^N x_i \quad \text{Equation 3-4}$$

The standard deviation of the mean indicates the spread of the experimental data about the mean value. It is calculated as shown in Equation 3-5

$$\text{Standard deviation} = \sqrt{\frac{\sum_{x=i}^N (x_i-x)^2}{N-1}} \quad \text{Equation 3-5}$$

The standard error associated with the repeated readings is calculated and represented as error bars on the plotted graphs. The standard error is calculated as shown in Equation 3-6.

$$\text{Standard error} = \frac{1}{\sqrt{N}} \sqrt{\sum_{x=i}^N \frac{(x_i - \bar{x})^2}{N-1}} \quad \text{Equation 3-6}$$

4. Results and Discussion

This chapter presents the results obtained from the experimental work conducted as discussed in Chapter 3 as well as the associated discussion of these results. The results elucidate work done on the mineralogical characterisation of a South African iron ore and a Brazilian iron ore and the flotation studies that were carried out on the ores. The chapter is divided into four sections.

Section 4.1 provides a detailed mineralogical analysis of the ores. It is important to highlight that the mineralogical analysis of the ores was only conducted after the unsuccessful initial flotation experiments of the South African iron ore. The mineralogical analysis was therefore conducted as a scoping study, with the chief aim being to identify the cause of the South African iron ore's poor flotation performance. However, in this thesis the mineralogical results and the discussion thereof is presented first to simplify the text for the reader. Section 4.2 elucidates results obtained from collector characterisation tests conducted on the amine collectors.

In Section 4.3, the effect of the different collectors on flotation performance was evaluated by analysing the grade and recovery of hematite after the reverse cationic flotation of a South African iron ore. Scoping tests through the flotation of pure quartz using the different collectors and a single frother are also presented. Section 4.4 focuses on the reverse cationic flotation of the Brazilian iron ore using the different collectors and three depressant types at varying dosages. In addition to the grade and recovery analysis, the extent of hematite entrainment in the system was determined.

4.1. Mineralogical Characterisation

The mineralogical characterisation of the iron ores under investigation was conducted using QEMSCAN. Key information retrieved from the instrument included the bulk mineralogy quantification, grain size distribution as well as analysis of particle size and the capture of images.

4.1.1. Bulk Mineralogy

Table 4-1 shows the quantitative abundance of minerals hosted in the iron oxide ores used in the study. The main minerals present in both ores are hematite and quartz. Quartz exists as the major gangue mineral associated with these hematite bearing ores. There is a marginal difference in quartz content between the two ores. The South African iron ore has a quartz content of 37.5 wt% compared to the 35 wt% present in the Brazilian iron ore. The gangue mineralogy of the two ores can be defined as simple since there is no enrichment in other gangue minerals besides that of quartz. A slight difference in the hematite content in the two

ores was noted. The South African iron ore had a hematite content of 57.6 wt% whereas the Brazilian iron ore had a hematite content of 63.5 wt%.

Table 4-1: The relative abundance of minerals in the iron oxide samples

	South African iron ore	Brazilian iron ore
Mineral	Mineral wt %	Mineral wt %
Hematite	57.6	63.5
Chlorite	1.6	0.08
Mica	0.0	0.2
Feldspar	1.2	0.2
Quartz	37.5	35.0
Apatite	0.1	0.0
Carbonates	0.1	0.01
BMS	0.01	0.02
Other	1.9	1.0

4.1.2. Elemental analysis

A detailed elemental analysis was established by means of chemical assaying by size in order to quantify the relative abundance of Fe and Si in the different size classes. Table 4-2 shows that there was a significantly high abundance of Fe in the fines size fraction (-53 μm) of the South African iron ore. Of note is the -10 μm size fraction which had the highest iron (Fe) content of 49.1 wt% in comparison to the other fine size fractions. The -53 μm size fraction made up about 50 wt% of the mill product after grinding to 80% passing 150 μm as shown in Figure 3-3. Given the high abundance of iron in the -53 μm size fraction, a decision not to deslime the South African mill product prior to flotation was justified. Desliming would lead to inherent losses in valuable mineral.

In the Brazilian iron ore, the Si content was significantly lower in the -10 μm size class but it was almost equally distributed in the coarser size fractions. Table 4-3 shows that for the Brazilian iron ore, the -53 μm size class had a high Fe content in comparison to the +53 μm size fraction. In the Brazilian iron ore, the differences in Fe content between the fines fractions and the coarser fraction was more distinct in comparison to the South African iron ore. The overall Fe content in the South African and Brazilian iron ores were 43 wt% and 45 wt%, respectively. Although the Brazilian iron ore exhibited much higher Fe content than the South African iron ore for the same size fraction in the fines, the South African iron ore had more fine material than the Brazilian iron ore as seen in Figure 4-1 and Figure 4-2, consequently evening out the overall iron content in the ore samples.

Table 4-2: Elemental composition of Fe and Si in the South African iron ore

Element	Size Fraction (μm)					
	-10	+10 to -25	+25 to -53	+53 to -75	+75 to -150	+150
Fe wt%	49.1	40.0	43.2	37.5	40.1	40.2
Si wt%	12.4	19.0	16.7	20.5	19.2	16.7
Combined Fe content: 43 wt %			Combined Si content: 17 wt %			

Table 4-3: Elemental composition of Fe and Si in the Brazilian iron ore

Element	Size fraction (μm)					
	-10	+10 to -25	+25 to -53	+53 to -75	+75 to -150	+150
Fe wt%	62.5	65.7	63.4	39.1	37.9	9.66
Si wt%	3.6	2.7	4.9	20.6	21.5	39.8
Combined Fe content: 45 wt %			Combined Si content: 16.5 wt %			

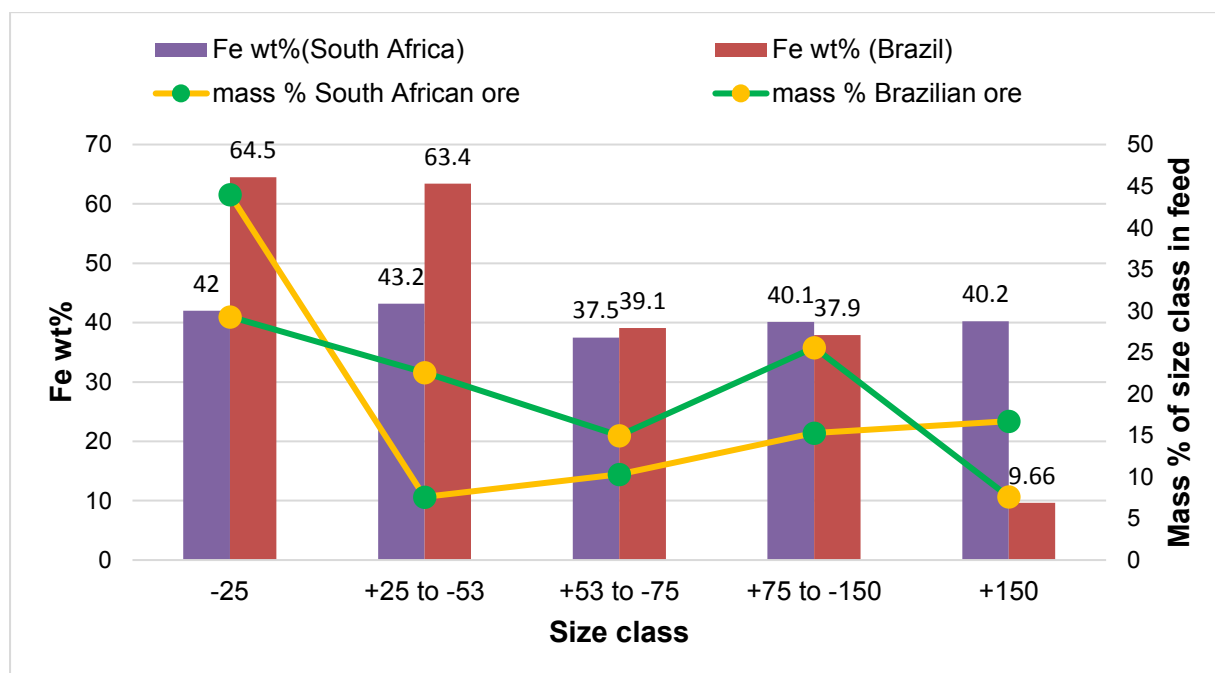


Figure 4-1: A comparison of the iron grade (Fe wt %) and weight contributions of different size classes in the South African and Brazilian feed ores

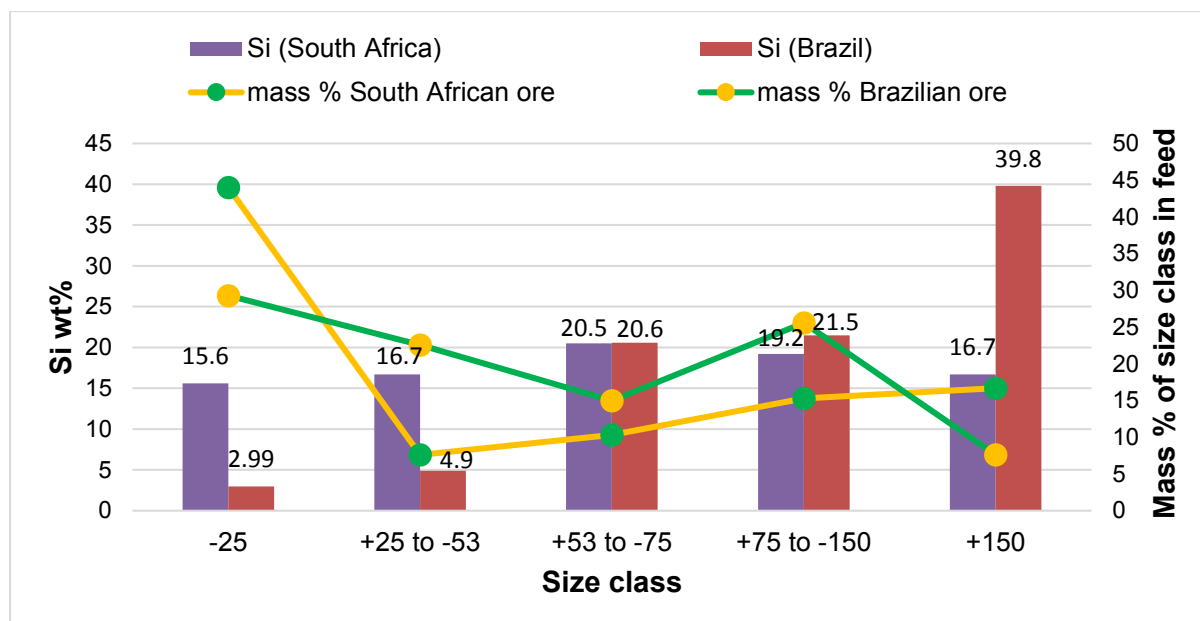


Figure 4-2: A comparison of the silicon grade (Si wt %) and weight contributions of different size classes in the South African and Brazilian feed ores

4.1.3. Quartz distribution

4.1.1. Quartz impurities

Table 4-4 shows the extent of iron impurities within the gangue mineral, quartz. It can be seen that some of the quartz within the South African iron ore is tainted with iron impurities. 58 wt% of the quartz is relatively pure whilst 22 wt% of the quartz is tainted with iron impurities. 93.8 wt % of the quartz in the Brazilian iron ore is pure.

Due to the presence of Fe atoms in the structure of some quartz grains in the South African iron ore sample, a possible interaction between starch and the iron atoms in the quartz mineral, could result in the depression of some quartz during flotation. Filippov, Filippova and Severov (2010) noted that the presence of iron impurities in a pargasite mineral reduced the flotation recovery of the silicate mineral which the author attributed to the interaction of starch with the Fe atoms essentially depressing the pargasite as if it were an iron oxide mineral. In the current study, the depression of quartz in the Brazilian iron ore due to starch adsorption on quartz was not expected since there were no iron atoms within the quartz structure to interact with the starch (depressant).

However, it should also be noted that the extent of depression of quartz or silicate minerals containing trace Fe impurities depends on the abundance of Fe atoms within the quartz or silicate structure. Enough iron (Fe) should be present to induce a significant amount of interaction with the starch molecules. Furthermore, textural complexities and liberation play a vital role in depressant efficacy, hence, their effects are noted to be more important.

Table 4-4: Quartz association with iron impurities

	South African iron ore	Brazilian iron ore
Quartz Type	Abundance wt%	Abundance wt%
Pure Quartz	58	93.8
Quartz-low Fe	11	0.5
Quartz-FeOx (75:25)	11	0

4.1.2. Particle and Grain size Analysis

Figure 4-3 shows selected QEMSCAN images of the South African iron ore. The light grey shade represents the hematite grains and the dark grey shade represents the quartz grains. It can be seen that both minerals were finely disseminated throughout the sample. On the image to the left, the quartz is disseminated within the hematite and in the picture to the right, more of the hematite was finely dispersed within the quartz. Based on the scale provided in the images, the disseminated quartz and hematite grain sizes were present in the fines size fraction, below 38 μm . Such a mineral texture with fine inclusions of minerals makes it challenging to fully liberate the minerals. It is well known that liberation of such fine material can only be realised after fine grinding. The difficulty in fine grinding is that excessive grinding can produce slimes which complicate the ore beneficiation further downstream (Wills & Napier-Munn, 2005).

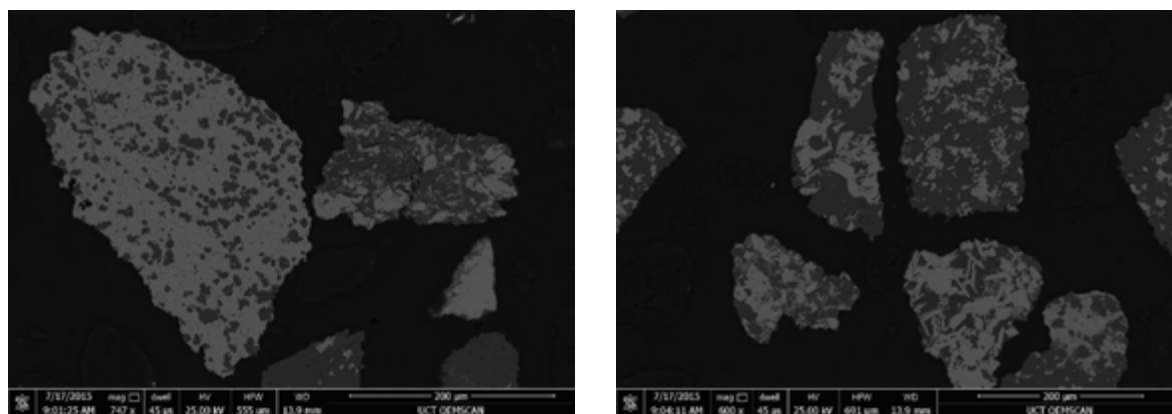


Figure 4-3: QEMSCAN grey scale images showing the distribution and texture of minerals within the South African iron ore sample. Light grey shade (Hematite); Dark grey shade (Quartz)

Particle images for selected size fractions in the two ores were analysed and a comparison of the particle false colour images is shown in Table 4-5. The particle images show that at coarse size fractions, the quartz in the Brazilian iron ore was almost fully liberated as seen by the high number of pink coloured single phase particles. In the finer size fractions, more iron was

liberated as indicated by the increase in single phases of the red coloured particles. The South African iron ore showed that at coarse size fractions the hematite represented by the red particles was either locked or disseminated within the quartz. More distinct hematite phases were only realised in the fine size fraction around 10 µm. The images in Table 4-5, indicate that at the same particle size, the Brazilian iron ore had more single phase minerals present in comparison to the South Africa iron ore and this has been ascribed to the ease in liberation of minerals in the Brazilian iron ore.

The grain size distribution for the flotation cell feed samples was plotted as part of the study. By definition a grain is a 3D entity consisting of one mineral. The grain size distribution provides an idea of the extent of full liberation. Figure 4-4 shows that very few quartz grains were present in the fine size classes (<38 µm) for the Brazilian iron ore, corroborating results from the images in Table 4-5. About 50 wt% of the hematite grains were present in the fines size fraction which is indicative of the presence of fully liberated minerals in the fines size fraction. In comparison to the Brazilian iron ore, the South African iron ore had more quartz and hematite grains in the fines size fraction. It can therefore be suggested that a finer grind size is required in order to liberate the quartz and hematite in the South African iron ore.

Table 4-5: Comparison of South African iron ore and Brazilian iron ore QEMSCAN false colour images at different particle size fractions. Key: Hematite ♦ Quartz ◆

Size fraction (µm)	Brazilian iron ore	South African iron ore
+150		
+53		
+10		

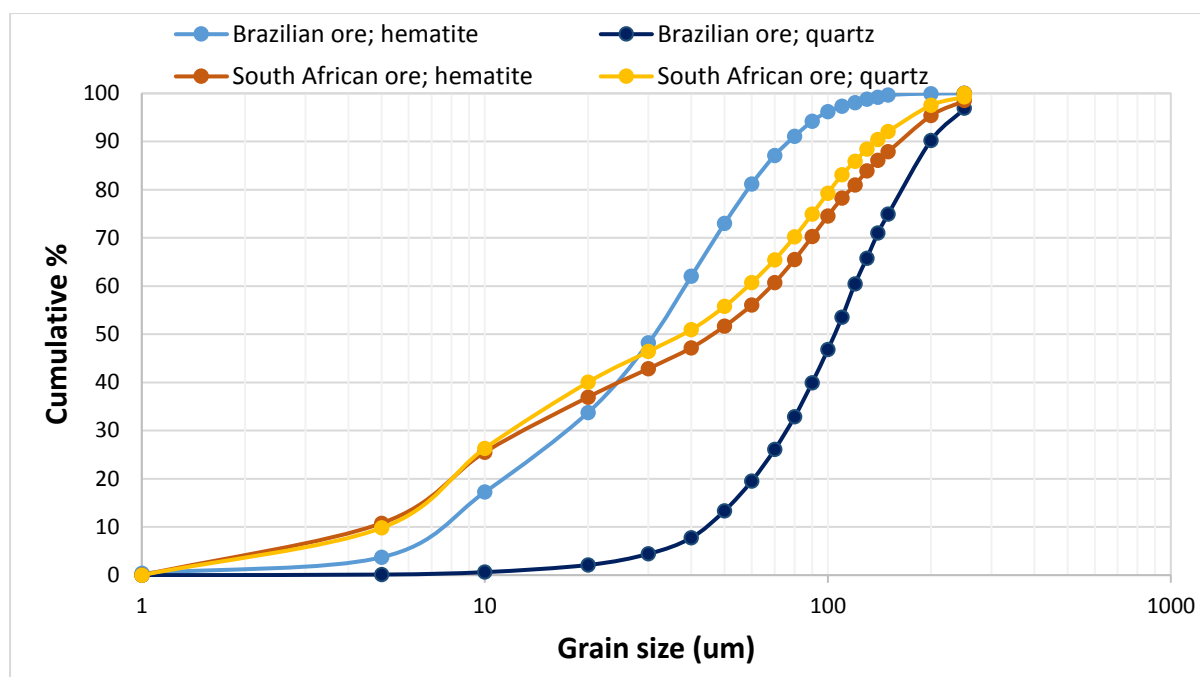


Figure 4-4: Grain size distribution of quartz and hematite in the South African iron ore and the Brazilian iron ore samples

4.1.3. Quantitative Liberation Analysis

A quantitative liberation analysis of both ores was conducted and a comparison of the liberation characteristics of the minerals hosted in the two ores is presented in Figure 4-5 to Figure 4-8. The particles were classified as locked (0-30 area %), low grade middlings (30-60 area %), high grade middlings (60-90 area %) and liberated (> 90 area %).

Figure 4-5 and Figure 4-6 show the liberation data for the quartz and hematite in the South African iron ore sample respectively. As seen in Figure 4-5, the full liberation of quartz was fairly poor in all the size ranges. A significant mass of quartz exists in the high grade and low grade middlings for all the size ranges analysed. The -25/+10 μm size fraction hosts the highest amount of fully liberated quartz material. The -10 μm size fraction, however, has most of its material located in the high grade middlings. The combined liberation shows that 39 % of the quartz mass was fully liberated at the initial grind size of 80 % passing 150 μm . Figure 4-6 shows that the liberation of hematite vastly improved at smaller size fractions. The -25/+10 and -10 μm size fractions have the highest amount of liberated material, with liberation values of 71 % and 85 % respectively. Overall, 60 % of the hematite was liberated.

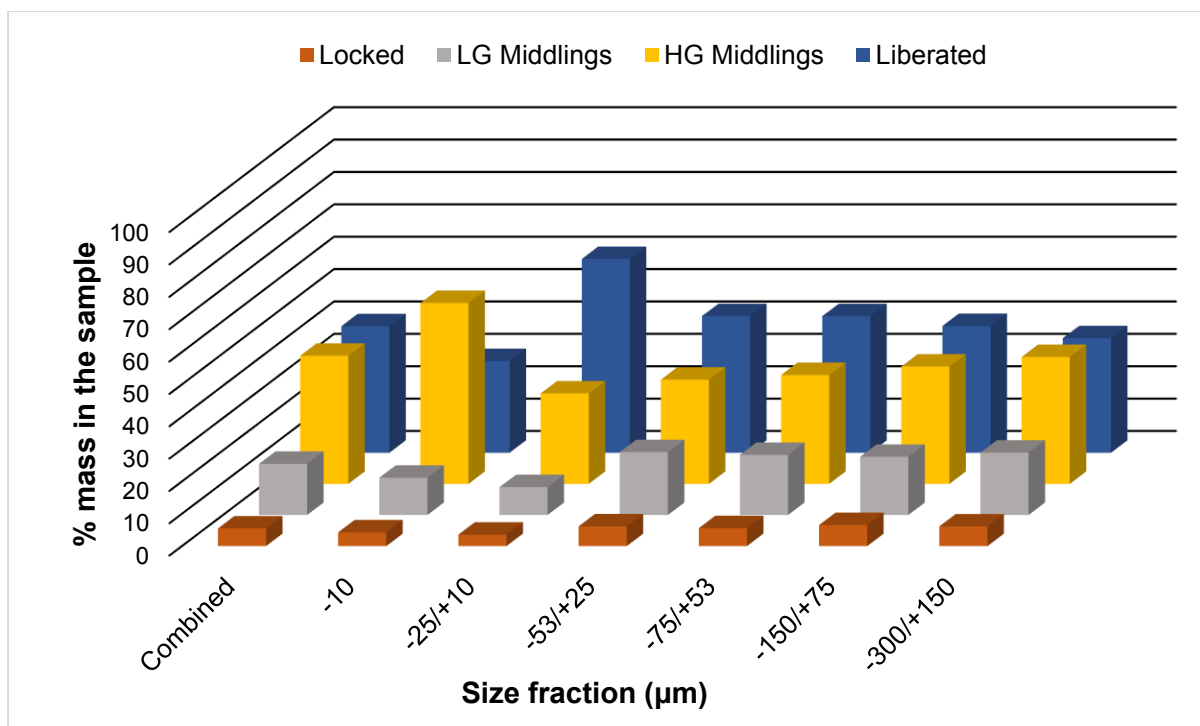


Figure 4-5: Liberation of quartz in the South African iron ore at a grid size of 80 % passing 150 µm.

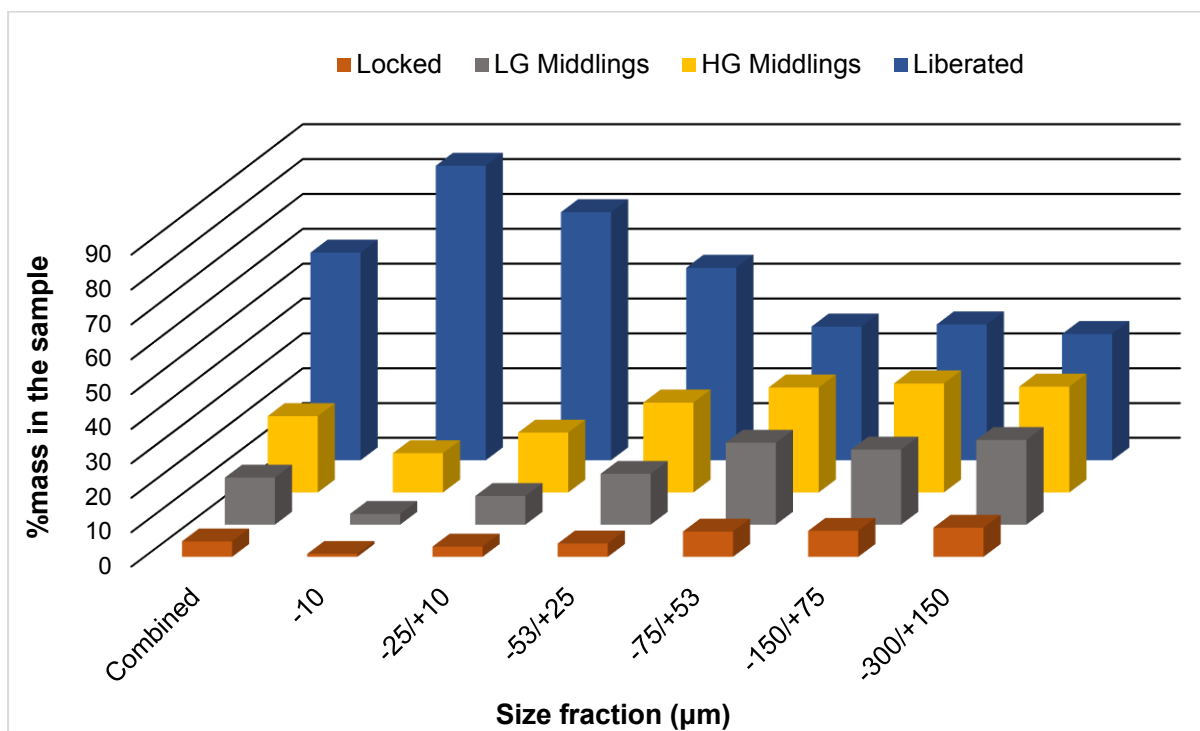


Figure 4-6: Liberation of hematite in the South African iron ore at a grind size of 80 % passing 150 µm.

For the Brazilian iron ore, there was a high degree of quartz liberation. Figure 4-7 indicates that in all but one size fraction, more than 85 % of the quartz was fully liberated. In the -10 μm size fraction, liberation was fairly poor with only 63 % of the quartz attaining full liberation. The combined sample had 98 % of the quartz fully liberated. Similar trends are noted for hematite liberation. In all size fractions, at least 80 % hematite was liberated.

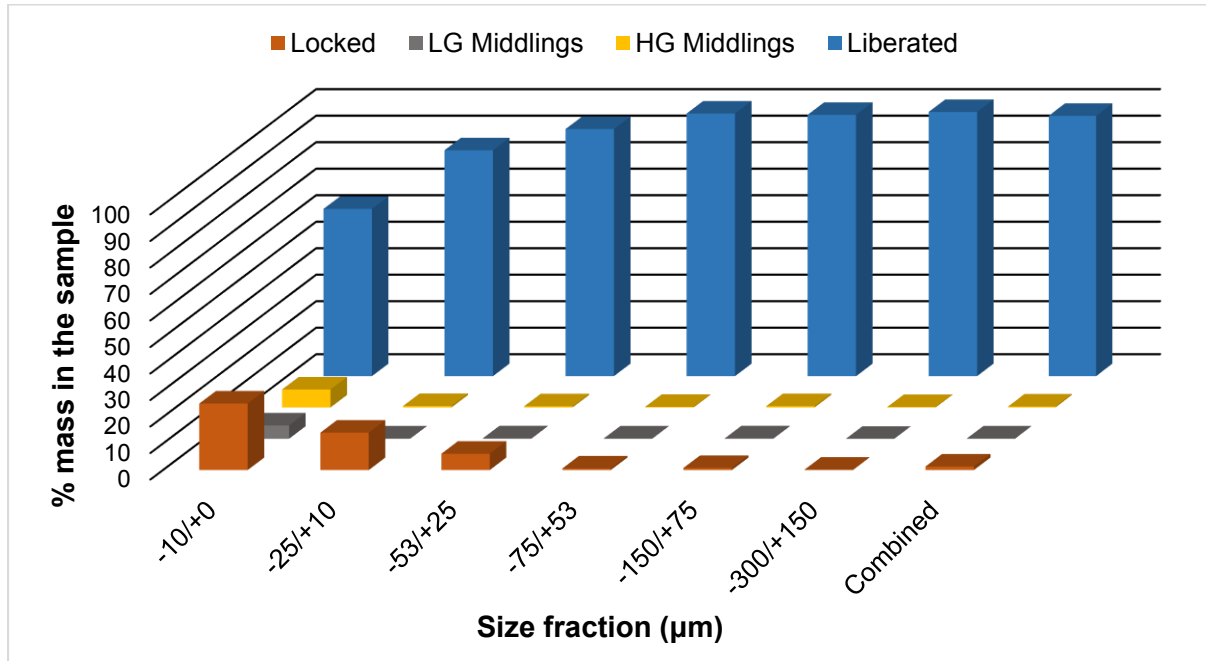


Figure 4-7: Liberation of quartz in the Brazilian iron ore at a grind size of 80 % passing 150 μm .

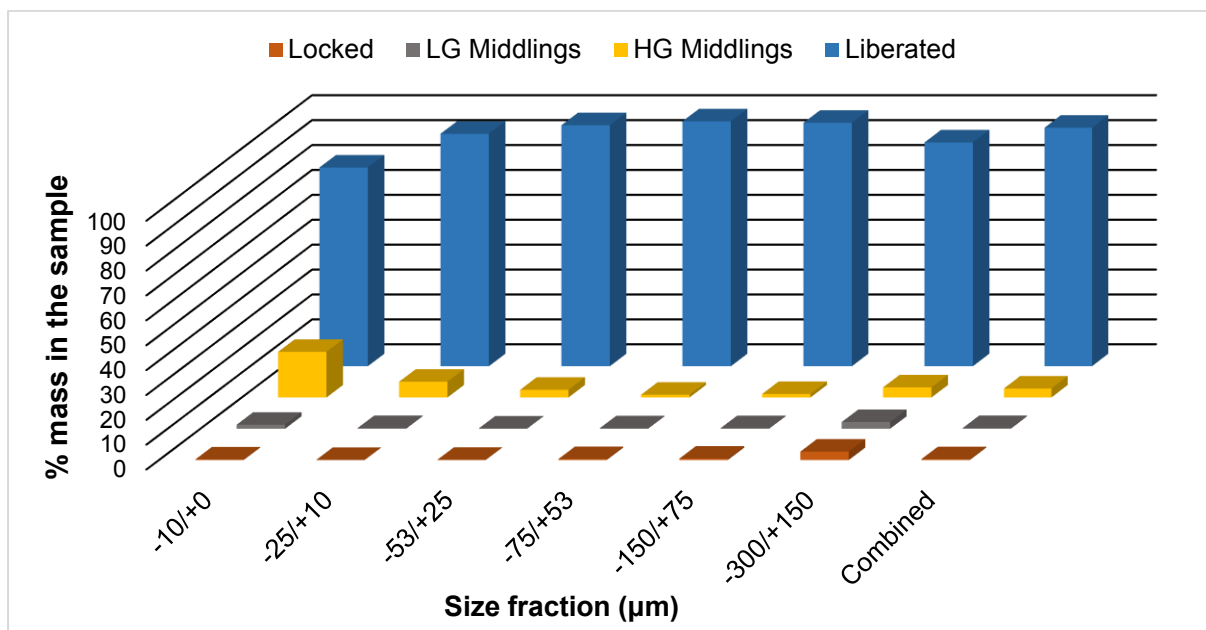


Figure 4-8: Liberation of hematite in the Brazilian iron ore at a grind size of 80 % passing 150 μm

4.1.4. Summary of iron ore characterisation

From the bulk mineralogy data presented, it is clear that the mineralogy of both ores is simple. The major iron bearing oxide is hematite and the significant gangue mineral present is quartz. As has been mentioned earlier, Prior (2015) highlighted that the ore deposits from the two different locations have similar genesis through supergene enrichment of BIFs. As a result, the major minerals abundant in the ores are relatively similar. However, upon analysis of the QEMSCAN images for the mineral distributions in the two ores, it can be seen that the ores differed significantly in their texture. The QEMSCAN particle images of the South African iron ore indicated that the ore had high proportions of finely disseminated quartz and hematite. The detrimental effect of such mineral texture is the complexity in attaining high liberation of locked particles. It is apparent that fine grinding is the most practical route to achieving liberation as suggested by Das et al. (2010) when studying the mineralogy and flotation behaviour of an Indian banded hematite quartz with similar textural complexities to those present in the South Africa ore used in the current study.

The quantitative liberation data for the South African iron ore as presented confirmed the effect of the aforementioned textural complexities. The current study has shown that at the initial grind size of 80 % passing 150 μm , there was generally poor liberation of both quartz and hematite in the South African iron ore. As illustrated in the results, most of the material existed as low grade and high grade middlings, indicative of significant amounts of composite materials. Such an ore body is challenging to process through reverse flotation as the addition of a depressant may result in the depression of hematite that is present in a composite particle together with the quartz. As such, there is little to no selective separation of the gangue minerals from the valuable minerals as will be shown in the flotation studies presented in Section 4.2.

As shown by the QEMSCAN studies, the hematite in the South African iron ore was more liberated than the quartz, particularly in the lower size classes ($-25 \mu\text{m}$) as indicated by the grain size distribution. QEMSCAN and flotation studies carried out by Rath et al. (2014) on a banded hematite quartz ore summarised that for ore samples with better hematite liberation, direct flotation yielded good grades, whereas in ore samples with better quartz liberation, reverse cationic flotation produced higher concentration grades. The authors also noted that finer grinding improved liberation corroborating observations made by (Roy & Das, 2008; Das et al., 2010; Fouchee, 2015). If a high grade of valuable mineral or removal of gangue mineral e.g. silica is to be attained, then finer grinding ought to achieve high liberation of the target material (Pease, Curry & Young, 2006).

On the contrary, the Brazilian iron ore had good liberation characteristics. Based on the quantitative liberation data and the QEMSCAN images presented, the ore has a relatively simple mineral texture. Almost all the quartz and hematite in the ore was fully liberated at the grind size of 80 % passing 150 μm . Araujo et al. (2003) reported that significant amounts of ore mined in Brazil do not present any textural complexities. As the ore is mined, it presents high degrees of liberation possibly due to extensive weathering patterns exerted on the ore. Grinding and milling are therefore mainly aimed at size reduction instead of liberation. Provided the Brazilian iron ore used in this particular study was sourced from an ore body representative of a naturally well liberated ore body, the results obtained showing ease in liberation of the hematite and quartz minerals are justified.

The study has revealed that liberation is the key issue that can explain differences in flotation behaviour of the two ores that were observed in the course of the study. Although 22% of the quartz in the South African iron ore is associated with iron impurities which could lead to the undesired depression of quartz after the impurities interact with starch, the quartz in general is poorly liberated. Texture and liberation will determine the extent of selective separation during the reverse cation flotation procedure.

4.2. Amine Characterisation

Owing to the proprietary nature of the cationic collectors used in this study, their detailed molecular structures could not be obtained for use in explaining the flotation performance obtained using the various collectors in the flotation tests. Collector characterisation was deemed necessary for establishing additional scientific parameters that could be utilised in explaining observations made in terms of the collectors' flotation behaviour and performance.

Collector characterisation tests identified the collectors' pKa values and the collectors' effect on the surface tension of an aqueous solution. Observations on the collectors' flotation behaviour and adsorption mechanisms on a quartz surface were explained using available knowledge on amine molecular chemistry, assumptions on electrostatic interactions between the charged quartz surface and cationic collectors, hydrogen bonding mechanisms and the micellization theory, which are all dependent on pH and pKa values. The surface tension measurement results also highlighted the frothing properties of the amine collectors.

For ease of collector class identification, Table 4-6 presents the trade name of the collectors investigated and their corresponding assigned names used throughout the remainder of this thesis.

Table 4-6: Assigned names for the Clariant collectors used in amine characterisation and flotation studies

Collector Trade Name	Assigned name
Flotigam EDA	Ether monoamine
Flotigam 3135	Ether diamine 1
Flotigam 2835	Ether diamine 2
Flotigam K2C	Quaternary ammonium salt (QAS)
Flotigam ITU	Imidazoline Salt

4.2.1. pKa measurements

pKa values were determined using potentiometric titration curves as described in Chapter 3. The change in the molecular structure of alkyl ether amines during an acid base reaction allows for the use of the potentiometric titration curve in establishing the alkyl ether amines' pKa values. The nature of their species in solution changes with changes in pH according to Equation 3-1, which in turn has an effect on the shape of the titration curves. However, the imidazolines and quaternary ammonium salts are fully ionized at all pH values and the change in pH does not produce any pronounced effect on titration curves that can be used in determining pKa values. The results were therefore only collated for the alkyl ether amines and shown in Table 4-7.

Table 4-7 shows that the pKa values of the alkyl ether amines lie in the alkaline range and they are close to those often reported in literature. A neutralised amine 50% dissociated in solution has a pH value of approximately 10.5 (Cassola, Silva & Bartalini, 2011), whereas Gaudin (1957) reports a pKa in the range of pH 9 to pH 9.5 for a primary alkyl amine, dodecyl ammonium chloride. At the pKa, it is reported that there is 50 % dissociation of the alkyl ether amine collectors i.e. a co-existence of the aminium ions and their neutral molecules which allows increased collector adsorption on the mineral surface leading to enhanced flotation recovery of solids (Chernyshova et al., 2001; Rao, 2004; Vieira & Peres, 2007).

Table 4-7: Collector pKa values determined from potentiometric titration curves.

Collector	pKa value
Ether monoamine	9.9
Ether diamine 1	10
Ether diamine 2	8.2

4.2.2. Surface tension measurements

The addition of an amine surfactant (frother/collector) to an aqueous solution results in a lowering of the surface tension at the liquid/gas interface which has an effect on the frothing ability of the system when air is introduced. Surface tension measurements on the supernatant obtained after conditioning and centrifuging the pulp were recorded and are shown in Figure 4-9. It was observed that the addition of a surfactant lowered the solution's surface tension.

A collectorless pulp had a surface tension of 70 N/m but the addition of alkyl ether amine collectors to the pulp zone resulted in centrifuged solutions with surface tension measurements well below 50 N/m. Flotation systems dosed with the quaternary ammonium salt or the imidazoline salt did not lower the surface tension of the solution to the same degree as the alkyl ether amine collectors. The surface tension of a collectorless system was only lowered from 70 N/m to 55 N/m and 53 N/m upon the addition of an imidazoline collector and a quaternary ammonium salt collector, respectively.

The increased lowering of the surface tension by the alkyl ether amines is indicative of the collectors' strong ability in generating more stable froths as will be shown in Section 4.3 and Section 4.4. This phenomenon can be interpreted in terms of the ability of alkyl ether amine solutions to form neutral amine molecules at specific pH ranges and the subsequent association with aminium ions forming an ion-molecular complex as expressed in Equation 2-6. The ion-molecular species which adsorb at the gas-liquid interface are highly surface active, decreasing the solution's surface tension (King, 1982; Rao, 2004).

The observation is supported by work carried out by Castro, Vurdela and Laskowski (1986). They showed that there is a correlation between the surface activity of an alkyl amine solution

and the precipitation of the alkyl amine. As seen in Figure 4-10, the surface tension of their system decreased as the pH increased and it reached a minimum in a pH range where the authors observed the presence of $\text{RNH}_2\text{-RNH}_3^+$ species. This occurred in a narrow range of alkaline pH values (pH 9 to pH 10.5), just before precipitation of the amine molecule (Finch & Smith, 1973; Castro, Vurdela & Laskowski, 1986; Rao, 2004).

Since the pH used for surface tension measurements in the current study has been equated to the pKa and lies within the ranges used by Castro and co-workers, it can be assumed that in that range, the alkyl ether amine solutions had also formed the neutral molecule. Adsorption of the ion-molecular complex, the aminium ion and the neutral molecule at the liquid/gas interface results in a closer packing of surfactant and hence the increased surface activity and hydrophobicity of the solid particles (Finch & Smith, 1973; Somasundaran, Moudgil & Soto, 1987).

In the case of the imidazoline salt and the quaternary ammonium salt which in nature are fully ionized at all pH values, there is no formation of neutral amine molecules in solution. Furthermore, the quaternary ammonium salt and imidazoline salt present well solvated systems such that even their long hydrophobic alkyl chains' surface activity is diminished. Adsorption of these surfactants at the liquid/gas interface is reduced because the surfactants are highly ionized and solvated. In addition, adsorption of purely cationic surfactants is hindered by electrostatic repulsion between the quaternary cations (Castro, Vurdela & Laskowski, 1986).

Interestingly ether diamine 2, with a molecular structure partly made up of a linear alkyl chain with between 12 and 15 carbon atoms did not lower the surface tension to the same extent as the ether monoamine and ether diamine 1 which possess branched alkyl chains with between 8 and 10 carbon atoms. Literature suggests that longer linear chain amphipathic molecules are thermodynamically more favoured to adsorb at the liquid/gas interface as they are more hydrophobic through the stronger interactions of their hydrocarbon chains via van der Waals forces, becoming more surface active (Rao, 2004). The results obtained in this study do not correlate with findings documented in literature.

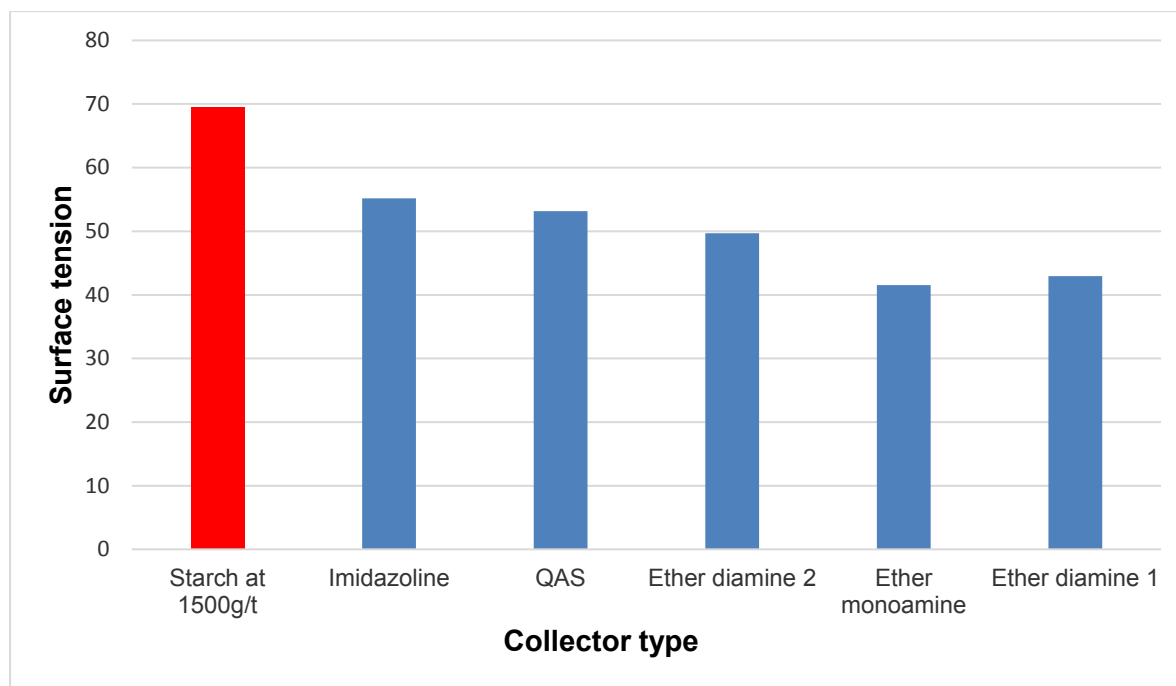


Figure 4-9: Surface tension measurements for the different supernatant solutions obtained after conditioning. Starch solution at 1500 g/t, was used as the base solution before collector was added. A collector dosage of 125 g/t was used for all surface tension measurements.

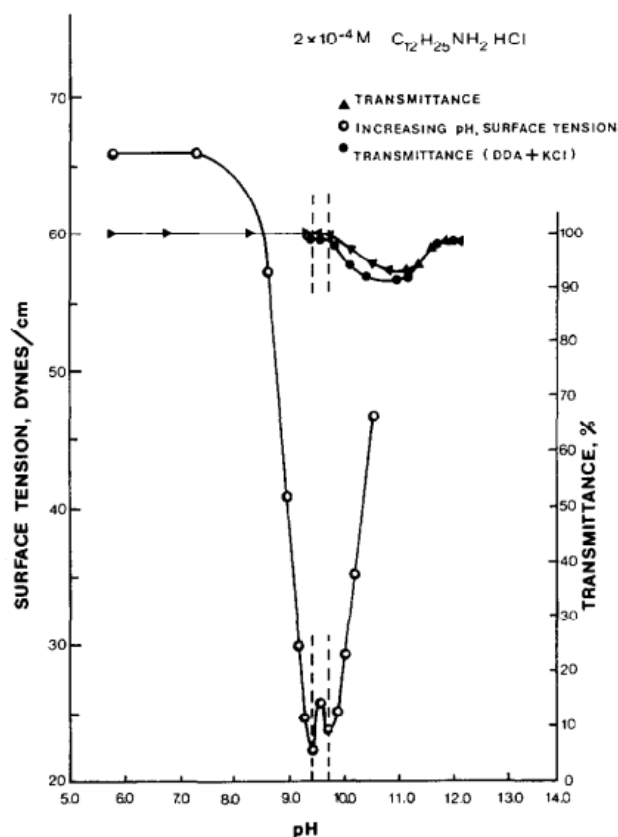


Figure 4-10: The effect of pH on the surface tension of an aqueous solution of dodecylamine hydrochloride solution (Castro, Vurdela & Laskowski, 1986)

4.3. Reverse Cationic flotation of a South African iron bearing ore

The initial aim of the test work in this study, was to assess the flotation performance obtained using five cationic collectors supplied by Clariant Chemicals. A standard reverse cationic batch flotation procedure of a South African iron ore was carried out as described in Chapter 3. As a result of the poor flotation performance of the South African iron ore obtained using the different collectors, scoping tests were conducted namely, the mineralogical analysis of the ore using QEMSCAN, which has been reported and discussed in Section 4.1 and secondly, decoupling the sub-processes and conducting batch flotation tests on a relatively pure quartz sample. The key findings from this series of test work are reported in this section.

4.3.1. Batch flotation

Batch flotation tests were carried out using five different collectors at a dosage of 125 g/t and a depressant at a dosage of 1500 g/t. The water and solids recovered after the reverse cationic flotation of the South African iron ore are summarised in Figure 4-11. At a constant collector and depressant dosage, there were marked differences in the amount of water and solids recovered in the froth zone as the collector type was varied.

An exception was in the systems using ether diamine 1 and the ether monoamine which exhibited similar solids recoveries i.e. 165 g and 159 g, respectively, corresponding to a mass pull of 16.5 % and 15.9 %. The same ether monoamine and ether diamine 1 exhibited the highest water and solids recovery to the froth phase. The results suggest that for the flotation system under investigation, the ether monoamine and ether diamine 1 were strong frothers which formed stable froth, leading to higher water retention when these reagents were used as collectors.

Interestingly, when ether diamine 2 was used as a collector, low amounts of water and solids were recovered in the froth yet ether diamine 2 is classified under the same molecular class as ether diamine 1. Only 17 g of solids (1.7 % mass pull) were recovered in comparison to the 16.5 % mass pull recovered when the ether diamine 1 was used as a collector. Using solely an imidazoline salt or a quaternary ammonium salt collector did not yield any solids or water recovery, hence, recoveries for systems employing these amine collectors are not shown. From visual observations during the experimental phase of the study, the bubbles reporting to the top of the flotation cell were barren and immediately burst as they reached the top of the cell, resulting in no froth formation. This suggested that these reagents were not acting as collectors and were not recovering quartz particles to the concentrate.

A commonly used neutral alcohol frother, methyl isobutyl carbinol (MIBC) was added at a dosage of 60 g/t together with the quaternary ammonium salt and the imidazoline salt in an attempt at introducing a frothing effect to the system. As shown in Figure 4-11, the introduction

of the frother slightly improved the water and solids recovery resulting in 27g of solids and 627 g of water being recovered in the froth concentrate. This further reinforced the theory that it was not a lack of frothing effect, but rather that the reagents were poor collectors. The solids and water recovery in the system dosed with the imidazoline salt and frother was insignificant and no results are presented for that system.

An investigation into the use of a combined ether amine mixture as a quartz collector at the same dosage i.e. 125 g/t, revealed that when the two best amine collectors were added to the batch flotation cell in a ratio of 1:1, there was a marked increase in froth stability evidenced by an increase in water recovery. The water recovered increased from 829 g and 1048 g (water recovered when the ether monoamine and the ether diamine were used in their pure state, respectively) to 1348 g when a blend of the aforementioned collectors was employed in flotation. The corresponding increase in solids recovered was a result of fine material being entrained in the stable froth thereby contributing to the total mass of solids recovered in the froth concentrate.

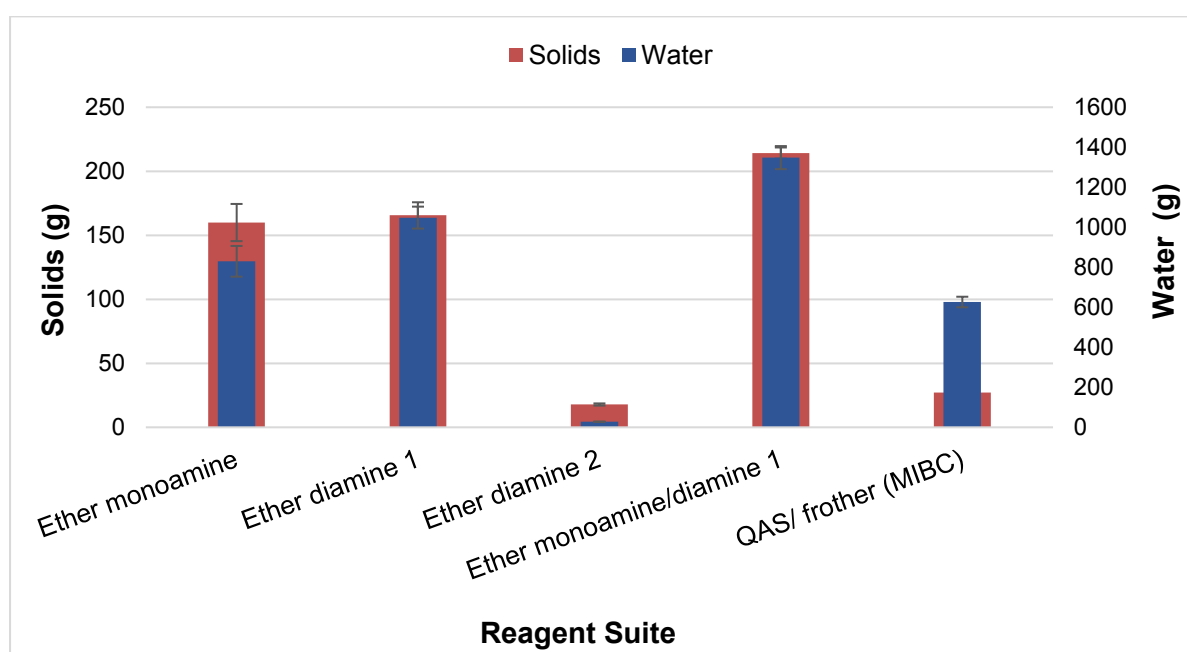


Figure 4-11: Final solids and water recovered after the reverse cationic flotation of a South African iron ore using the different amine collectors. A reagent suite consisting of starch at a dosage of 1500 g/t and collector at a dosage of 125 g/t was employed. Error bars show the standard deviation between duplicate tests.

Results for the cumulative solids versus the cumulative water recovered are shown in Figure 4-12. It can be seen that the lowest solids per unit water recovered was obtained when the quaternary ammonium salt collector was used in flotation. The highest solids per unit water recoveries were obtained when the ether diamine 1, ether monoamine or a combination of the

two collectors were used in flotation. Furthermore, the solids per unit water recoveries were similar for the three reagent suites.

The high water recoveries obtained when the ether diamine 1 or the combination of collectors was used in flotation is indicative of the strong frothing and froth stabilising effect of the collectors used. A linear relationship between the solids and water recovered is an indicator of the presence of the mechanism of entrainment, which contributed to the total mass of solids recovered in the pulp. An extrapolation of the plotted linear points produces an intercept close to zero. Neethling and Cilliers (2002) and Konopacka and Drzymala (2010) suggest that a linear, water versus solids relationship with a zero intercept alludes to solids recovery through entrainment of fine materials (sub 50 μm) in the froth zone. The flotation cell feed ore at a grind size of 80 % passing 150 μm was made up of about 40 % fine material (<25 μm). With such a significant amount of fine material, there was a high probability of the material reporting to the froth phase through entrainment. The addition of a high depressant dosage was not enough to depress all the fine hematite particles in this system.

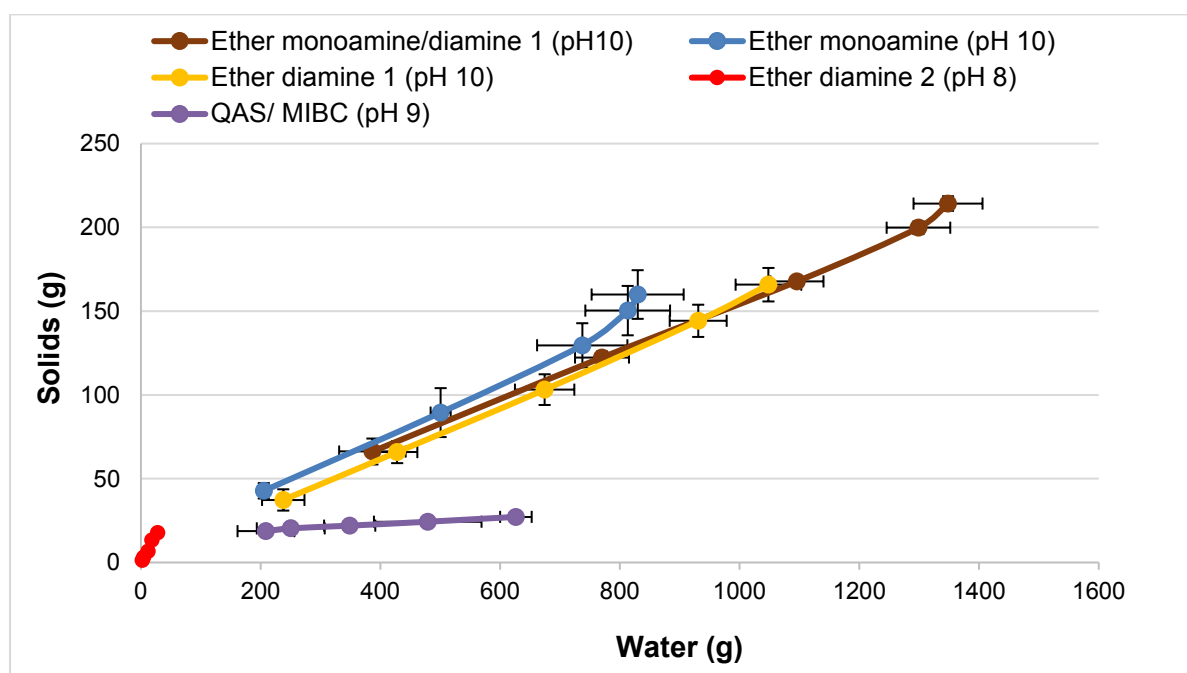


Figure 4-12: Cumulative solids versus cumulative water when different collectors were used in the reverse cationic flotation of a South African iron ore. A reagent suite consisting of starch at a dosage of 1500 g/t and collector at a dosage of 125 g/t was employed. Error bars show the standard deviation between duplicate tests.

The results for the solids recovered per unit time are shown in Figure 4-13. The results show that the ether monoamine, the ether diamine 1 and a combination of these two collectors resulted in high flotation recovery rates as seen by the steep gradients particularly in the initial two minutes of flotation. The same collectors resulted in the highest solids recoveries,

corresponding to previous suggestions that systems employing the alkyl ether amines exhibited stable froths with high solids recoveries and that the amines are good collectors of the solid particles. The use of quaternary ammonium salt with the MIBC frother and ether diamine 2 resulted in poor final solids recoveries whilst the use of an imidazoline salt did not yield any solids recovery.

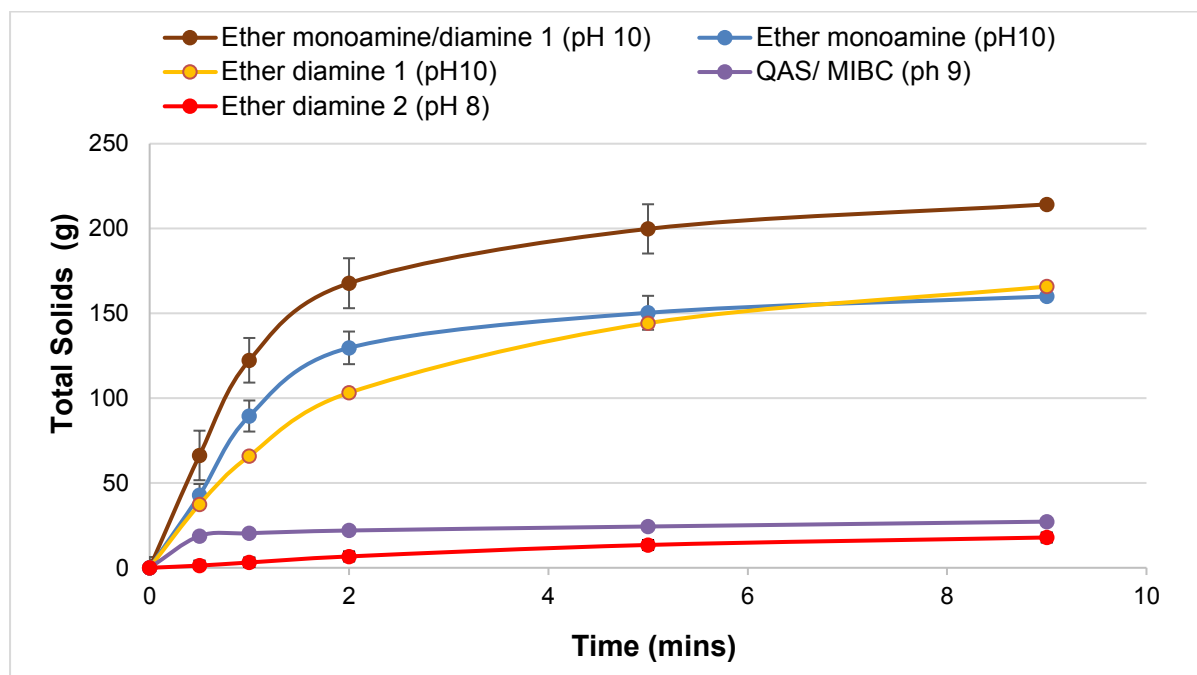


Figure 4-13: Recovery rate of total solids for the different amine collectors used in flotation studies on a South African iron ore. A starch dosage of 1500 g/t and collector dosage of 125 g/t was used in the test work. Error bars show the standard deviation between duplicate tests.

The reason for the analysis of the iron grade and recovery content after flotation was twofold. The analysis was intended to assess the collectors' effectiveness in recovering quartz in the froth zone as this builds on to the scientific discussion on the collectors' ability to recover quartz as well as the collectors' frothing ability. Secondly the analysis was intended to quantify the final hematite concentrate iron (Fe) grade and recovery which is of importance commercially, regarding obtaining a saleable product post flotation. Therefore, the grade and recovery results are presented for both the froth product (quartz concentrates) and the tails (hematite concentrate). Furthermore the grade and recovery analysis was only conducted on the products obtained when the most promising collectors' were used in the flotation of the South African iron ore.

As seen in Table 4-8, the quartz (SiO_2) grade and recovery to the froth zone was generally poor for all reagent suites that were employed in the study and the system had a low separation selectivity due to entrainment. A low quartz recovery, 26%, to the froth concentrate, was calculated when the alkyl ether amine collectors and the collector blend were used in

flotation. There was an increase in iron (Fe) recovery to the froth product i.e. from 15% to 20% and 24% when the collector was changed from an ether monoamine to ether diamine 1 and the collector blend, respectively. This result correlates with the increased water recovery seen in Figure 4-12. The increase in water recovered is related to an increased froth stability which contributed to the increased recovery of solid hematite particles through entrainment.

The results presented in Table 4-9 highlight that there was little quartz removal from the pulp zone as seen by the insignificant change in quartz grade in the hematite concentrate. The feed quartz grade only dropped from 38% to 36.1% and 35.8% when the ether monoamine and ether diamine were employed as collectors. As discussed in Section 4.1 the poor liberation at the initial grind size significantly contributed to the lack of separation of quartz from the hematite. As quartz was not well liberated and occluded within the hematite, starch addition resulted in the depression of the hematite together with the locked quartz.

Table 4-8: Grade and recovery results of the froth (quartz (SiO₂)) concentrate obtained after the reverse cationic flotation of a South African iron ore.

Collector	Collector Dosage	Froth (SiO ₂ Concentrate) Grades		Froth (SiO ₂ Concentrate) Recovery	
		SiO ₂ %	Fe %	SiO ₂ %	Fe %
Ether monoamine	125 g/t	54	32	26.2	15.2
Ether diamine 1	125 g/t	56.1	30	26.2	20.9
Ether diamine 1 & ether monoamine	125 g/t	49	36	25.9	24.2

Table 4-9: Grade and Recovery results of the tails (hematite (Fe₂O₃)) concentrate obtained after reverse cationic flotation of a South African iron ore.

Feed ore grade: Fe = 39 %; SiO ₂ = 38 %					
Collector	Collector Dosage	Tails (Fe ₂ O ₃ Concentrate) Grades		Tails (Fe ₂ O ₃ Concentrate) Recovery	
		Fe %	SiO ₂ %	Fe %	
Ether monoamine	125 g/t	40	36.1	84	
Ether diamine 1	125 g/t	37	35.8	78	
Ether diamine 1 & ether monoamine	125 g/t	37	37.1	75	

4.3.2. Column flotation

The results for column flotation tests conducted on a finely ground South African iron ore are presented in Table 4-10. As in the batch flotation tests, there was no significant improvement in iron grade after flotation. The quartz grade decreased from 38% in the feed to 33.1% in the hematite concentrates (pulp product), when the ether monoamine collector was applied. The quaternary ammonium salt and frother mixture was also not successful in reverse flotation of the iron ore. It can be seen that the grind size of 80% passing 75 μm was once again not sufficient to liberate the quartz and hematite.

Table 4-10: Iron and silica grade after column flotation tests on a finely ground South African iron ore

Feed ore grade: Fe = 39%; SiO ₂ = 38%		
Collector	Hematite Concentrate Fe Grade %	Hematite Concentrate SiO ₂ Grade %
Ether monoamine	41	33.1
QAS with Montanol frother	38	37.8

4.3.3. Extent of entrainment in reverse batch flotation of a South African iron ore

Entrainment studies in the reverse flotation of the South African iron ore showed that entrainment contributed significantly to the solids recovered in the froth phase during flotation. Figure 4-14 shows that in excess of 90% of the hematite recovered in the froth concentrate was done so through entrainment. The remaining fraction of hematite reporting to the froth zone was probably in composite particles with quartz.

The UCT entrainment method previously used by Wiese (2009) to quantify entrainment in a platinum bearing ore was employed in this study and assumes that at the high depressant dosage of 1500 g/t the hematite was completely depressed and any recovery of fine hematite in the froth concentrate was as a result of entrainment. Size by size assaying of the froth concentrate established that most of the hematite recovered was in the -38 μm size fraction. This observation conforms to suggestion by Wills and Napier-Munn (2005) which states that hydrophilic material in size classes below 50 μm recovered to the froth product is recovered through entrainment.

As expected the system employing the collector blend retained more hematite through entrainment as compared to the single collector systems. The system's highly stable froth, evidenced by high water recovery, prevented drainage of water and entrained solids in the bubble lamellae back to the pulp phase.

The calculated entrainment factors in the experimental systems, were reported as the amount of hematite entrained per unit water. Entrainment factors correspond to the gradient of an entrained hematite versus water recovered graph. Table 4-11 shows that the flotation systems had entrainability values between 0.05 and 0.072. The entrainability values are large in comparison to those attained in the flotation of the Brazilian ore as will be shown in Table 4-19.

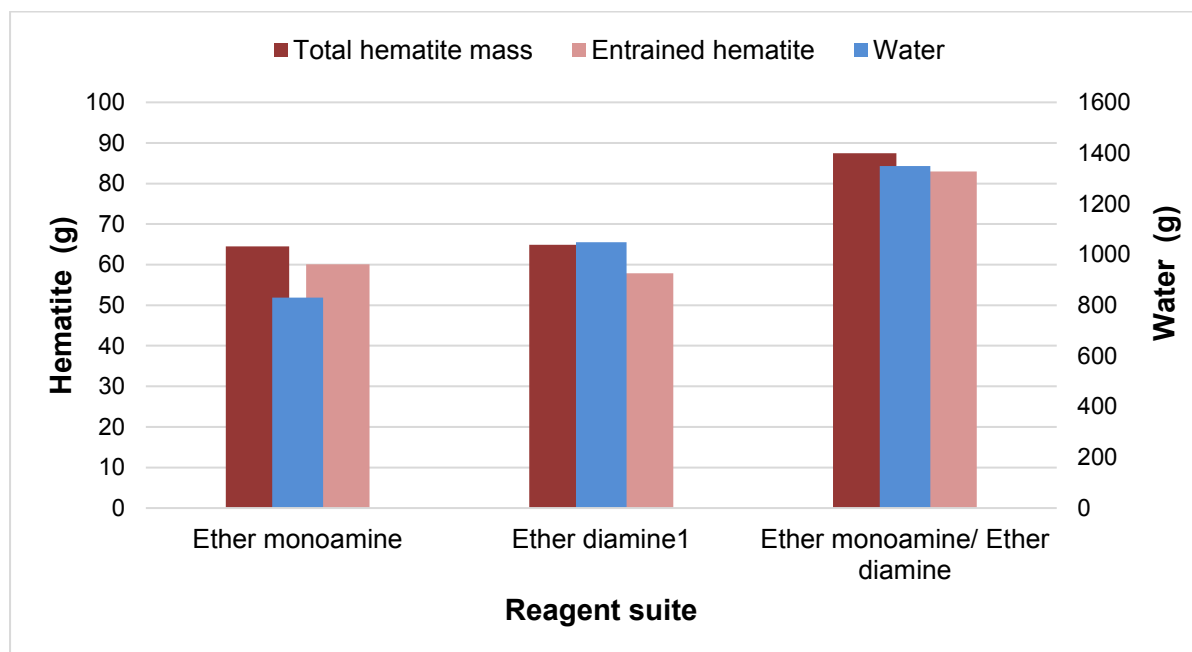


Figure 4-14: Effect of collector type on recovery of entrained hematite to the froth concentrate and the final water recovered after reverse cationic flotation.

Table 4-11: Entrainability values for the South African iron ore flotation system using alkyl ether amines collectors.

Reagent Suite	Entrainment (g of hematite/ g of water)
Ether monoamine	0.072
Ether diamine 1	0.056
Ether monoamine/ Ether diamine (mixture)	0.062

4.3.4. Residual amine analysis

Results for the amount of residual amine in solution after flotation are shown in Table 4-12. Alkyl amines responded well to the test method applied. It was observed that almost all the alkyl ether amine was used in flotation either as a collector or as a frother. 3% and 6.8% of the initial ether monoamine and ether diamine 1 added to the system, remained in the pulp zone after flotation, whereas 19% of the ether diamine 2 was in solution after flotation.

The residual amine analysis shows that the alkyl ether amines were generally strong collectors as a small amount of collector remains in solution after flotation. Ether diamine 1 and the ether

monoamine are stronger collectors than the ether diamine 2. Their collecting strength is evidenced by the high solids recoveries obtained in the froth product when the amines are employed as collectors as will be seen in Section 4.4

The ether monoamine and the ether diamine 1 possessed the lowest surface tension and therefore the best frothing ability. Due to their strong frothing effect, a larger amount of the ether monoamine and ether diamine 1 was used in flotation compared to the ether diamine 2 which was a weaker frother in the system under investigation.

Table 4-12: Residual amine in solution after the flotation of a South African iron ore.

Collector	% Amine remaining after flotation
Ether monoamine	3.0
Ether diamine 1	6.8
Ether diamine 2	19

4.3.5. Quartz batch flotation

Batch flotation tests using quartz were carried out as described in Chapter 3 and the values of the total water and solids recovered, are presented in Figure 4-15. Similar trends observed with the South African iron ore flotation were noted in this test work. Using the ether diamine 1 and the ether monoamine yielded the highest cumulative solids and cumulative water recoveries. The ether diamine 2 was a poor collector and had a low frothing strength and low solids recovery in the froth phase. Flotation using a pure quaternary ammonium salt or an imidazoline salt resulted in poor froth formation and no solids collection. As a result, the solids and water recoveries were too insignificant to present on the bar graph.

Montanol 800, an alcohol frother manufactured by Clariant Chemicals was added together with the quaternary ammonium salt and imidazoline salt. It was observed that the introduction of the frother resulted in solids and water recoveries previously not obtained in the frotherless systems, however, the solids and water recoveries remained significantly lower than those recovered using alkyl ether amine collectors. The results have shown that the alkyl ether amines are stronger quartz collectors and the alcohol frother contributed to the recovery of solids when the quaternary salts were used in quartz flotation.

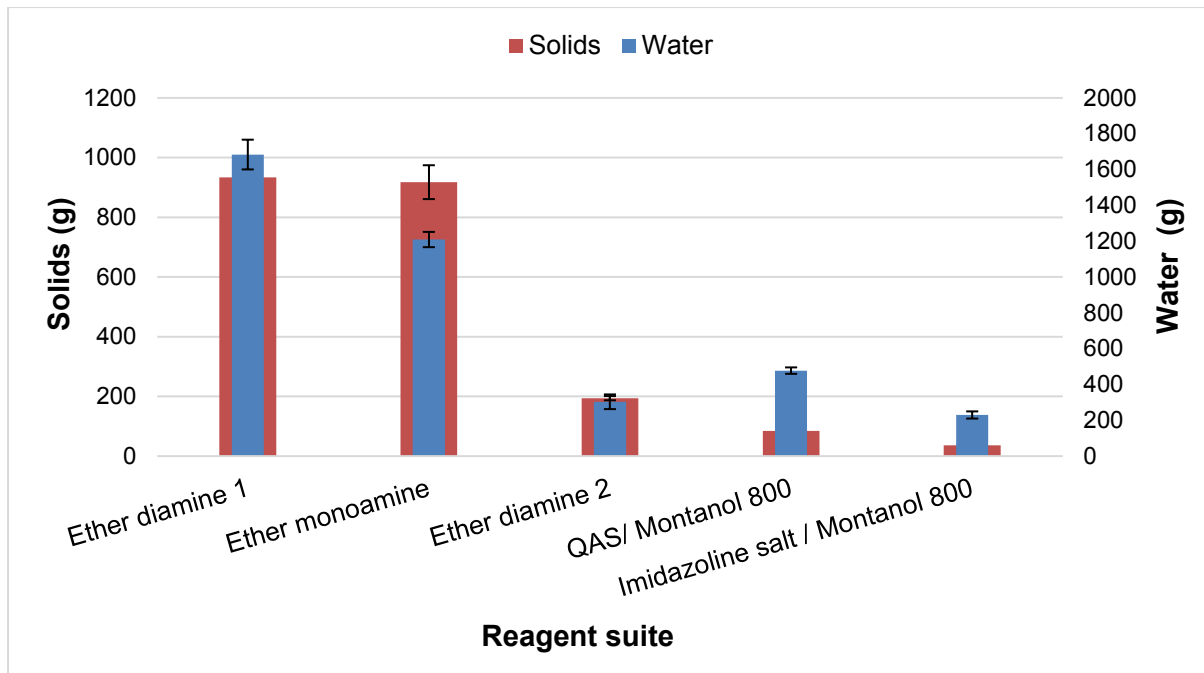


Figure 4-15: Final solids and water recovered after the flotation of quartz using different amine quartz collectors. A reagent suite consisting of starch at a dosage of 1500 g/t and collector at a dosage of 125 g/t was employed. Error bars show the standard deviation between duplicate tests.

The results for the cumulative solids versus cumulative water recovered are shown in Figure 4-16. The highest solids per unit water recovered was obtained when ether monoamine and ether diamine 1 were used as collectors. As expected the quaternary ammonium salt and the imidazoline salt had the lowest solids per unit recovery due to their low frothing properties.

The linear relationship between the cumulative solids and cumulative water recovered is indicative of the presence of the entrainment mechanism in the flotation system. Although entrainment of quartz would not be a problem during the separation of quartz from iron bearing minerals it is important to note that the collectors with the highest froth stability could contribute to recovery of quartz through entrainment and true flotation.

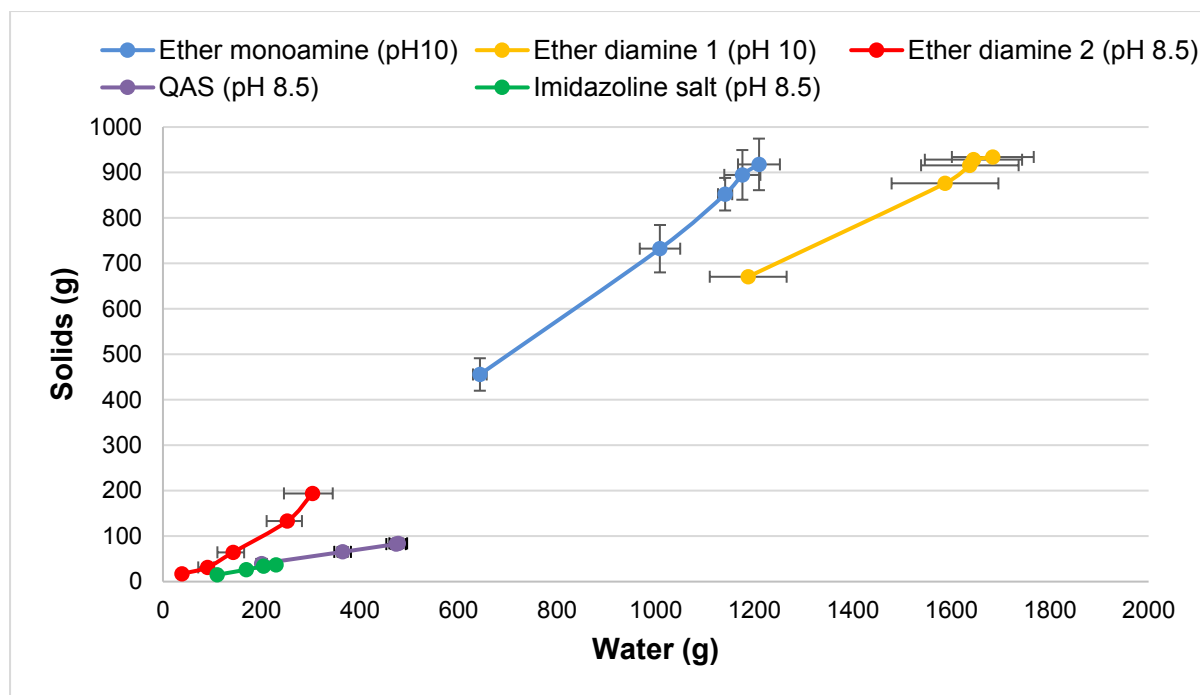


Figure 4-16: Cumulative solids versus water recovered after the flotation of quartz using different amine collectors. A depressant dosage of 1500 g/t and a starch dosage of 125 g/t were utilised. Flotation using the imidazoline and the quaternary ammonium salt was conducted in the presence of a frother. Error bars show the standard deviation between duplicate tests.

Figure 4-17 and Table 4-13 compare results obtained for total quartz recovery and the quartz recovery rate when the different reagent suites were used in the flotation tests. In a similar trend to that noted in the flotation of South African iron ore, the ether monoamine and the ether diamine 1 yielded the highest quartz recovery i.e. 94% and 74% recovery when the ether diamine 1 and the ether monoamine 1 are used, respectively. The same reagents also showed the highest flotation recovery rate, as seen in the steep gradient of the recovery versus time plots.

Based on the alkyl ether amine chemistry, the ether diamines which naturally have an extra $-NH$ group involved in collector adsorption of the quartz surface, should exhibit higher quartz collection rates than ether monoamines since they have more sites available for adsorption on the mineral surface (Araujo, Viana & Peres, 2005). The amine chemistry does agree with the result where the ether diamine 1 was more superior to the ether monoamine in quartz flotation, as predicted.

However, it does not hold in the case of the ether diamine 2 which performed poorly during flotation. By virtue of the ether diamine 2 having a long alkyl chain, the extent of solubility (solvation) could be considered as one of the limiting factors to the collector's adsorption on the mineral surface some long chain molecules are too hydrophilic to be solvated. However,

this assumption falls away as the same collector performs well in the flotation of the Brazilian ore as will be discussed in Section 4.4.

The imidazoline salt and the quaternary ammonium salt yielded the lowest quartz recovery, 3.6% and 8.6% quartz recovery, respectively. Their rate constants, however, are not very different to that of the ether monoamine, $k=1.5$. The ultimate recovery, R_{∞} values presented in Table 4-13 are similar to the experimentally observed recoveries, showing that the flotation of quartz was complete after 9 minutes of flotation time for all collectors except the ether diamine 2 which had an experimental recovery of 20% and ultimate recovery of 30%. Almost 90% of the recovered solids were recovered within the first 2 minutes of flotation. The standard laboratory flotation time for quartz in iron ore is between three and five minutes, however, a scale up by a factor of 2.6 is required for flotation using a larger scale machine (Nelson, Lelinski & Gronstrand, 2009). A first order kinetics recovery model was fitted to the data plots and the results show that the system agrees with a first order kinetic model. The model fit was statistically validated through residual plots provided in the appendix.

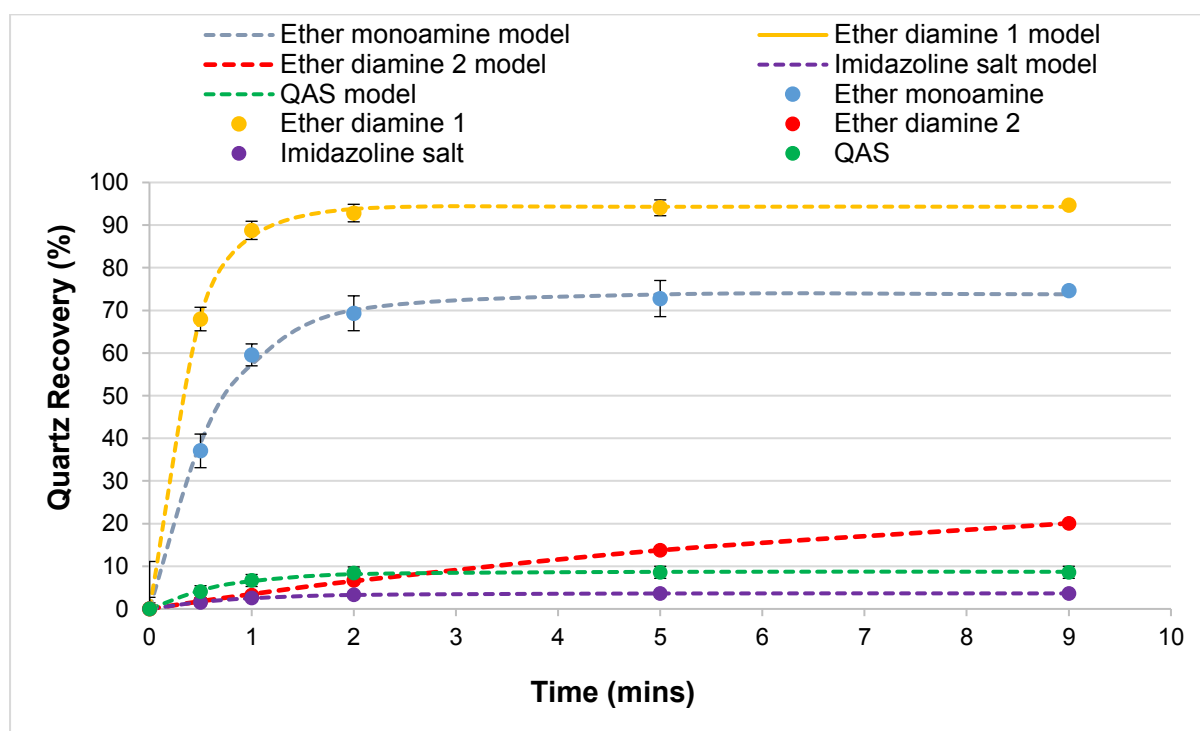


Figure 4-17: The recovery rate of quartz using different amine collectors. Tests were conducted at a collector dosage of 125 g/t. Flotation using the imidazoline and the quaternary ammonium salt was conducted in the presence of a frother. Error bars show the standard deviation between duplicate tests.

Table 4-13: Ultimate recoveries and the recovery rate of quartz when different amine collectors were used for flotation.

Collector	R_{INFINITY}	k
Ether monoamine	74	1.5
Ether diamine 1	94	2.6
Ether diamine 2	30	0.1
Quaternary ammonium salt (QAS)	8.7	1.4
Imidazoline salt	3.6	1.2

4.3.6. Summary of reverse cation flotation of the South African iron ore and Quartz

4.3.6.1. Mineralogy influence on flotation performance of a South African iron ore.

This section of the study focused on the reverse cationic flotation of a South African iron ore and the flotation of pure quartz using a range of collectors. The study showed that the batch flotation of a South African iron ore was challenging. The main problem being the lack of selective separation between the quartz and the hematite after reverse cationic flotation as demonstrated by the poor grade of iron (Fe) in the tails (hematite concentrate) coupled with a high retention of quartz in the tails.

Liberation data reported in Section 4.1 showed that the ore's textural complexity and the poor liberation of the minerals in the ore were the main causes of poor separation. The South African iron ore used in this study is made up of disseminated mineral phases with sizes of less than 20 μm which require liberation before flotation. The deleterious effect of poor liberation on flotation and mineralogical constraints in iron ore beneficiation have been reported previously (Nayak, 2013; Rath et al., 2014; Sahoo et al., 2016). In the direct flotation of banded hematite jaspers, Sahoo et al. (2016) attained a maximum grade of 45% iron from an initial grade of 29 % iron. To correlate the poor flotation performance to texture, electron mapping of the ore revealed the dissemination of hematite within the jasper, making liberation difficult.

Flotation studies on a Sishen iron ore sample conducted by Fouchee (2015) established that for the ore sample investigated, liberation in excess of 90% was only achieved at a grind size of 80% passing 18 μm . Reverse batch flotation using amine collectors, employed a modified beneficiation flow sheet consisting of rougher flotation for 18 minutes followed by regrinding, refloating (SiO_2 scavengers) for 12 minutes and additional depressant dosing, to achieve a hematite concentrate with an iron grade of 64.1% but an unacceptably low iron recovery of only 30%. Without circuit modifications the final iron grade was 54% from an initial 31% with a recovery of 48%, following 12 minutes of flotation. The majority of the hematite reported to

the SiO₂ concentrate through entrainment. Clearly the benefits of high grade are outweighed by poor recoveries making the batch flotation of ultra-fine material inefficient.

From Figure 4-5, Figure 4-6 and Figure 4-7, it is clear that full liberation of quartz and hematite in the South African iron ore would be expected in the -25 µm size fraction. However, milling finely to achieve that degree of liberation presents flotation operational challenges with regards to froth handling, the over stabilising effect of fines and the subsequent entrainment of fine hematite which overwhelmingly reduces the iron recovery in reverse cationic flotation of iron ores. Furthermore, fine grinding is an energy intensive process which can be costly.

4.3.6.2. Amine collector performance in the flotation of a South African iron ore and pure quartz

Interestingly, this study has shown the flotation superiority of branched alkyl ether amines (ether diamine 1 and the ether monoamine) over a linear alkyl ether amine (ether diamine 2) during the flotation of a South African iron ore and pure quartz flotation. Ether diamine 2 exhibited poor flotation performance for both systems that were investigated, contrary to what is reported in literature regarding the flotation behaviour of branched and linear alkyl ether amines. In fact Bleier, Goddard and Kulkarni (1976) mentioned that alkyl amines with linear chains are more effective at flotation than those with branched alkyl chains. However, reverse flotation studies on two martite ores conducted and reported in a patent by Shaw et al. (1982), demonstrated that for the same chain length, branched alkyl ether amines were superior to linear alkyl ether amines in the flotation of one of the ores.

The current study has also shown that, ether diamine 1 and the ether monoamine, both with chain lengths of between 8 and 10 carbon atoms, performed better than ether diamine 2 with a chain length of between 12 and 15 carbon atoms. Due to increased micellization and mineral surface coverage, resulting from stronger van der Waals interaction of long alkyl chains, long alkyl ether amine molecules are expected to impart more hydrophobicity to mineral particles. However, this study showed that shorter chain alkyl ether amines performed better for quartz flotation. Papini, Brandao and Peres (2001) and Vieira and Peres (2007) also reported that some short and medium chain alkyl ether amines perform better than long chain alkyl ether amines in the flotation of some ores although they had no scientific explanation for the observed results.

A recent publication on quartz separation from goethite by Quast et al. (2014) reported higher solids recoveries when using the ether monoamine collector compared to ether diamine 2. The researchers also used an imidazoline salt (ITU) but solids recoveries were poor, showing similarities to what was observed in the current study. At a collector dosage of 400 g/t, starch dosage of 300 g/t and pH 10, solids recoveries were 31%, 13% and 3.8% for the ether

monoamine, ether diamine 2 and imidazoline salt respectively. It can be deduced that the flotation performance of the collectors does not depend entirely on the collector chemistry but that ore chemistry and mineralogy contribute to the collectors' flotation performance.

The high water recovery obtained when alkyl ether amines were used as collectors in the flotation of quartz and the South African iron ore is indicative of the frothing strength and froth stabilising effect of the collectors. The alkyl ether amines which exhibited higher surface activities and hence, strong frothing effects, had the highest water and solids recoveries whereas the ammonium salt and the imidazoline salts with lower surface activities, had lower water and solids recoveries, corresponding to poor frothing and collecting abilities. This supports suggestions that water recovery can be applied as a measure of froth stability (Dhliwayo, 2005; Wiese, Harris & Bradshaw, 2011).

The presence of fine material reporting to the froth zone also enhanced froth stabilisation as noted by (Harris, 1982; Vieira & Peres, 2007; Filippov, Filippova & Severov, 2010). When the water recovery in the 2 phase system is compared to that recovered in a 3 phase system (see Figure 4-18), 3 phase systems attain higher water recoveries than two phase systems, confirming the substantial contribution made by fine solid particles to froth stability. Solid particles attached to bubbles, contributing to the froth viscosity. More viscous froths have higher elasticity, lower drainage rates and fewer bubbles bursting. The presence of ferric colloidal substances and $\text{SiO}_2\text{-Al}_2\text{O}_3$ hydrosols have also been reported to promote froth stability in flotation systems although fine mineral particles play a more significant role (Harris, 1982).

The effectiveness of using amine collectors in quartz flotation was assessed in this study and the results revealed that two out of three alkyl ether amines were good quartz collectors. Flotation was carried out at a pH equivalent to the pKa of the individual alkyl ether amine collectors. At the pKa there is co-existence of the aminium ions and their neutral molecules. This coexistence reduces electrostatic repulsions of aminium ions and promotes dense adsorption of the amine collectors on the mineral surface (Chernyshova et al., 2001; Kou, Tao & Xu, 2010).

The current study has revealed that the concentration of amine collectors in solution after flotation of the South African iron ore was close to zero. The Bromocresol method proposed by Araujo and Carvalho (2009) was successful at quantifying the alkyl ether amine collectors in solution after flotation. The fact that there was a small amount of collector remaining in solution shows that the ether amines strongly adsorb on the mineral surfaces and they also behave as strong frothers.

4.3.6.3. Effect of an alcohol frother on flotation performance

The imidazoline salt has a chain length of between 15 and 17 carbon atoms whilst the quaternary ammonium salt's carbon chains length varies between 8 and 18 carbon atoms. As previously mentioned, Papini, Brandao and Peres (2001) emphasized the need to add a frother when flotation is conducted employing fatty amine collectors e.g. imidazolines with such long chain lengths, as they have low surface activity, which was also noted in the current study. The quaternary ammonium salts, though not a fatty amine, exhibited a low surface activity which could indicate that the R- alkyl in its molecular structure has a carbon chain length closer to 18 carbon atoms in the alkyl chain as opposed to the lower value of 8 carbon atoms.

Montanol 800, an aliphatic alcohol, is a mixture of the commonly used hexanol and 2-ethyl hexanol frothers. Introducing an alcohol frother not only enhances froth generation and froth stability but assists the amine compounds' cationic species with adsorption on the quartz surface. The presence of the alcohol frother between the positively charged amine molecules reduces repulsion and increases collector density on the quartz mineral surface. This in turn promotes quartz flotation recovery (Comley et al., 2002; Liu et al., 2015). The neutral alcohol molecule functions in the same manner as the neutral amine molecule produced by alkyl ether amine collectors. The aliphatic alcohol frother has a straight chain structure which allows the formation a compact monolayer at the liquid/gas and solid/liquid interface. On the contrary, the branching in MIBC results in steric hindrance, preventing compact monolayer formation (Comley et al., 2002).

Quaternary ammonium salt cations and imidazoline salt cations are fully ionised at all pH values hence they are not capable of forming neutral amine molecules in alkaline systems. Vidyadharet al. (2002) and Filippov, Filippova and Severov (2010) made similar observations and conclusions when floating quartz using alkyl amines in the presence and absence of alcohols. Yuhua and Jianwei (2005) were successful at the flotation of quartz using a quaternary ammonium salt, CS-22, without any frother. However, this study has shown that some quaternary ammonium salts perform better in quartz batch flotation systems in the presence of a frother.

The presence of collector/frother interaction can be confirmed by 2 phase flotation results presented in Figure 4-18. The addition of the frother together with a quaternary ammonium salt or an imidazoline salt markedly improved the water recovery. There was a synergistic effect as the water recovery more than doubled after the frother addition to a 2 phase system dosed with an amine collector. This can be explained by the enhanced adsorption of non-ionic and ionic species at the air/liquid interface. The rheological properties of the adsorbed layers

of ionic and non-ionic molecules contribute to bubble elasticity, increasing froth stability (Harris, 1982).

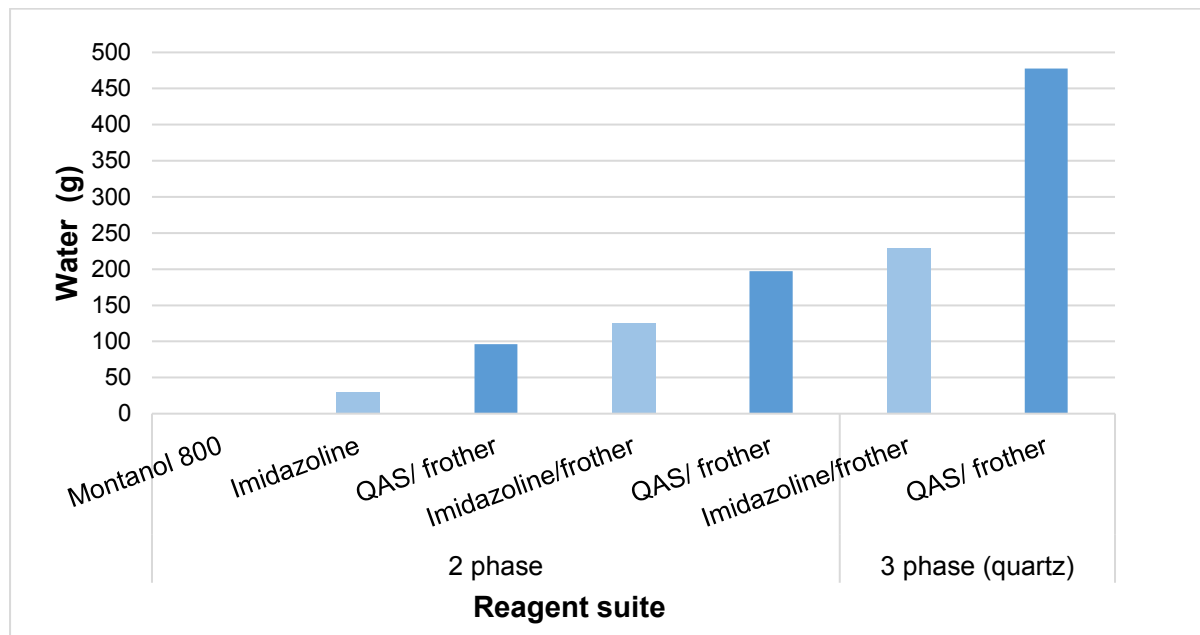


Figure 4-18: Water recovery in 2 phase and 3 phase (quartz) flotation using a quaternary imidazoline salt and a quaternary ammonium salt. A collector dosage of 125 g/t and a frother dosage of 60 g/t were employed in the flotation tests.

4.4. Reverse Cationic Flotation of a Brazilian iron ore

The reverse cationic flotation of a Brazilian iron ore served as a comparative study to the reverse cationic flotation of a South African iron ore. Flotation tests were carried out using the same collectors that were utilised in the reverse flotation of the South African iron ore as described in Chapter 3. Furthermore, an investigation into the reverse flotation of a Brazilian iron ore sample using different hematite depressants was conducted. The test work was sustainability driven, its aim being to identify alternative hematite depressants to replace corn starch.

4.4.1. Collector flotation performance

4.4.1.1. Effect of collector type on solids and water recovery

Reverse cationic batch flotation tests employing alkyl ether amines were carried out at a collector dosage of 125 g/t and a depressant dosage of 1500 g/t. Similar flotation tests using the quaternary ammonium salt and the imidazoline salt collector were conducted at collector dosages of 125 g/t and 250 g/t in the presence of 60 g/t of alcohol frother, after realising poor solid mass recoveries in frotherless systems.

The total solids and water recovered after flotation are presented in Figure 4-19. For the ore under investigation, high water and solids recoveries were noted for all alkyl ether amines at a collector dosage of 125 g/t. The solids recovery in all systems was above 30 %. The results also show that systems utilising the ether monoamine and ether diamine 2 exhibited almost similar water and solids recoveries, however, the system employing the ether diamine 1 had a far more superior solids and water recovery. Furthermore, ether diamine 1 had a superior froth stabilising effect as seen by the water recovery of 1257 g compared to the 735 g and 728 g of water recovered when the ether monoamine and ether diamine 2 were used as collectors.

Flotation using the imidazoline salt or the quaternary ammonium salt in their pure form did not yield any solids and water recovery. The addition of a frother at a dosage of 60 g/t improved the solids and water recovery for the quaternary ammonium salt at 125 g/t i.e. from a state of no recovery in the froth concentrate to a water recovery of 702 g and a mass recovery of 335 g corresponding to a froth concentrate solids pull of 33.5 %, however, the imidazoline salt still performed poorly in flotation. As illustrated in Figure 4-19, significant solids and water recoveries using the imidazoline frother were realised at a collector dosage of 250 g/t and a frother dosage of 60 g/t.

The high water and solids recoveries obtained when alkyl ether amine collectors were used are indicative of the frothing strength of the collectors. From visual observations, stable froths formed when alkyl ether amines were added in their pure form. Surprisingly, ether diamine 2

which performed poorly in the flotation of the South Africa iron ore and pure quartz performed exceptionally well in the flotation of the Brazilian iron ore in that high water and solids recoveries that were previously not observed in the flotation of a South African iron ore or the flotation of pure quartz, were now obtained in the flotation of a Brazilian iron ore.

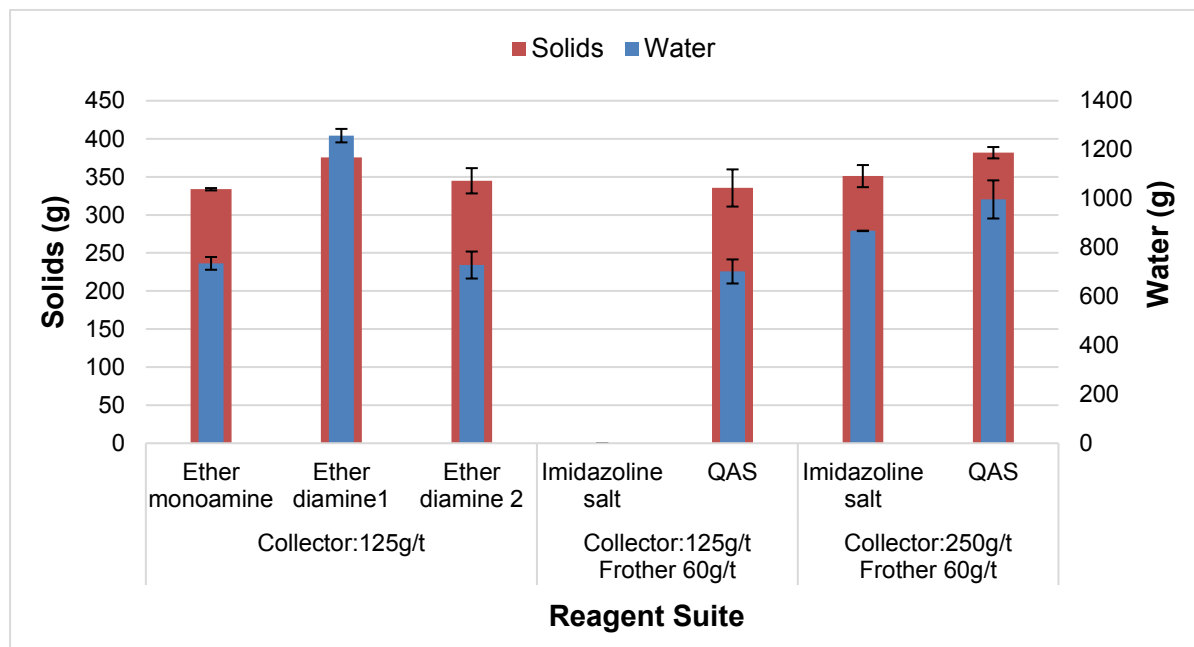


Figure 4-19: Final mass and water recovered after the reverse cationic flotation of a Brazilian iron ore using different reagent suites. Error bars show the standard deviation between duplicate tests.

Figure 4-20 illustrates the relationship between the cumulative solids recovered and the cumulative water recovered for the different reagent suites. The highest water recovery was obtained in a system dosed with the ether diamine 1 collector and shows that the ether diamine 1 had the strongest frothing ability in comparison to the other collectors. The aliphatic alcohol frother, Montanol 800, promoted froth generation and stability resulting in high water recoveries previously not attained in frotherless systems in which either the imidazoline salt or the quaternary ammonium salt were used as quartz collectors. Unlike the cumulative solids recovered versus cumulative water recovered graphs presented in Section 4.3, Figure 4-20 shows that the relationship between the solids and water recovered is nonlinear and extending the graphs does not yield an intercept at the origin. This is a clear indication that true flotation was prevalent in the Brazilian iron ore flotation systems, which is further supported by the high solids pull.

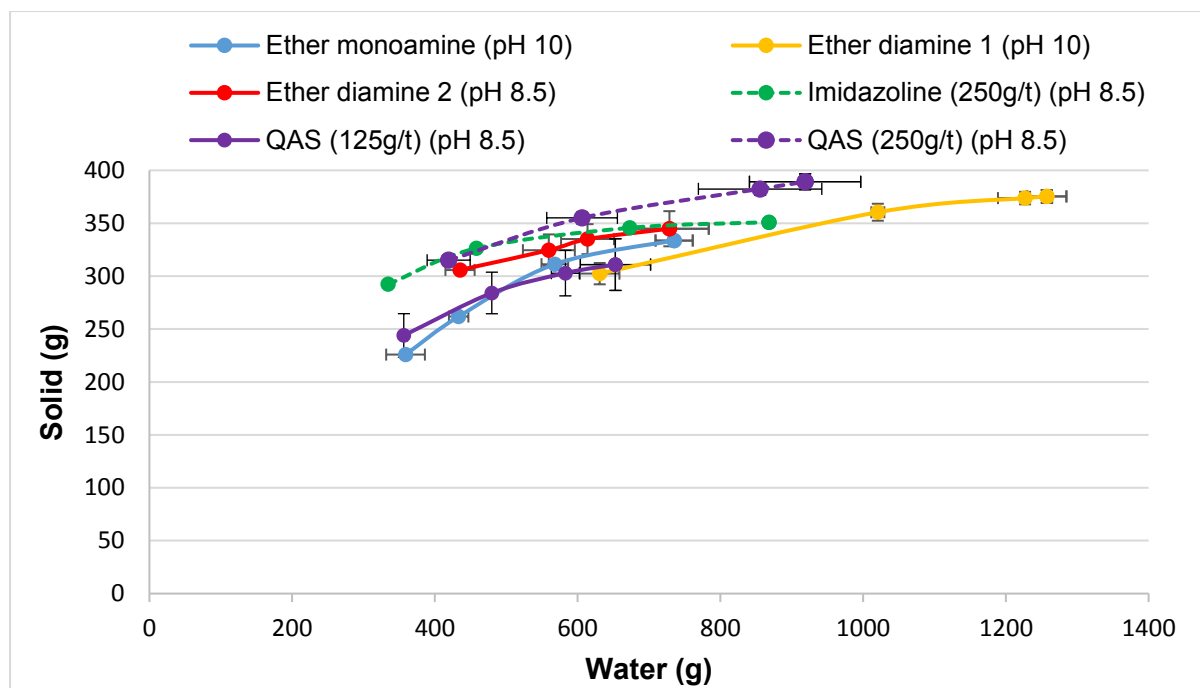


Figure 4-20: Cumulative solids versus water recoveries for the reverse cationic flotation of a Brazilian iron ore. Flotation tests were conducted at a starch dosage of 1500 g/t. pH conditions were determined from pKa values or standard flotation pH values sourced from literature.

A comparison of the solids recovery rate when different reagents suites were employed in the reverse cationic flotation of the Brazilian iron ore is shown in Figure 4-21. It is evident that the ore was fast floating, with most of the solids recovery occurring in the first two minutes of flotation. In the first 30 seconds of flotation, the system using alkyl ether diamines exhibited a faster recovery rate in comparison to the system employing the ether monoamine collector but as the flotation progressed, the ether monoamine exhibited faster recovery kinetics than the ether diamines. The results also established that the ether diamines attained a higher recovery of solids in comparison to the ether monoamine. After 9 minutes of flotation in systems employing alkyl ether amines the solids recoveries obtained were 375 g, 344 g and 333 g corresponding to mass pulls of 37.5%, 34.4% and 33.3% for the ether diamine 1, ether diamine 2 and ether monoamine, respectively.

The systems employing a reagent suite consisting of quaternary amine collectors and frother also showed solids recovery rates almost equivalent to those obtained for the alkyl ether amines. It can be seen that the frother positively contributed to the flotation kinetics of the system resulting in acceptable total solids recovery and recovery rates.

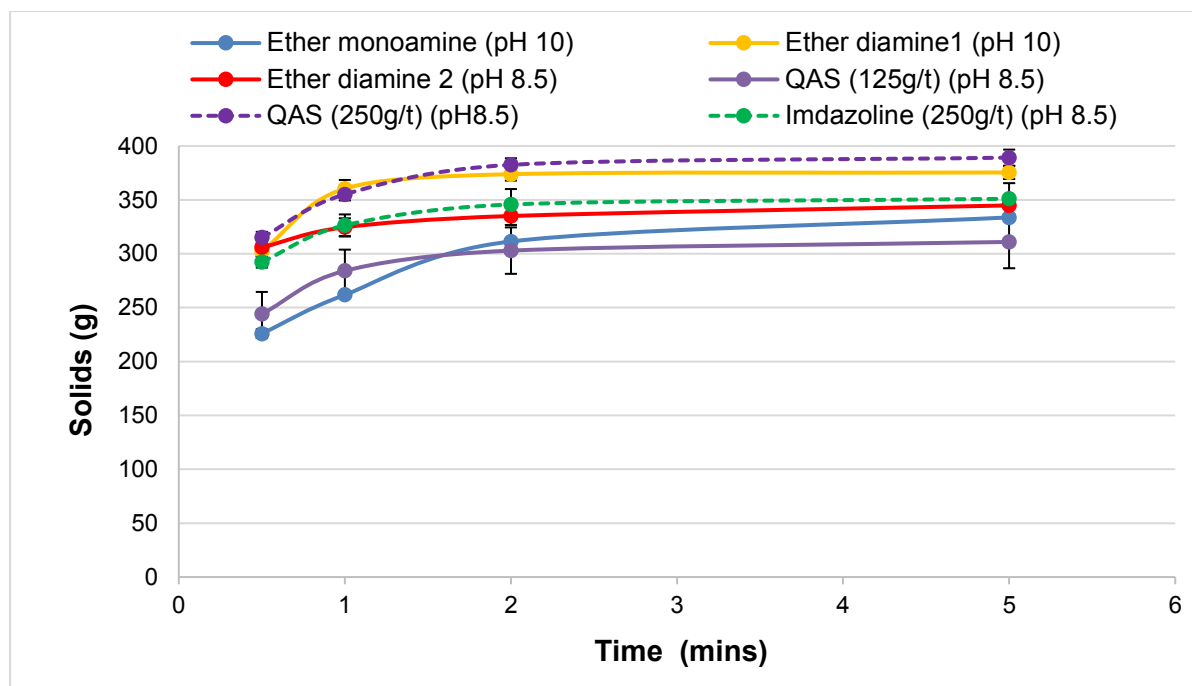


Figure 4-21: Solids recovery rates for the reverse cationic flotation of a Brazilian iron ore. Flotation tests using the quaternary ammonium salt (QAS) and the imidazoline salt included Montanol 800 frother (60 g/t). Error bars show the standard deviation between duplicate tests.

4.4.1.2. Collector effect on grade and recovery

The recovery and grade results of quartz in the froth concentrate collected after flotation, are presented in Table 4-14. For the same collector dosage (125 g/t), ether diamine 2 was the best collector with a quartz recovery of 97%, a quartz grade of 87% and a low iron content of 12%, contrary to what was observed in the studies on the flotation of a South African iron ore and the pure quartz sample, where it performed poorly as a collector.

Ether diamine 2 has an alkyl group with a chain length of between 12 and 15 carbon atoms. The long alkyl chain permits stronger interaction of the collector's non-polar ends through van der Waals forces forming longer and more hydrophobic aggregates, lowering the critical concentration for micellization and allowing for rapid flotation and high flotation recoveries to prevail (King, 1982). What is surprising is the collector's inability to behave in the same manner when used in the pure quartz system and the South African iron ore system reported in Section 4.3. As mentioned in Section 4.3, the collector chemistry alone has proved insufficient to describe the flotation performance. The mineral's surface chemistry and ore mineralogy possibly influence flotation performance.

The branched ether monoamine with an alkyl chain of 8 to 10 carbon atoms, performed equally as well as the ether diamine 2 with a quartz recovery of 95%, a quartz grade of 88% and an iron grade of 12%. The branched ether diamine 1 (alkyl chain length 8 to 10 carbon atoms) exhibited the poorest flotation performance as the froth concentrate contained the highest iron

grade of 26% and the lowest quartz grade at 74%. Given that the ether diamine 1 and ether monoamine are both branched and have a similar chain length range, the observed differences in quartz flotation are possibly due to the varying degrees of branching in the alkyl chains which subsequently determine the extent of adsorption on the quartz surface.

The use of the quaternary ammonium salt at a collector dosage of 250 g/t in the presence of a frother resulted in an improvement in recovery at a cost of a reduction in grade. The quartz grade reduced from 94% at a dosage of 125 g/t to 84% at a dosage of 250 g/t. This shows that the addition of the excess collector together with the collector's interaction with the frother markedly increased the froth stability, resulting in the recovery of more iron possibly through entrainment.

Table 4-14: Recovery and grade of iron and quartz in the froth (quartz (SiO₂)) concentrate after reverse cationic flotation of a Brazilian iron ore.

Collector	Collector Dosage	Frother Dosage	Froth (SiO ₂ Concentrate) Grades		Froth (SiO ₂ Concentrate) Recovery	
			SiO ₂ %	Fe %	SiO ₂ %	Fe %
Ether monoamine	125 g/t	-	88	12	95	6.6
Ether diamine 1	125 g/t	-	74	26	90	16.6
Ether diamine 2	125 g/t	-	87	12	97	7.5
QAS	125 g/t	60 g/t	94	6	90	3.0
QAS	250 g/t	60 g/t	84	15	99	9.4
Imidazoline	250 g/t	60 g/t	85	14	96	8.3

The primary interest of most iron ore research conducted by commercial researchers is the recovery and grade of iron in the hematite concentrates (tails), paying less attention to the SiO₂ concentrate. Observing the commercial approach, Table 4-15 shows the recovery of iron in the hematite concentrates recovered from the tails after flotation. It is evident that the ether diamine 2 is the best collector in the flotation of quartz in the Brazilian iron ore with an iron grade of 65% and a quartz content of 1.5%. The use of ether monoamine and imidazoline salt at dosages of 125 g/t and 250 g/t respectively, resulted in good flotation performance as their use achieved high iron grades i.e. 65% and 64% as well as high iron recoveries of 97% and 92%. Furnace specifications require a furnace feed ore to have a quartz content of less than 2%. This requirement was met with rougher flotation and no cleaning stages were employed.

Although increasing the quaternary ammonium salt dosage to 250 g/t rejected more quartz, it slightly increased iron losses. However, the increase in iron grade, from 63% at 125 g/t to

66% at 250 g/t and the associated decrease in the quartz content from 4.9% at 125 g/t to 0.6% at 250 g/t, overrode the small decrease in iron (Fe) recovery in the tails from 93% at 125 g/t to 89% at 250 g/t. The addition of the extra reagent is beneficial in that furnace specifications are met although rejecting more quartz is negated by the minimal iron losses.

At the same collector dosages of 125 g/t all the other collectors achieved iron recoveries above 90% except for the ether diamine 1. Due to high water recoveries, the ether diamine 1 is clearly a strong frother which formed a voluminous froth with low drainage leading to the entrainment of fine hematite and the subsequent low iron recoveries in the tails after flotation. Selectivity plots in Figure 4-22 indicate that generally all reagent suites used were selective in quartz separation from hematite. As expected from the high rejection of hematite through entrainment, the system using ether diamine 1 had the lowest selectivity.

Table 4-15: Recovery and grade of iron (Fe) in the tails (hematite (Fe₂O₃)) concentrate after the reverse cationic flotation of a Brazilian iron ore.

Feed ore grade: Fe = 45 %; SiO ₂ = 33 %					
Collector	Collector Dosage	Frother Dosage	Tails (Fe ₂ O ₃ Concentrate) Grades		Tails (Fe ₂ O ₃ Concentrate) Recovery
			Fe %	SiO ₂ %	Fe %
Ether monoamine	125 g/t	-	65	2.8	97
Ether diamine 1	125 g/t	-	61	5.7	83
Ether diamine 2	125 g/t	-	65	1.5	93
QAS	125 g/t	60 g/t	63	4.9	93
QAS	250 g/t	60 g/t	66	0.6	89
Imidazoline	250 g/t	60 g/t	64	2.3	92

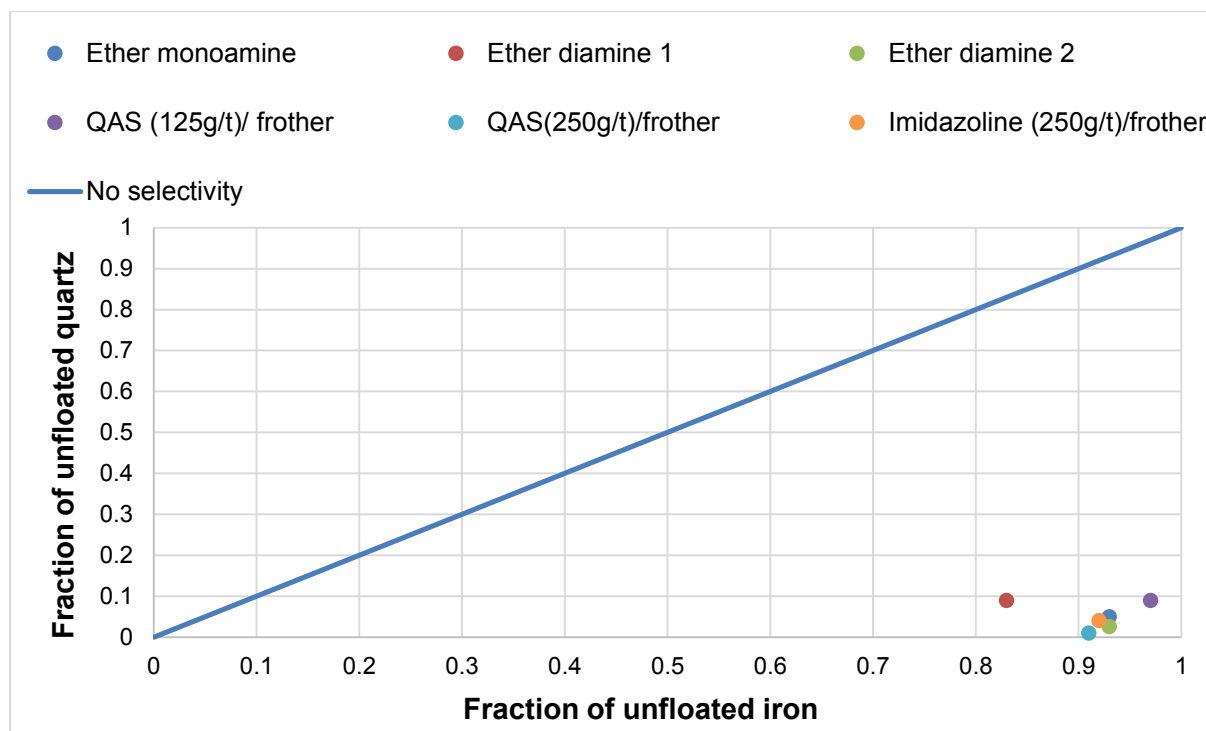


Figure 4-22: Selectivity plot for reverse cationic flotation of a Brazilian iron ore using different collectors

4.4.1.3. Collector effect on hematite entrainment

Figure 4-23 shows the percentage recovery of hematite into the froth concentrate. The UCT entrainment calculation method used in the entrainment studies on the South African iron ore was used to quantify the extent of entrainment in the flotation of a Brazilian iron ore. Particles in the sub 50 μm size fraction have been known to report to the froth concentrate through entrainment and are expected to form the bulk of hematite recovered in the froth zone.

The figure shows that the highest hematite recovery through entrainment was attained in systems with the highest froth stability. The system which employed ether diamine 1 as a collector had the largest amount of hematite reporting to the froth zone through entrainment corroborating the high water recoveries associated with the collector. Similarly the system that utilised the quaternary ammonium salt at a collector dosage of 250 g/t in the presence of a frother also resulted in high entrainment of hematite.

The calculated entrainment factors in the experimental systems, were reported as the amount of hematite entrained per unit water. Entrainment factors correspond to the gradient of an entrained hematite versus water recovered graph. Ether diamine 1 and the quaternary ammonium salt reagent suites have entrainment factors of 0.038 g hematite/ g of water and 0.047 g hematite/ g of water respectively as shown in Table 4-16. Ether diamine 2 at a dosage of 125 g/t and the imidazoline salt at a dosage of 250 g/t in the presence of a frother, have the

lowest entrainment factors, 0.023 g hematite/ g of water and 0.028 g hematite/ g of water respectively, thereby showing a low degree of entrainment.

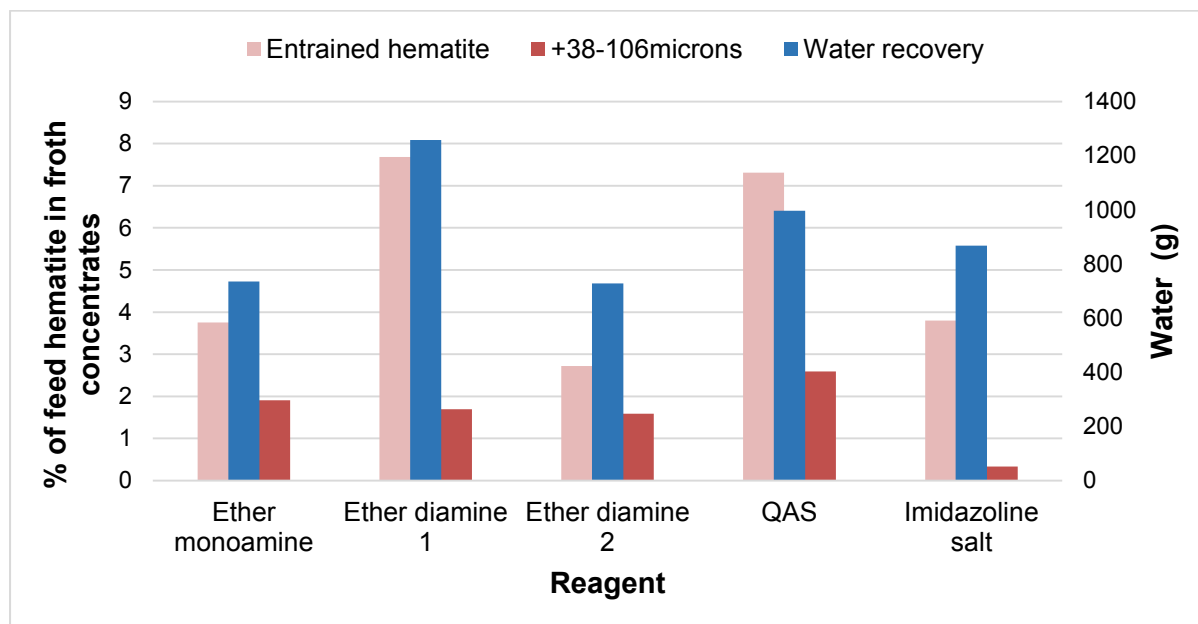


Figure 4-23: Effect of collector type on the percentage recovery of feed hematite to the froth concentrate and the final water recovered after reverse cationic flotation.

Table 4-16: Entrainability values for the Brazilian iron ore system using five amine collector reagent suites

Reagent suite	Entrainment factor (g hematite / g of water)
Ether monoamine	0.033
Ether diamine 1	0.038
Ether diamine 2	0.023
QAS (250 g/t) & frother (60 g/t)	0.047
Imidazoline salt (250 g/t) & frother (60 g/t)	0.028

4.4.2. Alternative depressant batch flotation tests

4.4.2.1. Effect of depressant type and dosage on solids and water recovery

Reverse cationic batch flotation tests were carried out using a carboxymethyl cellulose (CMC) and a guar depressant at three depressant dosages (250 g/t; 500 g/t and 1500 g/t) and a constant ether monoamine collector dosage of 125 g/t. The results were compared to those obtained when the standard depressant starch, at a dosage of 1500 g/t, was used to depress hematite. Figure 4-24 shows the total solids and water recovered after the reverse cationic flotation of a Brazilian iron ore under the different conditions.

Water recoveries decreased with an increase in depressant dosage for guar gum and starch depressant, which is attributed to a decrease in froth stabilising fine material and a subsequent decrease in froth stability as depressant dosage was increased. The water recovery increased when the CMC dosage increased from 250 g/t to 500 g/t. The water recovery, however, decreased when the CMC dosage was increased to 1500 g/t but the solids recovered increased. A comparison of the depressants at an equivalent depressant dosage of 1500 g/t shows that the highest water and solids recovery was obtained when the CMC depressant was used, indicating that the system had a more stable froth in comparison to the systems using a guar gum or starch as depressants.

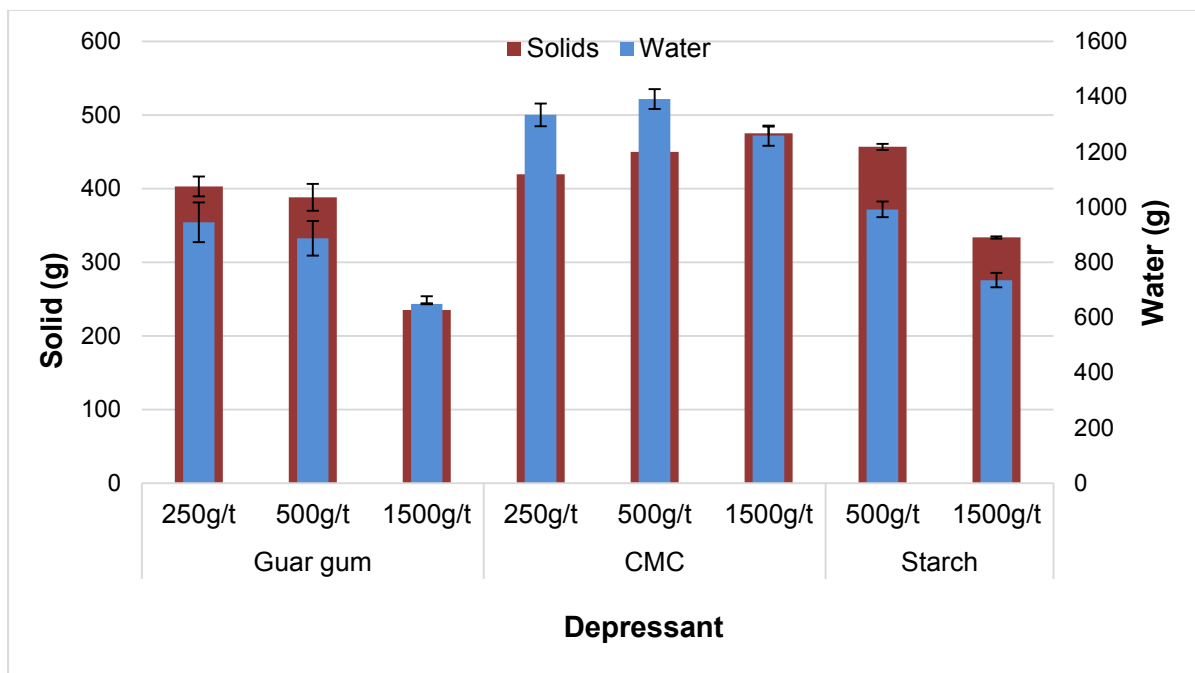


Figure 4-24: Total solids and water recovered after the reverse cationic flotation of a Brazilian ore. Flotation tests were conducted using 125 g/t of ether monoamine collector at pH 10. Error bars show the standard deviation between duplicate tests.

Figure 4-25 shows the cumulative solids versus cumulative water recovered during flotation. The ratio of the cumulative solids to cumulative water recovered decreases with an increase in depressant dosage from 500 g/t to 1500 g/t. This is more apparent for the starch and guar gum depressant as seen by the decrease in the slope of the curves particularly at a depressant dosage of 1500 g/t.

The slope of the CMC depressant curves does not change, in fact the solids per unit mass recovered is almost the same at all depressant dosages. The high water recoveries exhibited by the system in which the CMC depressant was used, indicates that the system had more stable froths than the systems in which starch or guar gum depressants were used.

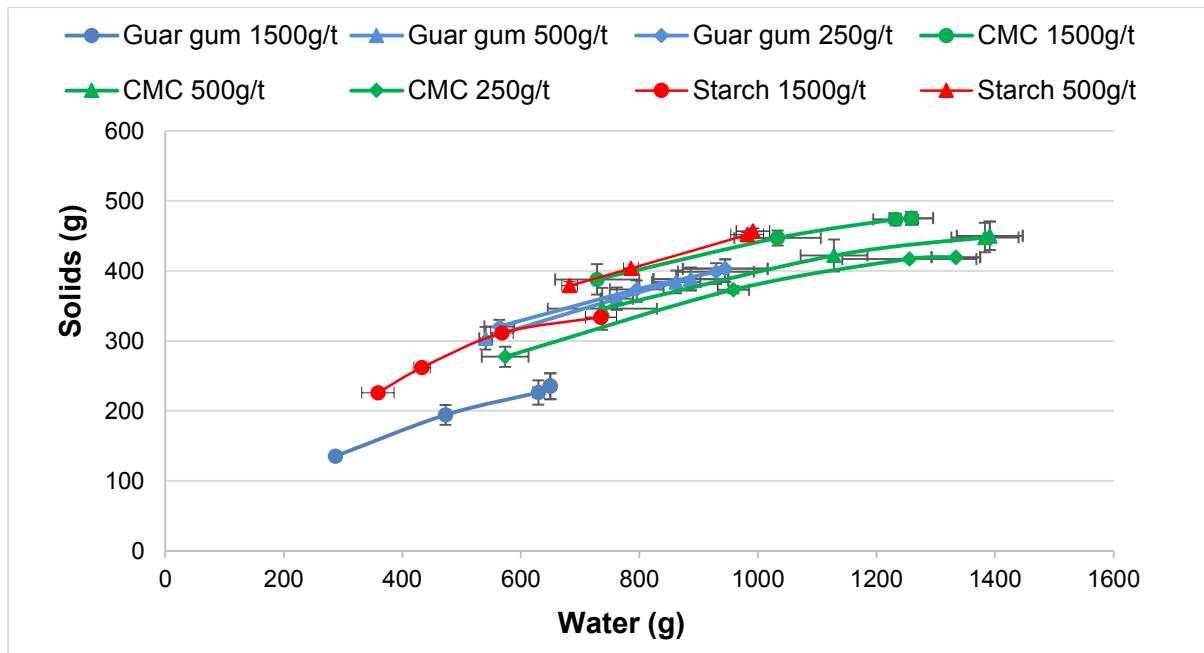


Figure 4-25: The relationship between the cumulative solids recovered versus the cumulative water recovered during the reverse cationic flotation of a Brazilian iron ore. Flotation was conducted with 125 g/t of an ether monoamine collector at pH 10. Error bars show the standard deviation between duplicate tests.

As seen in Figure 4-26, increasing the CMC depressant dosage only resulted in a small change in water recovered in the 5 minutes of flotation time in comparison to the guar gum. For example changing the CMC dosage from 500 g/t to 1500 g/t resulted in a decrease in water recovery by 133 g, whereas, a change in the guar gum dosage by the same degree resulted in a change in water recovery of 237 g.

This shows that for the system under investigation, the change in a guar gum dosage resulted in a significant depression of the fine solid material which would otherwise report to the froth zone and stabilise the froth, impacting on water recovery. Changing the CMC dosage, however, did not depress the solids material as much and as a result, the quantity of froth stabilising solid material reporting to the froth product did not change significantly resulting in a small change in froth stability and its associated water recovery.

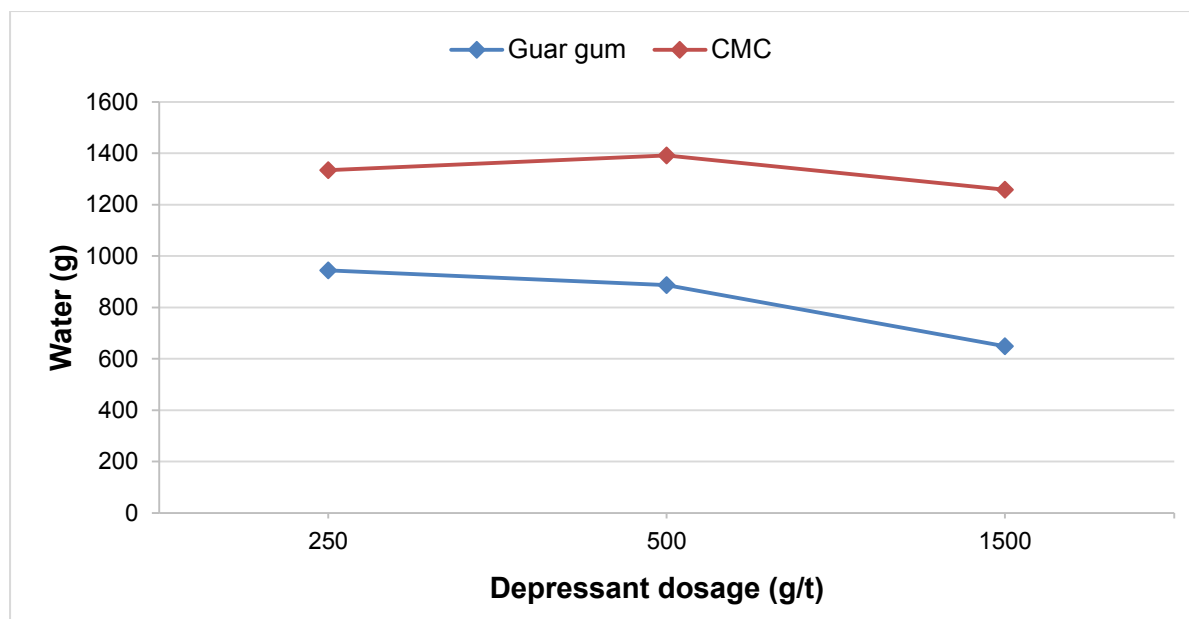


Figure 4-26: The effect of depressant dosage on water recovery

The rate of solids recovery and the total solids recovered after five minutes of flotation are shown in Figure 4-27. The results show that there was an insignificant change in the solids recovery rate as the depressant dosage was changed. This can be seen by a lack of change in gradient of the solids recovery versus time plots at different depressant dosages. As observed during flotation test work, the quartz mineral rendered hydrophobic by the collector, is fast floating, which enables its recovery rate to be less affected by the slight changes in froth stability, particularly when using a CMC and guar gum at depressant dosages of 250 g/t and 500 g/t.

The change in depressant dosage from 250 g/t to 500 g/t marginally changed the total solids recovered, however, the change from 500 g/t to 1500 g/t markedly changed the solids recovery when the guar gum and starch were used as depressants. As an example, changing the guar gum dosage from 250 g/t to 500 g/t resulted in the solids recovery changing from 40% to 39%, but the change in dosage from 500 g/t to 1500 g/t resulted in a pronounced drop in solids recovery from 39% to 23.5%.

The observed changes in the total solids recovered at the various depressant dosages suggest that the strongly frothing ether monoamine collector influenced froth stability more than the depressant did at low depressant concentrations and the effect of the depressant on froth stability was more apparent at high depressant dosages of guar gum and starch. In the case of the CMC, the increase in depressant dosage had a minimal effect on froth stability at all depressant dosages investigated.

The system using the CMC as a hematite depressant had the highest solids recovered in the given flotation time which correlates with the high water recoveries attained. The stable froth allows more material to be recovered as a result of entrainment. The system dosed with a CMC depressant exhibited the highest solids recovery rate.

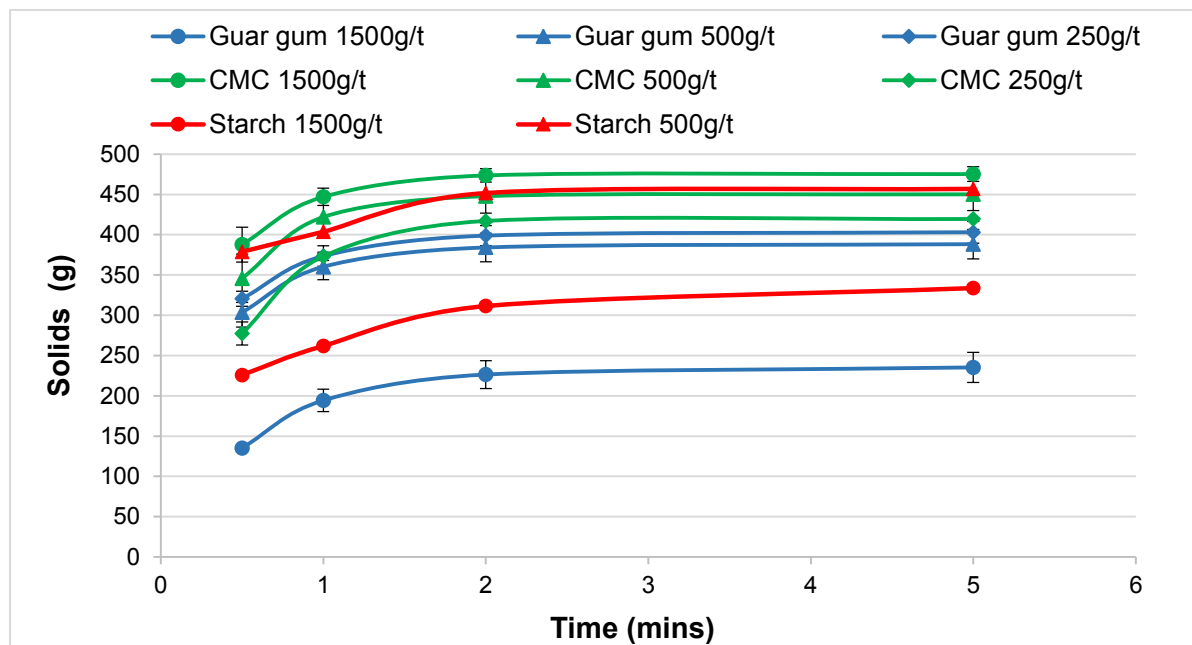


Figure 4-27: Solids recovery rate for the reverse cationic flotation of a Brazilian iron ore. Flotation tests were conducted using 125 g/t of ether monoamine collector at pH 10. Error bars show the standard deviation between duplicate tests.

4.4.2.2. Effect of depressant type and dosage on grade and recovery

Table 4-17 presents the quartz and iron recoveries in the froth concentrate after reverse cationic flotation of a Brazilian iron ore. The quartz recovery decreased with an increase in guar gum depressant dosage. The guar gum acts as a hematite depressant and also as a flocculant of fine mineral particles. As a result the fine quartz particles may aggregate, becoming too heavy to be transported out of the pulp zone into the froth zone by the bubbles.

The quartz recovery to the froth zone increased when a CMC was used as a hematite depressant. The addition of higher dosages of CMC may result in enhanced dispersion of particles in the system, with more quartz attaching to rising bubbles and reporting to the froth zone. CMCs have a strong negative charge which reduces the molecule's efficacy in attaching on negatively charged surfaces, instead dispersing minerals in the pulp (Wiese, 2009; Turrer & Peres, 2010).

This study has shown that employing a CMC as a hematite depressant resulted in stable froths and high solids recoveries when compared to systems using a guar gum or starch as depressants. The increase in froth stability is ascribed to the presence of undepressed

hematite fines and more hydrophobic fine quartz dispersed through the pulp resulting in fine mineral particles reporting to the froth zone where they have been reported to increase froth stability. A CMC and guar gum dosage of 1500 g/t and 250 g/t, respectively resulted in quartz recovery of 99.2% and 93.3% in the quartz concentrate, however, there was a significant recovery of iron of 20.4% and 14.5%, respectively. Starch remains superior as a hematite depressant since the iron recovery to quartz concentrate was only 3.2%.

Table 4-17: Recovery and grade of iron and quartz in the froth (quartz (SiO₂)) concentrate after reverse cationic flotation of a Brazilian iron ore.

Depressant type	Depressant Dosage	Froth (SiO ₂ Concentrate) Grades		Froth (SiO ₂ Concentrate) Recovery	
		SiO ₂ %	Fe %	SiO ₂ %	Fe %
Guar gum	250 g/t	76.9	23.1	93.3	14.5
	500 g/t	81.1	18.9	90.9	11
	1 500 g/t	69.5	30.4	52.7	12.1
CMC	250 g/t	69.2	30.8	89.1	20.6
	500 g/t	67.5	32.4	92.8	23.2
	1 500 g/t	71.7	28.3	99.2	20.4
Starch	1 500 g/t	93.8	6.2	94.7	3.2

The recovery and grade of iron in the tails (hematite concentrate) is shown in Table 4-18. Increasing the guar gum depressant dosage increased the recovery of iron with a detrimental effect on the grade. For example, increasing the guar gum dosage from 500 g/t to 1500 g/t resulted in a marked decrease in the hematite concentrate's Fe grade from 62% to 51% with a corresponding increase in the quartz content from 4.8% to 20.7%. The quartz agglomerates produced through flocculation, reduced the grade of hematite as the depressant dosage increased. The tabulated results have also shown that at the same dosage, the guar gum was more superior at depressing iron when compared to the CMC as shown by the higher iron recoveries in the tails concentrate. Tammishetti et al. (2014) conducted dispersion-flocculation tests and reported an increase in iron recovery but a decrease in iron grade as the dosage of a guar gum increased. The flocculation of fine iron ore particles into larger hydrophilic particles ensures that the particles have a lower tendency to entrain in the froth due to their large mass and inertia, allowing them to drain back to the pulp zone (Liu, Wannas & Peng, 2006).

At a CMC dosage of 1500 g/t, the quartz grade was 0.5 % which meets the preferred furnace specifications of less than 2% quartz in the furnace feed. At the same dosage of 1500 g/t, the

results show that only 79.6% of the iron was recovered, thus revealing a substantial loss in iron. It can be concluded that the starch at a dosage of 1500 g/t performed better than the other depressants since a hematite concentrate with an iron recovery of 96.8% and a quartz grade of 2.6% was achieved.

The presence of a negative charge on the hematite mineral surface and that of the CMC lowers the adsorption of the depressant on the mineral surface leading to poor depression of hematite. Turrer and Peres (2010) reported that some CMCs employed in their study were poor hematite depressants which was ascribed to the high negative charges exhibited by the CMC molecules, a result of the high DS introduced by COO⁻ substituents in the polysaccharide cyclic rings.

Table 4-18: Recovery and grade of iron (Fe) in the tails (hematite (Fe₂O₃)) concentrate after the reverse cationic flotation of a Brazilian iron ore.

Feed ore grade: Fe = 45 %; SiO ₂ = 33 %				
Depressant type	Depressant Dosage	Pulp Concentrate Grades		Pulp Concentrate Recovery
		Fe %	SiO ₂ %	Fe %
Guar Gum	250 g/t	63.3	3.7	85.4
	500 g/t	62.8	4.8	89.0
	1 500 g/t	51.8	20.7	88.0
CMC	250 g/t	61.8	6.32	79.4
	500 g/t	63	4.37	76.8
	1 500 g/t	66.1	0.5	79.6
Starch	1 500 g/t	65.4	2.62	96.8

4.4.2.3. Effect of depressant type and dosage on entrainment

The effect of changing the depressant type and dosage on the froth stability (water recovery) and entrainment was investigated and the results are shown in Figure 4-28 and Table 4-19. Depressant dosages of 500 g/t and 1500 g/t for the CMC and the guar gum, were considered as high depressant dosages with the strength to depress most of the hematite present in the system. More hematite was recovered through entrainment at depressant dosages of 500 g/t than at a depressant dosage of 1500 g/t. The system in which CMC was used as a hematite depressant achieved the highest hematite recovery through entrainment corresponding to the high water recoveries associated with increased froth stability.

The UCT entrainment calculation method which used high depressant dosages and normalised the mass of hematite recovered per unit mass of water, allowed for the flotation

performance of the different system conditions to be compared in terms of entrainment factors. The entrainment factors obtained at guar gum dosages of 500 g/t and 1500 g/t were 0.045 g of hematite/g of water and 0.023 g of hematite/g of water respectively.

For similar dosages of CMC, the system's entrainment factors were 0.055 g of hematite / g of water and 0.045 g of hematite /g of water. The high entrainment factors obtained in the presence of a CMC indicate a highly dispersed mineral system which equally explains the high iron recovery in the froth zone. A system using a guar gum and starch is coagulative in nature, the reagents behaving as flocculants in addition to acting as depressants of fine material thereby reducing the recovery of fine hematite through entrainment.

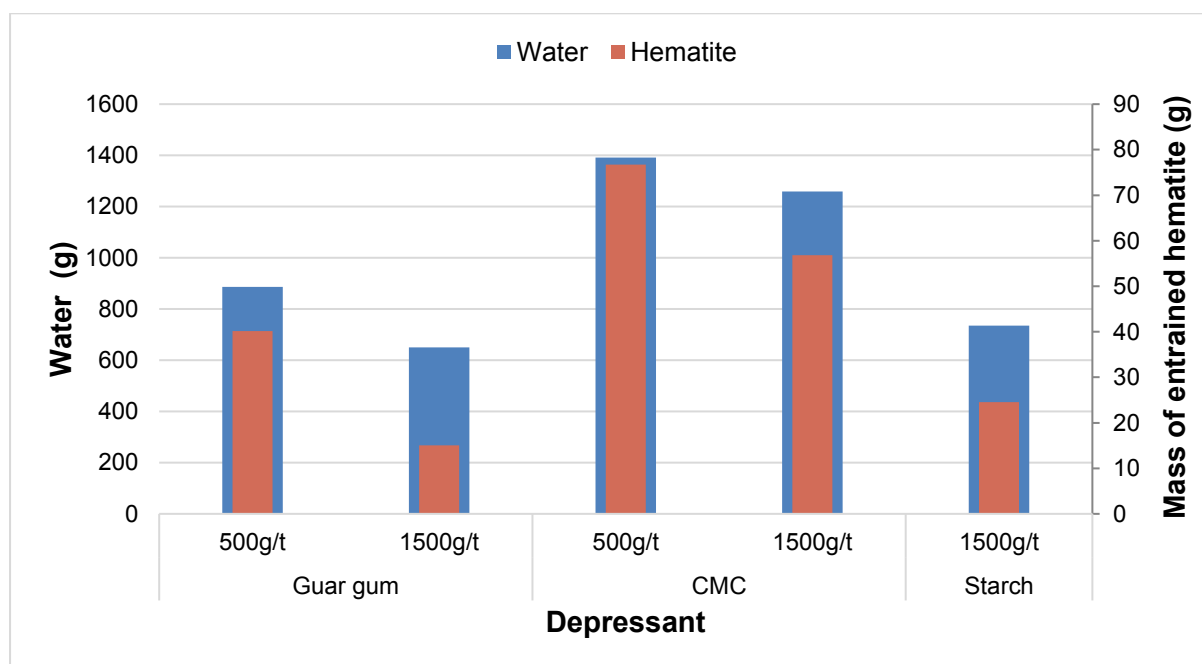


Figure 4-28: Effect of depressant type and dosage on the final water recovered and hematite entrainment during flotation

Table 4-19: Entrainment factors for the Brazilian iron ore system in the presence of guar gum, CMC and starch depressants.

Reagent suite	Entrainment factor (g hematite / g of final water)
Guar gum 500 g/t	0.045
Guar gum 1500 g/t	0.023
CMC 500 g/t	0.055
CMC 1500 g/t	0.045
Starch 1500 g/t	0.033

4.4.3. Summary of the reverse cationic flotation of a Brazilian iron ore.

4.4.3.1. Influence of mineralogy on the flotation performance of a Brazilian iron ore

The current study has shown that the Brazilian iron ore is amenable to flotation. The ease of separating quartz from hematite in this ore sample is attributed to the high degree of liberation of both minerals. As seen in Figure 4-7 and Figure 4-8, the overall liberation of quartz and hematite is 98% and 96% respectively. The flotation of quartz from iron oxide minerals requires a high degree of liberation of the target minerals as grade of the final tails concentrate affects further downstream processes. Owing to the abundance of highly liberated quartz, reverse cationic flotation is highly recommended and has been shown to produce high grade hematite for pellet production (Araujo et al., 2003; Ma, Marques & Gontijo, 2011; Rath et al., 2014).

A comparison of the Brazilian iron ore and the South African iron ore confirms the need for a highly liberated flotation feed if any separation is to be effected. The South African iron ore sample had a complex texture which affected the liberation of the mineral phases in the ore. Due to the ore's poor liberation, flotation was not selective and ultra-fine grinding would result in massive iron losses through entrainment of slimes, introducing froth rheological complexities which could result in processing difficulties.

4.4.3.2. Reagent suite effect on the flotation of a Brazilian iron ore

This study has shown that all alkyl ether amines tested in the reverse cationic flotation of a Brazilian iron ore i.e. the ether diamines and the ether monoamine, were successful at separating quartz from hematite by flotation. Interestingly, ether diamine 2 which was unsuccessful in the flotation of pure quartz and quartz in the South African iron ore performed well on the Brazilian iron ore. The difference in flotation performance has revealed that besides the reagent chemistry, the ore mineralogy and perhaps some complex surface chemistry equally impact the collector's flotation performance.

Ether diamine 2 is a long chain linear molecule with between 12 and 15 carbon atoms in its alkyl chain. Literature suggests that adsorption of the collector cations on the quartz surface is reinforced primarily because of the extra –NH group, available for electrostatic and hydrogen bonding (Shaw et al., 1982; Araujo, Viana & Peres, 2005). Furthermore, its linear structure leads to minimal steric hindrance thereby permitting a closely packed collector layer to adsorb on the mineral surface. The ether monoamine has also shown good flotation behaviour though it is a medium branched chain molecule (8 to 10 carbon atoms in the R – alkyl chain). In fact there is little difference in the total water and total solids recovered by these two collectors which can also be said of the recoveries and grades of iron and quartz both in the froth concentrate and the tails (hematite concentrate).

Papini, Brandao and Peres (2001) used ether diamine 2 and two forms of the ether monoamine used in the current study, with the same degree of neutralisation. Results from their study showed that one of the ether monoamine collectors performed as well as the ether diamine 2. Iron grades of 67.6% and 66.8% were achieved at iron recoveries of 91.4% and 90.6% for the ether monoamine and ether diamine 2 respectively. As has been mentioned before, Quast et al. (2014) used the ether monoamine and ether diamine 2 in the flotation of quartz from goethite and they observed that the ether monoamine produced concentrates with improved iron grade and recovery. The results from the studies of Papini, Brandao and Peres (2001), Vieira and Peres (2007) and Quast et al. (2014) as well as the current study suggest that the collector chemistry does not guarantee a straight forward prediction of flotation behaviour based on the reagent chemistry.

A key finding from this study is that improved flotation performance using amine collectors can be achieved in the presence of a neutral molecule. The need to add a neutral molecule in a system incapable of producing neutral molecules ought to be emphasized. As noted in the flotation studies using pure quartz (Section 4.3), the presence of a neutral alcohol frother improved the flotation recovery in a system using the quaternary ammonium salt or the imidazoline salt as quartz collectors. The same observation were made by Kou, Tao and Xu, (2010) and Liu et al. (2015) in the flotation of quartz in the presence of various alcohol frothers. The neutral molecule reduces electrostatic repulsion between the amine cationic heads attaching on the mineral surface. This results in a densely packed collector coverage on the mineral surface (Vidyadhar et al., 2002). Similarly the neutral molecule of an alkyl ether amine formed at alkaline pH values around pH 9 to pH 11 carries out the same function as the alcohol frother (Rao, 2004; Cassola, Silva & Bartalini, 2011).

The higher iron grades and iron recoveries achieved when starch was employed as a depressant in comparison to the grades and recoveries achieved when the guar gum and the CMC were used, have shown that starch was a better depressant than the guar gum and the CMC. Turrer and Peres, (2010) noted similar trends in their studies on alternative iron oxide depressants. However, the current study has not exhausted all guar gums and CMCs available. It should be emphasized that some CMCs and guar gums have also been reported to be better iron oxide depressants than starch. Araujo, Viana and Peres (2005) experimented with 3 CMCs of varying molecular weights and degrees of substitution.

Results from the studies showed that CMCs with high molecular weights and low degrees of substitution performed as well as starch. From the studies, it was apparent that the molecular weight and the degree of substitution influence the depressant efficacy. Nanthakumar, Grimm and Pawlik (2009) comparatively studied the effect of starch and guar gums in the depression

of iron in iron-phosphate minerals. In their study, guar gums performed better than starch. The ability of guar gums and CMCs to perform as iron ore depressants is due to the presence of the glucopyranose ring which provides the –OH groups to interact with the hydroxylated metal species on the mineral surface (Araujo, Viana & Peres, 2005; Nanthakumar, Grimm & Pawlik, 2009; Turrer & Peres, 2010)

The flotation test work has also revealed that at the operating conditions chosen for the current project, the guar gum is a stronger depressant than the CMC. The depression of iron bearing minerals e.g. pyrite using guar gum and CMC depressants has been previously studied (Bicak et al., 2007). Similar observations were made as the guar gum depressed the pyrite more than the CMC did. The poor depression of pyrite by the CMC has been ascribed presence of negatively charged –OH and –COO⁻ groups in the CMC molecules which reduced adsorption on the pyrite surface due to electrostatic repulsions. This observation suggests that besides Bronsted acid base interaction suggested by Laskowski, Liu and O'Connor (2007), CMC adsorption is also governed by electrostatic interactions.

Guar gums have been reported to adsorb through interactions between their –OH groups and the metal hydroxylated species on the mineral surface (Rath, Subramanian & Pradeep, 2000; Bicak et al., 2007). A study on a guar gum/talc system by Wang, Somasundaran and Nagaraj (2005) and a guar gum/pyrite system by Bicak et al. (2007) showed that the depression of talc and pyrite, respectively, in the systems, was marginally affected by changes in ionic strength, prompting the authors to rule out electrostatic interactions as a determining factor in guar gum adsorption on a mineral surface.

The current study did not consider the effect of cations (ionic strength) in the water used for flotation, however, Khraisheh et al. (2005) noted that an increase in concentration of divalent cations improves CMC adsorption and subsequent depression of pyrite using CMC depressants. Possibly due to interactions of the Ca²⁺ ions with the CMC molecules resulting in charge neutralisation. Investigating the effect of ionic concentration in the CMC/iron oxide system on the adsorption of CMC and depression of hematite could provide different results on depression of hematite using CMCs.

The UCT entrainment calculation method previously used to quantify entrainment in sulphide mineral systems has never been applied to iron ore flotation. The choice of this method over the ones reported in literature is substantiated by its ease of application as no sophisticated equipment is required. Size by size assaying revealed that the highest amount of hematite recovered in the quartz concentrates was in the -38 µm size fraction. It is well established that entrainment is common for particle sizes below 50 µm (Wills & Napier-Munn, 2005; Wang et

al., 2015), hence, it was expected to find a high prevalence of hematite below 50 μm in the froth concentrate.

The entrainment factors calculated for the Brazilian iron ore systems investigated, range from 0.025 to 0.05 depending on the reagent suites used. These entrainment factors are of the same numerical order as the 0.023 to 0.026 calculated by Wiese, (2009) in the study of entrainment in a base metal sulphide Merensky ore using the UCT method. As this study had never been applied iron ore flotation, the promising entrainment values calculated can be verified using a different entrainment analysis techniques. The preliminary values established in this study have shown that the UCT method could potentially be used in other mineral systems besides the sulphide ore flotation systems.

A comparison of the entrainability values presented in Table 4-11 and Table 4-16 has shown that the South African iron ore's flotation system had a more pronounced entrainment mechanism than the Brazilian iron ore's flotation system. This is confirmed by higher entrainability values obtained when the South African ore is floated. When both flotation systems used the ether monoamine and the ether diamine 1 as quartz collectors, more hematite mass was recovered through entrainment in the South African iron ore's flotation system. A possible explanation for this observation is that there are more fines present in the South African iron ore's pulp. When transported to the froth zone, the fines increase froth stability and subsequently there is less water drainage but more hematite entrainment in the froth zone. The entrainability data for both ores corroborates the solids versus water results presented in Figure 4-12 and Figure 4-20. The linear relationship between the solids and water recovered in Figure 4-12, shows the presence of entrainment in the South African iron ore's froth zone and the nonlinear relationship between the solids and water recovered in Figure 4-20, hints at minimised entrainment in the Brazilian iron ore's froth zone.

The froth zone is indirectly affected by changes in conditions in the pulp zone as mentioned by Wiese, Harris & Bradshaw (2011). The largest amount of entrained hematite was recorded in systems in which high water recoveries were obtained i.e. systems at low depressant concentrations as well as in systems employing a depressant (CMC) with a pulp dispersing effect in which more froth stabilising fine material reports to the froth zone. The study also showed that collectors with lower surface tensions and inherently strong frothing properties resulted in froths that retained fine hematite. The study confirms that the collector type, depressant type and depressant dosages affect the flotation mechanism in the froth zone.

5. Conclusions

5.1. Effect of ore mineralogy and texture on flotation performance

The mineralogy and texture of a low grade South African iron ore and a Brazilian iron ore were investigated using QEMSCAN and the results showed that these two parameters play a significant role in the flotation of the gangue mineral (quartz) from the hematite.

The laboratory flotation test work on the two ore samples showed that the quartz and hematite in the Brazilian iron ore were well liberated. Consequently, the Brazilian iron ore was amenable to flotation using the range of amine collectors investigated, whereas, the poor liberation of hematite and quartz in the South African iron ore rendered the ore not amenable to flotation. It was concluded that the poor flotation performance of the South African iron ore is a result of poor liberation brought about by the textural complexity of the ore. The texturally complex South African iron ore is characterised by finely disseminated mineral phases rendering it difficult to liberate the minerals through milling. The primary and secondary grind sizes of 80% passing 150 μm and 75 μm , respectively were not sufficient to liberate the quartz and the hematite. However, the Brazilian iron ore with a simple texture was easily liberated at a grind size of 80% passing 150 μm .

Ultra-fine grinding to a grind size of 80% passing 20 μm could be considered as a possible beneficiation route, however, this will require more energy input in the milling stage. A more advanced flotation circuit incorporating conventional flotation cells and column cells with different points of reagent addition must be designed. Considering the current low iron prices, the capital and operational expenditure may not justify the implementation of this processing route. However, in the long run, a well-designed flotation circuit which suits the South African iron ores may be profitable provided the iron prices surge back to their previous highs.

5.2. Effect of collector type on the flotation of quartz and the entrainment of hematite

This study has effectively shown that changing the collector type had a pronounced effect on the flotation recovery of quartz and the associated entrainment of hematite fines. Using the alkyl amines as quartz collectors yielded a high quartz recovery, whereas, using the pure quaternary ammonium salt collector or the pure imidazoline at the same collector dosage of 125 g/t did not yield a significant quartz recovery. It was concluded that the alkyl amine collectors exhibited a more superior flotation performance in comparison to the quaternary ammonium salt collector and the imidazoline collector which confirms the first hypothesis presented in Chapter 2.

Amongst the alkyl ether amine collectors, the superiority of ether diamines over ether monoamines is still to be proven. The test work has shown that the performance of these

collectors is not only defined by their molecular chemistry i.e. chain length but may also be affected by the mineral surface chemistry. The ether diamine 2 performed poorly in the flotation of pure quartz and in floating quartz from hematite in a South African iron ore, however, it excelled at floating quartz from hematite in a Brazilian iron ore. The flotation performance of these collectors differs depending on the mineral system, a phenomenon also noted by Papini, Brandao and Peres (2001). The ether monoamine (Flotigam EDA) has proved to be the most reliable collector as it consistently performed well in all binary mineral systems and the quartz system.

The observed differences in the flotation performance of alkyl ether amines and quaternary salts were ascribed to the differences in the molecular structures of the amine collectors which in turn affect the adsorption of the collectors onto mineral surfaces. At the alkaline flotation pH, alkyl ether amine collectors exist as dissociated cations in solution, co-existing with neutral amine molecular species which are self-generated by the system at alkaline conditions. Furthermore, the collectors are characterised by the presence of an –NH group which partakes in hydrogen bonding. Adsorption of alkyl ether amines on to quartz surfaces is achieved through electrostatic interactions between the cations and the negatively charged mineral surface and through hydrogen bonding between the collectors' –NH groups and the silanols on the quartz surface. Collector coverage is enhanced due to the presence of the neutral amine molecules that reduce electrostatic repulsion between cationic heads, thereby, increasing the collector species on the quartz surface leading to higher flotation recovery.

On the contrary the quaternary ammonium salt and the quaternary imidazoline salt fully dissociate in solution and these systems are not capable of generating neutral amine molecules. Attachment of the collector species onto the mineral surface is only through electrostatic interactions between the cations and the mineral surface. Due to the absence of neutral amine species in the system, the collector coverage density on the mineral surface is reduced as a result of electrostatic repulsion between the quaternary cations leading to poor quartz flotation.

The addition of a neutral amine species in the form of an alcohol frother has proved that neutral molecules are necessary to enhance flotation performance imparted by amine collectors. When an alcohol frother was added together with the quaternary ammonium salt and the imidazoline, there was a marked increase in the quartz recovery which had previously not been present in the absence of the alcohol frother. Through studies on the flotation of the Brazilian iron ore, it has been shown that employing a reagent suite consisting of a quaternary ammonium salt or imidazoline and a frother can yield almost similar results to those obtained when alkyl ether amines are used in the absence of a frother. The alcohol frother not only

induced the frothing effect but also assisted with the adsorption of the collector cations onto the mineral surface. The neutral alcohol behaved in a similar manner to the neutral amine molecular species generated by alkyl ether amines in that it reduced electrostatic repulsion between cations, increasing the collector density on mineral surfaces which leads to a higher collection of quartz (Kou, Tao & Xu, 2010; Liu et al., 2015).

The entrainment of hematite was influenced by the type of collectors employed in the batch flotation tests. From the calculated entrainment factors and iron grades in the froth concentrates, it can be concluded that systems employing alkyl ether amines as collectors, exhibited a higher degree of hematite entrainment than systems using the quaternary ammonium salt or the imidazoline salt. This statement is supported by surface tension results where, the ether amine collectors exhibited the strongest frothing strength and froth stabilising effect in comparison to the quaternary salts. The strong froth stability increases the probability of hematite entrainment as a result of poor froth drainage. Entrainment in systems using the quaternary salts only becomes significant when high collector dosages are added.

Entrainment mainly occurred in particles sizes less than 38 μm as confirmed through the size by size analysis of the quartz concentrates. The UCT entrainment calculation method assumes that at high depressant dosages, effectively all the hematite is depressed and any hematite recovered to the froth zone does so through entrainment. The UCT method has shown that it can provide a reliable rough estimate of the degree of entrainment in the flotation system. The calculated entrainment factors were of the same degree as the ones calculated by Wiese (2009) in the flotation of a Merensky ore.

5.3. Depressant type and dosage on the recovery of hematite

A guar gum and a CMC were tested as alternative hematite depressants. The study has shown that the tested depressants were not as effective as starch in depressing hematite although they show promise in replacing starch as a hematite depressant. The guar gum depressant behaved better as a depressant in comparison to the CMC.

Using low guar gum dosages of 250 g/t and 500 g/t resulted in good iron grades as reported in Chapter 4, however, at a high depressant dosage of 1500 g/t there were low iron grades. It seems that there is a threshold dosage where the guar gum's flocculating effect becomes significant, leading to the agglomeration of quartz particles which become too heavy to report to the froth zone. As a result the quartz agglomerates report to the pulp zone which subsequently lowers the hematite concentrate grade. The dispersive effect of the CMC has also been noted in the study. At higher CMC dosages i.e. 1500 g/t, more hydrophilic hematite fines reported to the froth zone which resulted in the stabilisation of the froth and subsequent entrainment of hematite. At low depressant concentrations, the froth zone was marginally

affected by changes in depressant dosage in the pulp zone. The effect of changing pulp conditions on the froth zone was only noted when the dosage was changed from 500 g/t to a higher depressant dosage i.e. 1500 g/t

6. Recommendations

The reverse cationic flotation of low grade South African iron ores is still in its infancy and there is significant work to be completed before the technology can be fully implemented. With that in mind, the following recommendations for future work are suggested in order to add knowledge to the field of iron ore beneficiation, particularly in the South African industry:

- A detailed feasibility study into the economic viability of conducting reverse cation froth flotation in the beneficiation of low grade South African iron ores.
- The development of ore specific cationic collectors and testing other cationic collectors which were not explored in this study.
- Modification of the processing route possibly through finer grinding and stage wise flotation i.e. using rougher and scavenger stages whilst incorporating column flotation in the flotation circuit with the aim of achieving a high grade hematite concentrate with minimal losses of hematite to the froth zone through entrainment.
- Investigating a wider range of guar gum and CMC depressants as alternative hematite depressants. Future studies could also consider the possible use of dispersants and coagulants in combination with the polysaccharide depressants.
- Assessing the liberation of quartz and hematite after ultra-fine grinding and employing reverse anionic flotation which has been reported to be less sensitive to the presence of slimes.
- Verification of the degree of entrainment of hematite by using other entrainment calculation techniques to validate the UCT method. Entrainment remains an unwanted mechanism which hampers recovery of hematite particularly in the batch flotation of fine material. It therefore requires attention in order to minimise losses of hematite.
- Floating ores from different ore bodies in order to assess whether the South African ore is generally difficult to process. In addition, a deeper investigation of the significance of mineral surface chemistry flotation performance using the amine collectors must be investigated.

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8. Appendices

Appendix A: Experimental Procedures

Appendix A1: Qemscan block preparation

1. The sample was split into seven particle size classes defined by the PSD as represented in Table 3-1. After screening, the samples were split, using a rotary splitter, into 4 g aliquots in preparation for making vertical sections for QEMSCAN analysis.
2. Milled graphite that is one size fraction smaller than the iron ore sample size fraction, was added to the iron ore sample, in a mass ratio of 1:1 (graphite: iron ore sample). The graphite was added to minimise touching particles in addition to assisting with electron conductivity.
3. Moulds for vertical sections were prepared using ice cubes. The moulds were labelled and lubricated then the previously prepared graphite-iron ore mixture was added to the moulds. A desired amount of resin was carefully added to the each of the moulds and the mixture in the mould was thoroughly mixed in a figure 8 pattern.
4. After mixing, the moulds were placed in a vacuum chamber for 10 minutes, thereby, breaking the vacuum in between to release the trapped air bubbles. After 10 minutes, the moulds were removed from the vacuum chambers and placed in a pressure pot overnight to cure. The sample blocks were subsequently removed from the moulds and sliced into smaller sections. The sliced sections were remounted into 30 mm round moulds. In each size fraction 3 sliced sections are added to the moulds.
5. The moulds with the new sliced sections were mixed with resin and returned to the vacuum chamber. Thereafter, they were placed in the pressure pot to cure overnight. Once the moulds had cured, a printed label and more resin were placed at the back of the mould. The blocks with the sliced sections were removed from the moulds in preparation for polishing.
6. Polishing was conducted in series of grinding and polishing. The blocks were rinsed with distilled water between each grinding and polishing step. After the polishing was complete, the polished blocks were placed in an ultrasonic water bath for 10 minutes. Thereafter, the blocks were rinsed with acetone, taking care not to scratch the polished surface.
7. The polished blocks were placed in an oven to dry at 30°C for 1 hour. As a quality control check, the polished blocks were analysed using a microscope. This was done to ensure that there were no plucked grains or cracked looking grains on the sample surface.

8. The final step was applying a carbon coating using the Emitech carbon evaporator, The carbon coat was essential, as it diffuses electrons off the surface of the samples when the block are in the QEMSCAN machine.

Appendix B: Statistical analysis of first order kinetic model fit: Residual plots

A linear regression analysis using the first order flotation recovery kinetic model was used to fit the model to the experimental data. Below are the formulae used to evaluate the fit of the data and the corresponding results are shown in Table 8-1 and Figure 8-1.

$$\text{Root Mean Square Error (RMSE)} : \sqrt{\frac{\sum_{i=1}^n (y_i - f(x)_i)^2}{n}} \quad \text{Equation 8-1}$$

$$\text{Residual Sum of Squares (RSS)} : \sum_{i=1}^n (y_i - f(x)_i)^2 \quad \text{Equation 8-2}$$

$$R^2 \text{ value} : \frac{1 - \text{RSS}}{\sum (y - \text{mean})^2} \quad \text{Equation 8-3}$$

Table 8-1: Input values used to evaluate the first order recovery kinetic model fit to experimental data

Flotigam EDA (Ether monoamine)						
Time	Experimental Recovery	Kinetic model recovery	Residual	Residual R ²		
0	0.0	0.0	0.0	0.0		
0.5	37.1	38.9	1.8	3.3	SSE	10.8
1	59.6	57.3	-2.3	5.2	RMSE	1.5
2	69.3	70.1	0.8	0.6	Mean	62.7
5	72.8	73.7	1.0	0.9	Sstotal	955.2
9	74.7	73.8	-0.9	0.8	R ²	1.0

The residual plots presented in Figure 8-1 are randomly displaced along the x-axis. This is the same trend observed for all the reagent suites employed in the study. The observed result implies that the linearized first order kinetic model fits the experimental data collected.

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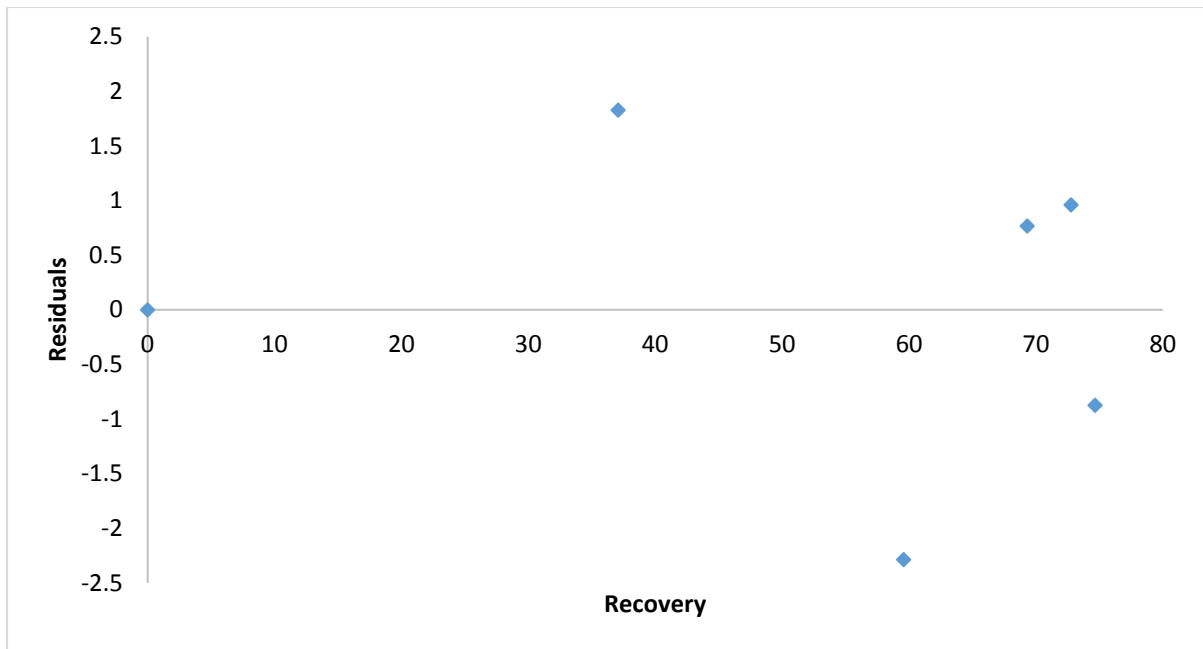


Figure 8-1: Residual plots comparing the first order recovery kinetics model to the experimental recovery.

Appendix C: Determination of residual amines in solution

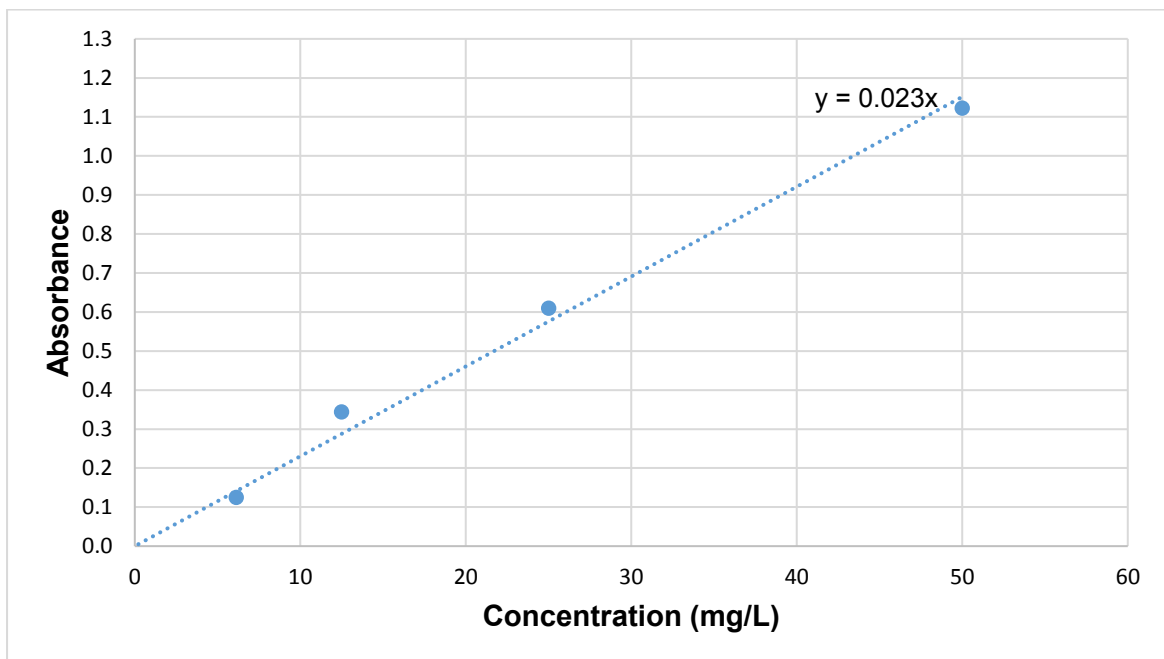


Figure 8-2: Sample calibration curve employed in determining the residual amine in solution after flotation using the ether monoamine collector. Serial dilution was used to prepare the known concentration solutions.

Initial amine content = 125mg

Absorbance supernatant = 0.065

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Final amine concentration = $0.065/0.023 = 2.83\text{mg/L}$

Final amine in solution = $2.83\text{mg/L} * 3\text{L} = 8.47\text{ mg}$

Percentage amine remaining after flotation = $8.47\text{mg} / 125\text{mg} * 100 = 6.78\%$

Appendix D: Determination of the amine compound's pKa

Table 8-2: Input variables used to determine the ether monoamine's pKa value using the calculus method.

NaOH Vol (cm ³)	ph	dpH	dVol	dpH/dVol	dVol/dpH
0.0	1.34				
0.5	1.56	0.22	0.5	0.44	2.27
1.0	1.84	0.28	0.5	0.56	1.79
1.5	2.12	0.28	0.5	0.56	1.79
2.0	2.50	0.38	0.5	0.76	1.32
2.5	3.00	0.50	0.5	1	1.00
3.0	3.49	0.49	0.5	0.98	1.02
3.5	3.75	0.26	0.5	0.52	1.92
4.0	3.90	0.15	0.5	0.3	3.33
4.5	4.07	0.17	0.5	0.34	2.94
5.0	4.42	0.35	0.5	0.7	1.43
5.5	5.10	0.68	0.5	1.36	0.74
6.0	6.76	1.66	0.5	3.32	0.30
6.5	8.00	1.24	0.5	2.48	0.40
7.0	8.30	0.30	0.5	0.6	1.67
7.5	8.50	0.20	0.5	0.4	2.50
8.0	8.75	0.25	0.5	0.5	2.00
9.0	9.24	0.49	1	0.49	2.04
9.5	9.38	0.14	0.5	0.28	3.57
10.0	9.51	0.13	0.5	0.26	3.85
10.5	9.67	0.16	0.5	0.32	3.13
11.0	9.75	0.08	0.5	0.16	6.25
11.5	9.79	0.04	0.5	0.08	12.50
12.0	9.95	0.16	0.5	0.32	3.13
12.5	10.36	0.41	0.5	0.82	1.22
13.0	10.65	0.29	0.5	0.58	1.72
13.5	11.12	0.47	0.5	0.94	1.06
14.0	11.62	0.50	0.5	1	1.00
15.0	12.25	0.63	1	0.63	1.59
16.0	12.48	0.23	1	0.23	4.35
17.0	12.51	0.03	1	0.03	33.33
18.0	12.53	0.02	1	0.02	50.00

APPENDIX D: Sample Batch Flotation Data

Table 8-3: Determination of the iron content and recovery in the tails (hematite concentrates) after flotation of a Brazilian iron ore with amine collectors

Reagent suite	Mass of Tails (g)	SiO ₂ wt %	Fe ₂ O ₃ wt%	Mass of Fe ₂ O ₃ in (g)	Moles of Fe ₂ O ₃ (mol)	Moles of Fe (mol)	Mass of Fe (g)	Fe% grade	Fe % Rec
Ether monoamine (125 g/t)	654.05	2.62	93.45	611.2	3.8	7.7	427.5	65.4	93.4
Ether diamine 1(125 g/t)	599.29	4.9	86.68	519.5	3.3	6.5	363.3	60.6	83.3
Ether diamine 2 (125 g/t)	607.21	1.35	92.77	563.3	3.5	7.1	394.0	64.9	92.5
QAS (125 g/t) Frother (60 g/t)	684.81	4.38	90.19	617.6	3.9	7.7	432.0	63.1	97.0
QAS (250 g/t) Frother (60 g/t)	627.98	0.55	93.85	589.4	3.7	7.4	412.2	65.6	90.6
Imidazoline (250 g/t) Frother (60 g/t)	616.62	2.16	92.05	567.6	3.6	7.1	397.0	64.4	91.7

Table 8-4: Determination of the Si content and recovery in the tails (hematite concentrate) after flotation of a Brazilian iron ore with amine collectors

Reagent suite	Mass of tails (g)	SiO ₂ wt %	Fe ₂ O ₃ wt %	Mass of SiO ₂ in (g)	Moles of SiO ₂ (mol)	Moles of Si (mol)	Mass of Si (g)	Si grade (%)	SiO ₂ Rec (%)
Ether monoamine (125 g/t)	654.05	2.62	93.45	17.1	0.3	0.3	8.0	1.2	5.0
Ether diamine 1(125 g/t)	599.29	4.9	86.68	29.4	0.5	0.5	13.7	2.3	9.0
Ether diamine 2 (125 g/t)	607.21	1.35	92.77	8.2	0.1	0.1	3.8	0.6	2.6
QAS (125 g/t) Frother (60 g/t)	684.81	4.38	90.19	30.0	0.5	0.5	14.0	2.0	9.0
QAS (250 g/t) Frother (60 g/t)	627.98	0.55	93.85	3.5	0.1	0.1	1.6	0.3	1.0
Imidazoline (250 g/t) Frother (60 g/t)	616.62	2.16	92.05	13.3	0.2	0.2	6.2	1.0	4.1

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Table 8-5: Determination of quartz and hematite mass and % recovery in the froth concentrates

Reagent suite	Mass of concentrates (g)	SiO ₂ wt %	Fe ₂ O ₃ wt %	Mass of SiO ₂ in concentrates (g)	Mass of Fe ₂ O ₃ in concentrates (g)	SiO ₂ Recovery (%)	Fe ₂ O ₃ Recovery (%)
Ether monoamine (125 g/t)	366.51	88.28	11.72	42.94	323.57	94.97	6.56
Ether diamine 1(125 g/t)	399.03	73.99	26.01	103.79	295.24	90.95	16.65
Ether diamine 2 (125 g/t)	354.36	87.17	12.83	45.47	308.88	97.41	7.47
QAS (125 g/t) Frother (60 g/t)	320.75	94.04	5.96	19.11	301.64	90.96	3.00
QAS (250 g/t) Frother (60 g/t)	396.36	84.60	15.40	61.05	335.30	98.98	9.39
Imidazoline (250 g/t) Frother (60 g/t)	360.07	85.80	14.20	51.13	308.93	95.87	8.26

Table 8-6: Determination of the quartz content in the tails (hematite concentrates) after flotation of a Brazilian ore using polysaccharide depressants

Depressant	Mass of tails (g)	SiO ₂ wt %	Fe ₂ O ₃ wt%	Mass of Fe ₂ O ₃ (g)	Moles of Fe ₂ O ₃ (g)	Moles of Fe (g)	Mass of Fe (g)	Fe grade (%)	Fe ₂ O ₃ Rec (%)
KU9 (250 g/t)	612.94	3.70	90.53	554.9	3.5	6.9	388.1	63.3	85.4
KU9 (500 g/t)	670.65	4.76	89.85	602.6	3.8	7.5	421.5	62.8	89.0
KU9 (1500 g/t)	745.45	20.72	74.03	551.9	3.5	6.9	386.0	51.8	88.0
DEP (250 g/t)	565.17	6.32	88.42	499.7	3.1	6.3	349.5	61.8	79.4
DEP (500 g/t)	539.92	4.37	90.02	486.0	3.0	6.1	339.9	63.0	76.8
DEP (1500 g/t)	555.79	0.5	94.44	524.9	3.3	6.6	367.1	66.1	79.6
STARCH (1500 g/t)	654.28	2.62	93.45	611.2	3.8	7.7	427.5	65.4	96.8

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Table 8-7: Determination of the quartz content in the tails (hematite concentrates) after flotation of a Brazilian ore using polysaccharide depressants

Depressant	Mass of hematite (g)	SiO ₂ wt %	Fe ₂ O ₃ wt%	Mass of SiO ₂ (g)	Moles of SiO ₂ (g)	Moles of Si (g)	Mass of Si (g)	SiO ₂ grade (%)	SiO ₂ Rec (%)
Guar (250 g/t)	612.94	3.7	90.53	22.68	0.38	0.38	10.57	3.7	6.7
Guar (500 g/t)	670.65	4.76	89.85	31.92	0.53	0.53	14.88	4.76	9.1
Guar (1500 g/t)	745.45	20.72	74.03	154.46	2.57	2.57	71.98	20.72	47.3
CMC (250 g/t)	565.17	6.32	88.42	35.72	0.59	0.59	16.65	6.32	10.9
CMC (500 g/t)	539.92	4.37	90.02	23.59	0.39	0.39	11.00	4.37	7.2
CMC (1500 g/t)	555.79	0.5	94.44	2.78	0.05	0.05	1.30	0.5	0.8
STARCH (1500 g/t)	654.00	2.62	93.45	17.13	0.29	0.29	7.99	2.62	5.2

Table 8-8: Determination of the quartz and hematite recovery to the froth concentrate after flotation using various depressant suites.

Reagent suite	Mass of concentrates (g)	SiO ₂ wt %	Fe ₂ O ₃ wt %	Mass of SiO ₂ in concentrates (g)	Mass of Fe ₂ O ₃ in concentrates (g)	SiO ₂ Recovery (%)	Fe ₂ O ₃ Recovery (%)
Guar (250 g/t)	410.48	76.91	23.09	315.70	94.78	93.30	14.59
Guar (500 g/t)	395.25	81.15	18.85	320.74	74.51	90.95	11.00
Guar (1500 g/t)	247.40	69.59	30.41	172.16	75.24	52.71	12.00
CMC (250 g/t)	422.11	69.23	30.77	292.21	129.90	89.11	20.63
CMC (500 g/t)	453.15	67.56	32.44	306.13	147.02	92.84	23.22
CMC (1500 g/t)	474.95	71.71	28.29	340.59	134.37	99.19	20.38
STARCH (1500 g/t)	332.31	93.84	6.16	311.84	20.46	94.79	3.23

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Table 8-9: Determination of the quartz and hematite recovery to the froth concentrate after the flotation of a South African iron ore

Reagent suite	Mass of froth concentrate (g)	Fe ₂ O ₃ Grade %	SiO ₂ Grade %	Mass of Fe ₂ O ₃ in concentrate (g)	Mass of SiO ₂ in concentrate (g)	Fe ₂ O ₃ Recovery (%)	SiO ₂ Recovery (%)
Ether monoamine (125 g/t)	159.94	45.74	54.24	73.16	86.75	14.47	26.20
Ether diamine 1 (125 g/t)	165.79	43.39	56.10	71.94	93.01	13.27	26.19
Ether diamine 1 & Ether monoamine (125g/t) (1:1 ratio)	214.22	51.01	48.98	109.27	104.92	17.69	25.93

Appendix E: Raw Liberation data

Table 8-10: Raw Quartz liberation data for a Brazilian iron ore

Liberation	<= 10%	<= 20%	<= 30%	<= 40%	<= 50%	<= 60%	<= 70%	<= 80%	<= 90%	< 100%	100%
Size Fraction(μm)	Quartz Mass % within the different liberation classes										
-300/+150	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.15	54.08	45.59
-150/+75	0.74	0.03	0.01	0.00	0.01	0.14	0.00	0.16	0.18	48.58	50.15
-75/+53	0.57	0.03	0.00	0.03	0.01	0.05	0.00	0.00	0.17	37.52	61.61
-53/+25	5.79	0.35	0.03	0.04	0.00	0.11	0.05	0.00	0.30	41.92	51.41
-25/+10	12.82	1.04	0.24	0.09	0.04	0.00	0.21	0.11	0.24	34.32	50.89
-10/+0	15.68	6.51	3.20	2.16	1.80	1.13	1.14	1.63	2.95	25.53	38.27
Combined	1.21	0.10	0.03	0.02	0.02	0.07	0.01	0.08	0.19	47.18	51.09

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Table 8-11: Combined quartz liberation data for a Brazilian iron ore

	Locked <= 30%	30% < LG Middlings <= 60%	60% < HG middlings <= 90%	90% < Fully Liberated
Size Fraction (µm)	Quartz Mass % within the different liberation classes			
-300/+150	0.14	0.00	0.18	99.68
-150/+75	0.78	0.15	0.48	98.59
-75/+53	0.60	0.10	0.23	99.07
-53/+25	6.16	0.15	0.45	93.24
-25/+10	14.10	0.13	0.56	85.21
-10/+0	25.10	5.03	6.78	63.09
Combined	1.33	0.11	0.36	98.20

Table 8-12: Raw hematite liberation data for a Brazilian iron ore

Liberation	<= 10%	<= 20%	<= 30%	<= 40%	<= 50%	<= 60%	<= 70%	<= 80%	<= 90%	< 100%	100%
Size Fraction(µm)	Hematite Mass % within the different liberation classes										
-300/+150	1.81	0.39	1.22	1.86	0.00	0.87	0.00	0.39	2.84	89.40	1.22
-150/+75	0.45	0.04	0.09	0.06	0.16	0.04	0.17	0.17	1.03	84.35	13.43
-75/+53	0.31	0.06	0.02	0.02	0.13	0.03	0.11	0.16	0.82	92.63	5.71
-53/+25	0.06	0.02	0.01	0.02	0.03	0.03	0.09	0.35	2.62	89.28	7.49
-25/+10	0.03	0.01	0.02	0.02	0.09	0.20	0.45	1.13	4.57	86.66	6.82
-10/+0	0.07	0.06	0.10	0.22	0.49	0.94	1.69	4.29	11.62	63.60	16.92

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Table 8-13: Combined hematite liberation data for a Brazilian iron ore

Liberation	Locked <= 30%	30% < LG Middlings <= 60%	60% < HG middlings <= 90%	90% < Fully Liberated
Size Fraction (µm)	Quartz Mass % within the different liberation classes			
-300/+150	3.40	2.70	4.06	89.84
-150/+75	0.58	0.26	1.41	97.74
-75/+53	0.39	0.19	1.12	98.31
-53/+25	0.09	0.08	3.08	96.74
-25/+10	0.06	0.30	6.34	93.30
-10/+0	0.23	1.63	18.36	79.78
Combined	0.34	0.31	3.61	95.74

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Table 8-14: Raw quart liberation data for a South African iron ore

Liberation	<= 10%	<= 20%	<= 30%	<= 40%	<= 50%	<= 60%	<= 70%	<= 80%	<= 90%	< 100%	100%
Size Frac (µm)	Quartz Mass % within the different liberation classes										
-150/+75	0.88	1.91	3.75	5.14	5.53	7.34	8.62	12.30	15.37	39.00	0.17
-300/+150	0.83	1.77	3.50	5.20	6.30	7.78	10.46	13.46	15.31	35.39	0.00
-75/+53	0.73	1.60	3.24	5.27	5.84	7.49	8.87	10.17	14.62	41.56	0.63
-53/+25	1.09	1.94	3.09	5.14	6.66	7.66	7.88	10.24	14.09	41.48	0.74
-25/+10	0.72	1.43	1.40	2.01	2.81	3.80	5.25	8.45	14.28	59.09	0.76
-10	1.10	1.48	1.68	2.55	3.59	5.38	9.18	16.77	29.94	26.33	2.00
Combined	0.90	1.70	2.86	4.21	5.03	6.60	8.64	12.68	18.28	38.39	0.70

Table 8-15: Combine quartz liberation data for a South African iron ore

Liberation	Locked <= 30%	30% < LG Middlings <= 60%	60% < HG middlings <= 90%	90% < Fully Liberated
Size Fraction(µm)	Quartz Mass % within the different liberation classes			
-150/+75	6.54	18.01	36.28	39.17
-300/+150	6.10	19.28	39.23	35.39
-75/+53	5.56	18.59	33.66	42.19
-53/+25	6.12	19.45	32.21	42.22
-25/+10	3.55	8.62	27.98	59.85
-10	4.26	11.52	55.89	28.33
Combined	5.46	15.84	39.60	39.09

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Table 8-16: Raw hematite liberation data for a South African iron ore

Liberation	<= 10%	<= 20%	<= 30%	<= 40%	<= 50%	<= 60%	<= 70%	<= 80%	<= 90%	< 100%	100%
Size Frac(μm)	Hematite Mass % within the different liberation classes										
-150/+75	0.80	2.53	4.24	5.06	8.04	8.71	10.41	9.48	11.63	28.07	11.03
-300/+150	0.99	2.54	4.93	6.52	8.66	9.42	10.16	8.35	12.09	30.70	5.64
-75/+53	0.85	2.44	4.07	6.19	7.81	9.81	10.13	9.44	10.79	23.71	14.77
-53/+25	0.40	1.29	2.18	3.16	5.07	6.52	7.50	7.91	10.62	28.43	26.91
-25/+10	0.32	1.00	1.65	2.22	2.83	3.28	3.87	4.63	8.89	29.71	41.59
-10	0.05	0.32	0.49	0.72	1.03	1.37	2.13	3.27	6.02	19.08	65.52
Combined	0.48	1.47	2.55	3.34	4.81	5.50	6.45	6.44	9.26	25.16	34.54

Table 8-17: Combined hematite liberation data for a South African iron ore

Liberation Degree	Locked <= 30%	30% < LG Middlings <= 60%	60% < HG middlings <= 90%	90% < Fully Liberated
Size Fraction(μm)	Hematite Mass % within the different liberation classes			
-150/+75	7.57	21.81	31.52	39.10
-300/+150	8.45	24.60	30.60	36.34
-75/+53	7.36	23.80	30.36	38.48
-53/+25	3.88	14.75	26.03	55.34
-25/+10	2.97	8.33	17.39	71.30
-10	0.86	3.13	11.42	84.60
Combined	4.49	13.66	22.15	59.70

EBE Faculty: Assessment of Ethics in Research Projects

Any person planning to undertake research in the Faculty of Engineering and the Built Environment at the University of Cape Town is required to complete this form before collecting or analysing data. When completed it should be submitted to the supervisor (where applicable) and from there to the Head of Department. If any of the questions below have been answered YES, and the applicant is NOT a fourth year student, the Head should forward this form for approval by the Faculty EIR committee: submit to Ms Zakiya Chikte (Zakiya.chikte@uct.ac.za); New EBE Building, Ph 021 650 5739). Students must include a copy of the completed form with the dissertation/thesis when it is submitted for examination.

Name of Principal Researcher/Student:
Ngoni Mhonde

Department: Chemical engineering

If a Student: yes

Degree: MSc Chemical Eng

Supervisor: Jenny Wiese

If a Research Contract indicate source of funding/sponsorship: Clariant

Research Project Title: Reagent suite investigation and optimisation for iron ore.

Overview of ethics issues in your research project:

Question 1: Is there a possibility that your research could cause harm to a third party (i.e. a person not involved in your project)?	NO
Question 2: Is your research making use of human subjects as sources of data? If your answer is YES, please complete Addendum 2.	NO
Question 3: Does your research involve the participation of or provision of services to communities? If your answer is YES, please complete Addendum 3.	NO
Question 4: If your research is sponsored, is there any potential for conflicts of interest? If your answer is YES, please complete Addendum 4.	NO

If you have answered YES to any of the above questions, please append a copy of your research proposal, as well as any interview schedules or questionnaires (Addendum 1) and please complete further addenda as appropriate.

I hereby undertake to carry out my research in such a way that

- there is no apparent legal objection to the nature or the method of research; and
- the research will not compromise staff or students or the other responsibilities of the University;
- the stated objective will be achieved, and the findings will have a high degree of validity;
- limitations and alternative interpretations will be considered;
- the findings could be subject to peer review and publicly available; and
- I will comply with the conventions of copyright and avoid any practice that would constitute plagiarism.

Signed by:

	Full name and signature	Date
Principal Researcher/Student:	Ngoni Mhonde Signed	4/12/2015

This application is approved by:

Supervisor (if applicable):	Signed	07/12/2015
HOD (or delegated nominee): Final authority for all assessments with NO to all questions and for all undergraduate research. Chair: Faculty EIR Committee	J. Pedersen Signed	6/1/2016
For applicants other than undergraduate students who have answered YES to any of the above questions.		

ADDENDUM 1:

Please append a copy of the research proposal here, as well as any interview schedules or questionnaires:

ADDENDUM 2: To be completed if you answered YES to Question 2:

It is assumed that you have read the UCT Code for Research involving Human Subjects (available at <http://web.uct.ac.za/depts/educate/download/uctcodeforresearchinvolvinghumansubjects.pdf>) in order to be able to answer the questions in this addendum.

2.1 Does the research discriminate against participation by individuals, or differentiate between participants, on the grounds of gender, race or ethnic group, age range, religion, income, handicap, illness or any similar classification?	YES	NO
2.2 Does the research require the participation of socially or physically vulnerable people (children, aged, disabled, etc) or legally restricted groups?	YES	NO
2.3 Will you not be able to secure the informed consent of all participants in the research? (In the case of children, will you not be able to obtain the consent of their guardians or parents?)	YES	NO
2.4 Will any confidential data be collected or will identifiable records of individuals be kept?	YES	NO
2.5 In reporting on this research is there any possibility that you will not be able to keep the identities of the individuals involved anonymous?	YES	NO
2.6 Are there any foreseeable risks of physical, psychological or social harm to participants that might occur in the course of the research?	YES	NO
2.7 Does the research include making payments or giving gifts to any participants?	YES	NO

If you have answered YES to any of these questions, please describe how you plan to address these issues (append to form):

ADDENDUM 3: To be completed if you answered YES to Question 3:

3.1 Is the community expected to make decisions for, during or based on the research?	YES	NO
3.2 At the end of the research will any economic or social process be terminated or left unsupported, or equipment or facilities used in the research be recovered from the participants or community?	YES	NO
3.3 Will any service be provided at a level below the generally accepted standards?	YES	NO

If you have answered YES to any of these questions, please describe how you plan to address these issues (append to form)

ADDENDUM 4: To be completed if you answered YES to Question 4

4.1 Is there any existing or potential conflict of interest between a research sponsor, academic supervisor, other researchers or participants?	YES	NO
4.2 Will information that reveals the identity of participants be supplied to a research sponsor, other than with the permission of the individuals?	YES	NO
4.3 Does the proposed research potentially conflict with the research of any other individual or group within the University?	YES	NO

If you have answered YES to any of these questions, please describe how you plan to address these issues(append to form)