DERIVATION OF METHODOLOGY CAPABLE OF IDENTIFYING SUITABLE COLLECTORS FOR COAL FLOTATION BY USING SURFACE DEPENDANT TECHNIQUES

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By
Susanna Gertruida Elizabeth de Jager

Cape Technikon
Cape Town
8000
South Africa

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Synopsis

The aim of the study was to develop an understanding of fine coal flotation emphasizing developing methodology capable of selecting the optimum flotation reagent. A secondary aim was to use the experimental data in a statistical program to validate the findings and investigate correlations between flotation performance and coal characteristics.

The predictions that were made from the coal characterisation results were confirmed. Oleic acid, iso-decanol and dodecene resulted in the best flotation performance on the coal samples that were evaluated. This is in agreement with previous research findings, that oleic acid is a good collector for coal and that branched hydrocarbons also increase flotation yields. The ability of unsaturated hydrocarbons to increase flotation yield was also confirmed.

The study included 5 coal samples from different collieries - Twistdraai (Highveld seam 3 and 4), Waterberg (Zone 10 -11), Syferfontein seam 5 upper (Highveld) and Witbank seam 2 and seam 4. Twistdraai, Waterberg and Syferfontein seam 5 upper were all found to be vitrinite rich coals. The Witbank coals are both more inertinite rich. The feed ash contents determined for the flotation feed samples were 28.8% for Twistdraai coal, 13.9% for Syferfontein seam 5 upper, 28.8% for Waterberg coal, 16.1% for Witbank seam 2 coal and 33.8% for Witbank seam 4 coal.

The coal characterisation study included petrographic analysis, proximate analysis, float-sink analysis, oxygen-containing functional groups, surface extraction, flotation release analysis and contact angle measurements. The primary characterisation parameters that influence flotation performance can be obtained from oxygen functional group determination (carboxylic group content), contact angle measurements on density separated coal and flotation release analysis (optimum flotation performance).

there was no correlation between the surface extraction values and the flotation recovery or ash content of the float products. The absorption values showed that Waterberg coal should be the easiest to float and need the least reagents. This, however, did not seem to be the case. Witbank seam 2 coal was the easiest to float at an absorbency of 0.388. Syferfontein seam 5 was the most difficult to float, but had an absorbency value (0.182), larger than that of Twistdraai (0.162).

It was found that contact angle measurements on density separated coal can be applied as a reagent screening tool, but the reagents need to be validated on flotation performance. An important conclusion is that the contact angle on the coal-rich fraction (ρ <1.5 g/cm^3) should be as low as possible, with no contact angle for the mineral-rich (ρ >1.5 g/cm^3) fraction. This results in a very selective reagent. Larger angles on the coal-rich fraction resulted in higher product yields during flotation. The best flotation performance was obtained when the contact angle between the oil and the coal-rich sample was about 90°.

The flotation tests showed that the best reagents for all of the coal samples studied were iso-decanol and dodecene. These reagents produced flotation products that were near to the release curve, and thus the optimum flotation results (obtained when using iso-paraffin as collector). Dodecene resulted in low ash products and iso-decanol in high yield products. The flotation data from the release analysis for Waterberg coal showed that iso-paraffin should also be considered as a collector for these coals.

An equation that was derived for predicting the ash and yield that can be obtained for a certain coal type and collector was used to confirm the experimentally obtained ash content and yield during flotation. The accuracy of the yield relationship was above 95% (p-value below 0.05) with a linear regression of 0.9289. The accuracy of the ash relationship was slightly lower, with a linear regression of 0.7841, but also above 95%.

The predictions that were made from the characterisation of the coal samples were confirmed in terms of flotation performance and the use of the methodology can be recommended.

It is recommended that, to improve the understanding of the flotation process of ultra-fine coal, the coal samples should be screened into individuall maceral groups to test the effect of maceral content on flotation. It is also recommended that the influence of contact angles on density separated coal and the effect of the contact angle size be further investigated. Interfacial chemistry and the effect of mixtures of collectors (for example dodecene and iso-decanol) on flotation could be the subject of a further investigation.

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Chapter 1

Introduction

The aim of this thesis is to develop an understanding of fine coal flotation emphasizing developing methodology that can be applied to the different coal types in South Africa. The methodology must be able to predict with high certainty what kind of reagent will be suitable for a certain coal type. This methodology will be developed using coal and reagent characterisation information that was obtained from the test work presented in this thesis. Since characterisation of a coal sample is very time-consuming, the statistical evaluation of the data may show which parameter has the largest effect on coal flotation; and it may be necessary to measure only one or two parameters to be able to ascertain as to which reagent will be suitable for a specific coal.

Since the Witbank no. 2 seam is nearing depletion and mainly the no. 4 seam is mined, it will be in the interest of the Witbank Collieries to determine the floatability of the no 4-seam coal (Powell, 1999). In general, no. 2-seam coal, being more vitrinite rich (brighter) is easier to float than no 4 seam coal (duller) which is more inertinite rich (Horsfall, 1993). The current study will therefore include coal from the no. 2 and 4 seams. Twistdraai colliery coal (Highveld seams 3 and 4 coal) and Syferfontein seam 5 upper (Highveld) coal.

Numerous companies recommend flotation reagents on the basis of trial and error. This is not the ideal modus operandi if the needs of the customer are to be addressed (i.e. the recommendation of the best reagent should be based on scientific principles). The collector that is used for floating a particular coal plays a very important role in the effectiveness of the floatation process.

A methodical approach is urgently needed by industry in order to obtain the optimum results from the flotation test work, thereby minimising the number of experiments whilst still obtaining the maximum value from the study. This will ensure that the effect of every flotation parameter is taken into consideration in order to determine which parameter or reagents are suitable.

1.1 Background

The mining industry in South Africa is currently examining the beneficiation propensity of previously discarded coal fines, particularly in the Witbank coalfield. In the past, beneficiation of coal fines was not considered economically viable due to the low price of coal and the high cost of the treatment processes e.g. drying of the coal fines (Du Preez, 1990). The use of modern mining methods has been shown to produce a large amount of fine coal, and the quality of the coal is also deteriorating (Powell, 1999).

A large amount of fine coal is created annually (12% of the ROM is finer than 0.5mm) and it is becoming necessary to beneficiate the large quantity of discarded coal fines. Apart from adding value to a waste product, ther is also an environmental issue (the fines are generally dumped into large ponds). A lot of carbonaceous material of export quality is still present in the fines (Rex and Prinsloo, 1987).

Spirals are generally used in fine coal beneficiation circuits for the treatment and separation of fine particles with a size range between 1mm and 150 µm (Powell, 1999). Goodman et.al. (1985) report that spirals tend to separate particles on the basis of mass and not density; and spirals are therefore applied on narrow size ranges. They also state that it is sometimes necessary to use spirals in conjunction with other cleaning processes such as froth flotation rather than replacing the spirals for optimum utilisation.

Operating studies by Franzidis and Harris (1995) indicated that there has been a dramatic change in the type of spirals that are employed. The spiral capacity ranges between 2-3 tph (tons per hour) dry solids per start, and it is common to find two or more starts per unit, i.e. the units are aligned one into the other to occupy the same space.

It is evident from the recently installed flotation Turbo column plants at Koornfontein colliery (1997), Rietspruit colliery (1995) and Kleinkopjie colliery (1996/97); as well as the Jameson cell plant at Atcom colliery (1996) that the implementation of coal flotation in the Witbank area is increasing. Second and third flotation modules are also being installed at certain plants e.g. Koornfontein.

In the Witbank coal field, seams 1, 2, 4 and 5 are usually mined together with a lot of impurities (minerals). This requires that the ROM (Run-of-mine) coal must first be beneficiated if it is to be prepared as an export grade thermal coal (28 MJ/Kg CV), (Horsfall, 1993).

The price for thermal grade export coal (F.O.B. Richards bay) is between R144 and R168/ton (Powell, 1999), which renders the possibility for coal flotation more positive. Froth flotation is a beneficiation method that discriminates on the basis of the surface characteristics of the coal. The characteristics of a coal include its floatability (which depends on the coal hydrophobicity), the amounts and types of minerals that are present in the coal matrix; and the presence of surface oxygen functional groups (Du Plessis, 1983). The optimum floatation performance (ideal separation) for a specific coal is also determined by means of release analysis, and flotation results are compared to this data (Dell, 1964).

The characterisation of coal samples provides a fundamental understanding of the oxidation state of the coal (Bunt, 1997). The data that is obtained usually indicates whether a coal is easily floated or difficult to float. By understanding the synergism between the coal and the flotation reagents, it may be possible to determine which reagent to use for flotation of a specific coal type. It should be mentioned that coal differs from seam to seam and from mine to mine (Horsfall, 1993).

1.2 Project:

A fundamental knowledge regarding the reagents and coals that are used for flotation is necessary to determine why certain reagents cause coal particles to float and others don't. The possibility of synergistic effects also needs to be investigated.

The coal samples that will be subjected to surface characterisation will be evaluated together with the pre screened model component flotation reagents (collectors) using froth flotation to determine the influence of the various compounds. The use of aromatic compounds (creosote) and paraffin type compounds (power paraffin) is very popular. The reagents will be characterised using contact angle measurements of the oil samples on the coal samples.

The results obtained from coal and reagent characterisation analysis will be used in a statistical design program to evaluate possible model fitting. The primary parameters influencing the flotation of fine coal will be evaluated and compared to actual flotation performance.

1.3 Objectives

The aim of this thesis is to develop a methodology for coal flotation that can be applied to the different coal types in South Africa. The methodology must be able to predict with a high amount of certainty what kind of reagent will be suitable for a certain coal type. This methodology will be developed using coal and reagent characterisation information that was obtained from the test work presented in this thesis. Since characterisation of a coal sample is very time-consuming; the proposed methodology will determine the parameters that have the largest effect on coal flotation. It may be possible to select a suitable reagent for a specific coal by measuring only one or two parameters.

Chapter 2

Literature review

2.1 Introduction

In this chapter an overview is given of the literature relevant to the project described in this thesis. This will include the origin of coal, coal surface characterisation, as well as froth flotation and the parameters that influence froth flotation.

2.2 What is coal?

Coal is a complex heterogeneous solid consisting predominantly of altered plant material (Osborne, 1988) originally growing between 200 and 300 million years ago (Horsfall, 1993).

The Northern Hemisphere (Laurasian) coals were formed by sedimentation of plant material in swamps in warm, moist climatic conditions. The accumulated plant material decayed under anaerobic conditions (due to accumulation beneath the surface of swamps), and after a gel-like phase, eventually metamorphosed into coal.

Elevation changes and accumulation of water-borne mud and silt periodically interrupted the growth and decay cycle, resulting in the formation of a number of coal seams.

The vegetation that formed coal in the Southern Hemisphere (Gondwana) the coal formation vegetation differed from the Northern Hemisphere vegetation. Coal-forming vegetation grew in shallow lakes that were fed by rivers flowing from elevated lakes. Glaciers fed the rivers during the formation phase, which resulted in a greater degree of aerobic decay. Due to the rivers being glacier fed, a lot of mineral matter was introduced. When the water drained from the gel-like phase, the peat was buried. The increase in temperature and pressure initiated the coalification process. The coalification process consists of 3 stochia called:

- Sedimentation Stage - deposition of organic plants in woody mashes.
- Diagenetic Stage - (biochemical change of the decaying debris via banded layers together with an accompanying compaction).
- Metamorphic Stage - (geochemical conversion to the final coal).

Because the plant matter decayed aerobically, Southern Hemisphere coal has a higher proportion of inertinite and mineral matter and lower proportions of vitrinite and exinite (Horsfall, 1993).

2.3 Classification of coal

During the coal formation process, coal acquires the most important characteristics that are used for coal classification, namely: Coal Grade, Coal Type and Coal Rank (Fullard, 1986).

2.3.1 The coalification process

The transformation process of peat via the steps of lignite, sub-bituminous, bituminous, anthracite and graphite is known as coalification. Falcon (1997) has presented data indicating the main chemical changes that occur during coalification. The chemical changes from peat through to graphite are listed in Table 2.1

Table 2.1: Chemical changes during coalification (Falcon, 1977)

Rank	Carbon (%)	Hydrogen (%)	Oxygen (%)	Nitrogen (%)
Wood	50	6	43	0.5
Peat	59	5	33	2.5
Lignite	70	5.5	23	1
Bituminous	82	5	10	2
Anthracite	93	3	2.5	1
Graphite	100	0	0	0

2.3.2 Grade of Coal

The grade of coal is determined by the amount of inorganic material that is left as residue after combustion (mineral ash content). The higher the amount of inorganic residue, the lower the grade of the coal. (Fullard, 1986).

2.3.3 Coal Type

The type of plant material from which the coal formed determines the type of coal. During the process of decay, the cellulose is biochemically converted to peat in the presence of adequate air and restricted decomposition, with a gradual increase in carbon rich compounds. During this coalification process, microscopic constituents called macerals can be distinguished.

Coal has a heterogeneous composition, which can be seen from the macerals (Smith, 1984; Coetzee, 1976).

Four main groups of macerals can be distinguished in SA coals:

1 Vitrinite
2 Exinite
3 Reactive semi-fusinite (RSF) and
4 Inertinite.

Reactive semi-fusinite can be found only in the Gondwana Coal area (Smith, 1984).

The group macerals are also subdivided as shown in the following table (Tsai, 1982:4 and Smith, 1984).

Table 2.2: Sub division of main maceral groups

Vitrinite	Colinite
	Telinite
Exinite	Sporinite
	Cutinite
	Algenite
	Resinite
Inertinite	Schleronite
	Semifusinite
	Fusinite
Reactive semi fusinite	Micrinite
	Macrinite

Vitrinite is the main maceral found in Northern hemisphere coal, and constitutes 70 - 80% of the seam (Meyers, 1982). The hydrogen content as well as the oxygen content of Vitrinite is average (Meyers, 1982). Exinite contains the highest hydrogen content (Meyers, 1982) and the lowest oxygen content of all the macerals. Inertinite contains the lowest amount of hydrogen and the highest oxygen content of all the macerals (Meyers, 1982).

From an isometamorphic maceral group evaluation on a 84 % (m/v) carbon content coal, it was clear that the larger aromatic clusters are present in vitrinite and that the aromaticity in a certain coal rank is the highest for inertinite (Tsai, 1982). This was confirmed by Van Nierop (1986).

2.3.4 Rank of Coal

The rank of coal is determined by the degree of change within the coal. The change is the result of metamorphism that the coal layers undergo over a period of millions of years. Pressure within the sediment layer, heat from the mantle of the earth and secondary heat as a result of weathering of the earth's crust causes the combustibles and moisture content to decrease. This results in higher carbon contents. High Rank coal has lower oxygen contents and lower rank coal can have oxygen contents up to 30 % (Fuerstenau, 1976).

With an increase in rank the structure of the coal tends to become less porous and the carbon more aromatic. An increase of aromaticity is found with an increase in rank, therefore anthracite will be more aromatic than brown coal (Meyers, 1983). The structure of the coal becomes more ordered for higher rank coals (see Figure 2.1), the aromatic lamellae grow in proportion and size and their alignment becomes more perfect (Horsfall, 1993).

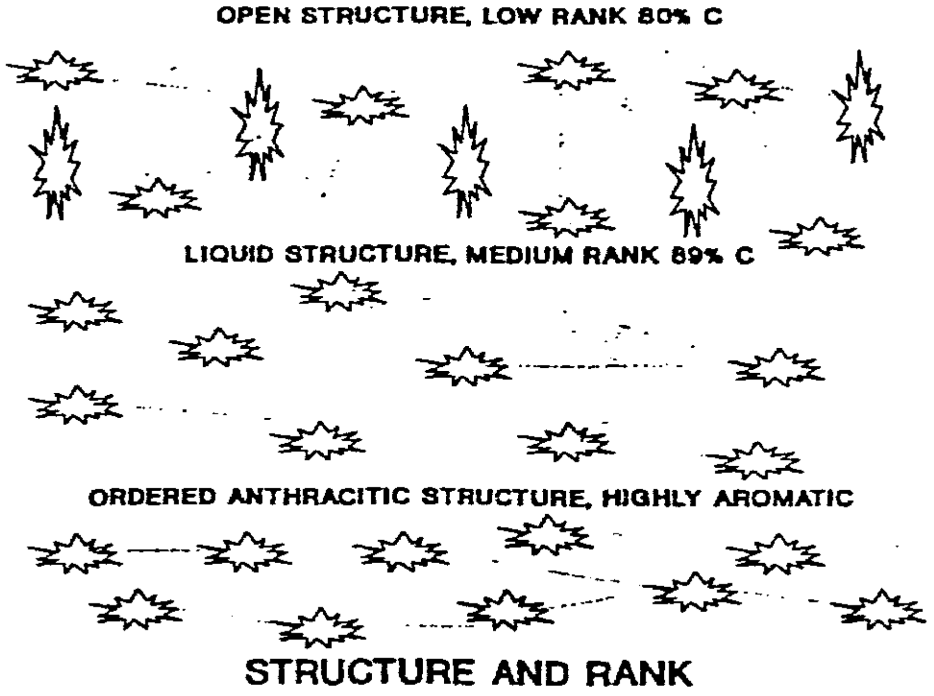


Figure 2.1: Structure and rank changes within coal (Horsfall, 1993)

2.4 Mineral matter in coal

The inorganic constituents of coal consist mainly of minerals and to a lesser extent organometallic components and exchangeable cations. When coal is burned at high temperature in the presence of O_2, the inorganic components are left behind as residue called ash.

The presence of minerals in coal is due to finally divided minerals that are captured during the sedimentation phase and are bonded to the organic structure of the coal. There are two ways in which the minerals are captured, namely:

(1) Syngenitic (minerals that formed part of the structure during the coalification process)

(2) Epigenetic (minerals were introduced into the structure via holes and cracks after coalification was completed)

The difference is made clear in Figure 2.2 (Horsfall, 1993).

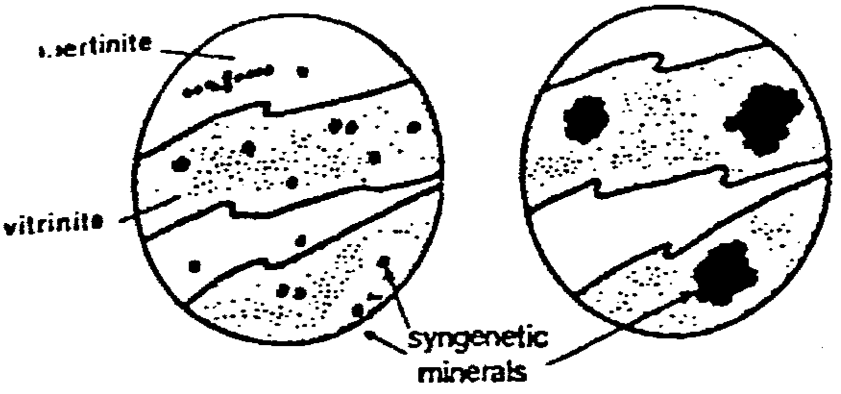


Figure 2.2(a) Syngenetic mineral matter (formed with closely bound)

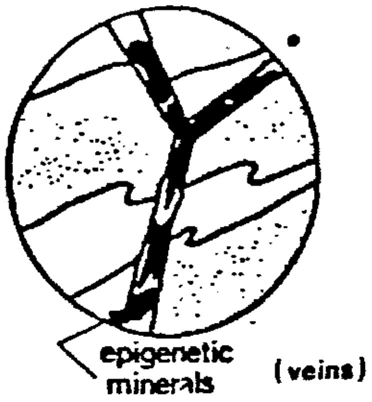


Figure2.2(b) Epigenetic (formed after coalification)

The removal of minerals from the coal matrix depends on the type of mineral (Horsfall, 1993). Syngenetic minerals are more difficult to remove than epigenetic minerals.

South African coals differ from Northern Hemisphere coals in mineral content - the South African coal has a higher percentage of fine included minerals in the coal, and requires extensive milling to very small particle sizes for liberation of the minerals (Botha, 1980).

2.5 Chemical structure of coal

The structural ordering of coal increases as the coalification process increases till the formation of organic macromolecules that have a flat form with carbon atoms in the centre (Bouska, 1981).

The carbon atoms show a two dimensional ordering, i.e. they lie in one plane, in the edges of more or less regular hexagons, which are not connected but flat in the disordered gel matter of a disc like molecule (Figure 2.3). Only a part of the matter is made up of regularly arranged molecules. In the remaining part, the molecules are unordered [(Kasatochkin (1969), Lazarov and Angelova (1976)]. The carbon hexagons are considered as embryos of the graphite arrangement.

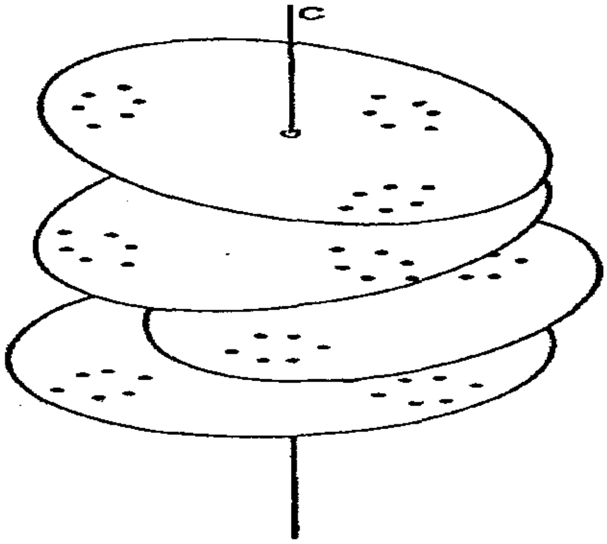


Figure 2.3: Turbostratic ordering of two dimensional molecules with hexagonal carbon embrya (Bouska, 1981)

Every macromolecule has several carbon hexagons, which make up a planar pattern. At the beginning of coalification, the aromatic systems are probably linked through the non-aromatic layers (Bouska, 1981).

Flat polynuclear aromatic molecules aggregate to form the turbostratic lamellar system (Blayden et al., 1944). The turbostratic arrangement is not typical of the crystalline matter but is found in colloidal gels. During coalification, the size of molecules increases as well as the degree of ordering. Macro molecules arrange themselves laterally or vertically to form a lamellae system. X-ray studies by Hirsch (1954), Brown and Hirsch (1955) and Cartz et al (1956) determined that most coal types consists of 2 - 3 lamellae; the maximum number of lamellae rises from 4 - 5 with 80% carbon to 8 - 10 lamellae with 94 % carbon.

The infrared spectra of coal have confirmed its aromatic and probably also its polycyclic character. The following were substantiated: OH-groups, aromatic CH groups, aliphatic CH_2 and CH_3 groups, polycondensed aromatic groups and benzene rings (Bouska, 1981).

The relation between the intensities of IR-adsorption bands of the aromatic and aliphatic CH groups shows that the number of aliphatic groups decreases greatly with the increase in coalification (Van Krevelen, 1963).

Now that an understanding of coal formation has been obtained, it is important to review the status of coal characterisation techniques that have relevance to this dissertation.

2.6 Coal characterisation

The coal characterisation techniques that will be reviewed in this section include petrographic analysis, proximate and ultimate analysis, calorific value, float sink analysis and oxygen-containing functional groups.

2.6.1 Petrographic analysis

Each maceral group has unique characteristics and surface properties as discussed in section 2.3.3. Since flotation is a surface dependant separation technique, the floatability of each maceral group differs.

During the metamorphism of coal, the reflecting properties of the different macerals changes in reflecting properties, as the process progresses, and the reflectivity of the maceral also increases. Using this reflectance phenomenon, it is possible to study the different macerals present in a coal sample using microscopy.

The reflectivity that is obtained is associated with chemical changes that occur in the coal as the carbon content and aromatisation of the carbon linkages increase (Horsfall, 1993). Metamorphism into anthracite increases the reflectivity of the macerals to such an extent that individual macerals can no longer be identified.

For low rank coals, the degree of reflectivity is an important measure for the degree or rank of coal, and therefore for predicting the properties associated with it.

2.6.2 Proximate and ultimate analysis

Proximate analysis includes the analytical determination (%) of the moisture content, volatile matter and ash content in the coal sample. The fixed carbon content is calculated by subtracting the ash, moisture and volatile matter content from 100 (percentage).

Ultimate analysis consists of the measuring of carbon, hydrogen, sulphur and nitrogen. The oxygen content of the coal is calculated by subtracting the sum of the carbon content, hydrogen content, sulphur content and nitrogen content from 100%.

2.6.3 Calorific value (CV)

The calorific value of coal is the energy value that the coal possesses. CV is generally used as one of the specifications for a certain application; for example, export thermal grade coal requires a heating value of 28 MJ/kg (mega Joules per kilogram).

2.6.4 Float-sink analysis

Coal can be separated into two fractions by using liquids of relative densities between that of coal and the impurities associated with it.

Coal varies in relative density from anthracite (rd 1,5 g/cm^3) to bituminous coal (rd 1,25 g/cm^3). The relative density of non-pyritic minerals is between 2,2 and 3,9, and that of pyrite is 5,0 g/cm^3 (Horsfall, 1993).

By using liquids with a known density it is therefore possible to separate the coal and waste minerals. By mixing two liquids with known densities it is possible to obtain a required density liquid. For example, Bromoform (ρ = 2.83 g/cm^3) and toluene (ρ = 0.87 g/cm^3) can be mixed in a specified ratio to obtain a density of 1.6 g/cm^3. The volumes of each pure liquid that are used determine the density of the solution. Some of the liquids that are usually used are listed in Table 2.3 together with naphtha with a density of 0,70 g/cm^3.

Table 2.3: Liquids used for density separation of coal (Horsfall, 1993)

LIQUID	DENSITY (g/cm^3)
Petroleum Spirit	0,73
White Spirit	0,77
Toluene	0,87
Perchlorethylene	1,61
Bromoform	2,79
Tetrabromomethane	2,96

An inorganic mixture that is often used separating bulk solutions is zinc chloride, which is dissolved in water to obtain the required density. The effectiveness of zinc chloride as a dense medium is between 1,3 g/cm^3 and 1.75 g/cm^3 above which the zinc chloride starts precipitating (Bunt 1997).

Coal particles are immersed in the liquid (of a specific density) and two fractions are separated - a 'sink' fraction (density of the material is higher than the density of the liquid) and a 'float' fraction (the density of the particles is lower than the density of the liquid).

The density separations are done on a range of densities and should be as comprehensive as possible. Usually the densities range from as low as 1,2 or 1,3 g/cm^3 to as high as 2,0 g/cm^3 or higher. The data (fractional yield of floated particles) is plotted against the relative density of the liquid to construct a washability curve. From the curve, the yield at a certain density can be determined.

An example of a typical washability curve for Witbank seam 2 (after Horsfall, 1993) is given in Figure 2.4.

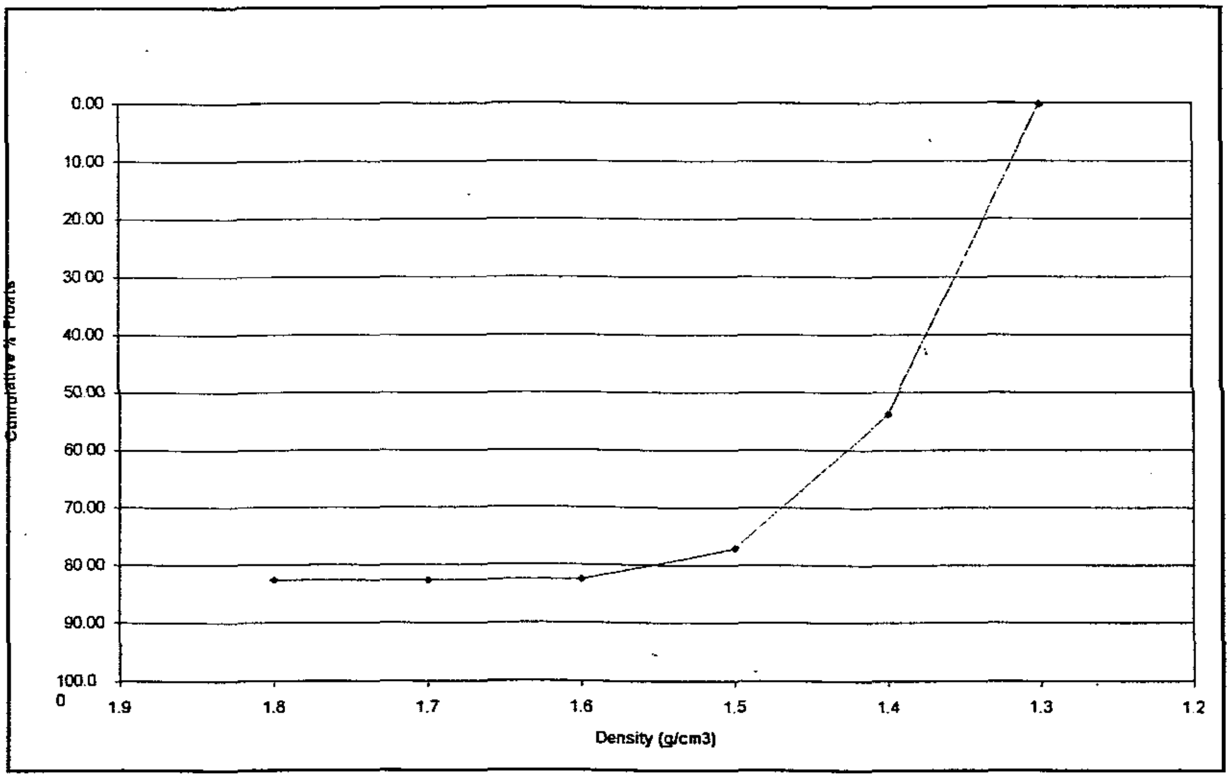


Figure 2.4: Washability curve for Witbank seam 2 coal (horsfall, 1993)

2.6.5 Oxygen-containing functional groups

Du Plessis (1983, 1985), Swart (1987) and Matthyser (1984) showed that there is a linear relationship between the composition of the surface functional groups and the surface properties of coal. A decrease in functional groups was noted with a decrease in coal rank by Blom et al (1957).

The surface properties of coal are not only determined/influenced by mineral inclusions, but also by the surface functional groups present on the coal surface. These surface functional groups were distinguished by Blom et al (1957) as ester, carboxylic, hydroxyl, carbonyl (cetonic and cinonic), peroxide, hydroperoxide and ether groups (aliphatic and cyclic). These will be further discussed below.

2.6.5.1 Carboxylic Groups

Blom et al (1957) compared brown coal with different vitrinite-rich coals, and found that carboxylic acid groups decrease from 8 % to 0 % with an increase in carbon content from 65,5 % to 85,5 %. This was confirmed by Fuerstenau (1982).

Du Plessis (1983) used SA coals and also found that an increase in carbon content (45 % to 88 %) was associated with a decrease in carboxylic oxygen content (1,0 % to 0,1 %).

2.6.5.2 Hydroxyl Groups

This functional group is present in all coal ranks. Tarzab et al (1979) found that the hydroxyl content of coal depends on the grade and rank as well as on the geochemical and geological origin of the coal. The hydroxyl groups in coal are of phenolic alcohol and aliphatic in nature (Meyers, 1982).

An increase in carbon content leads to a decrease in the hydroxyl group content (Blom et al, 1957).

2.6.5.3 Carbonyl Groups

Blom et al (1957) found that with an increase in carbon content from 65,5 % to 85,5 %, the carbonyl content of the coal decreases from 5,6 % to 0,1 %. The presence of carbonyl groups in high rank coal is ascribed to cinonic groups. The low carbonyl group content in coal was confirmed by Van Krevelen (1957).

2.6.5.4 Ether Groups

Blom et al (1957) noted a decrease in ether groups with an increase in carbon content from 65,5 % to 85,5 %.

However, Du Plessis (1983) could not obtain a relationship between the carbon content and the percentage ether groups in SA coals, although the same experimental procedure was used.

Painter et al (1980) found that ether groups are above all found in highly oxidised coals. This can possibly be ascribed to condensation between carboxylic and hydroxylic groups on the coal. This was confirmed by Du Plessis (1983).

Now that an understanding of the relevant coal characterisation techniques has been obtained, it is important to review the surface dependent beneficiation techniques are relevant to this dissertation

2.7 Factors affecting surface properties and hydrophobicity

There are differences in the surface properties of coal and associated minerals. Coal is hydrophobic and the associated minerals are hydrophilic. This is the basis for separation of the coal and the minerals.

Methods that include the use of surface dependant techniques are froth flotation and oil agglomeration.

Oil agglomeration is applied to coal with a particle size of less than 100 µm (Capes et al, 1976 & Mehrotra et al, 1983). Oil agglomeration includes high shear mixing of coal-water slurry in the presence of an oily liquid. The separation is caused by adsorption of the hydrophobic oil on the coal particles, forming carbon spheres. The mineral particles remain in the water phase. Separation is noted as grey and black streaks in the slurry (Capes et al, 1976 & Mehrotra et al, 1983).

Sastech R & D has investigated the possibility of oil agglomeration as a beneficiation method for fine coal, but concluded that the price of the oils (called bridging liquids), and the volumes required, renders the process economically unfavourable.

Froth flotation is a process in which coal-water slurry is mixed in a flotation cell, collectors and frothers are added and air is introduced to the cell. The hydrophobic coal particles float and are removed as a concentrate and the hydrophilic mineral particles stay in suspension in the water (Hindmarch et al, 1991 - 52 & Horsley, 1951 - 52). Two phases can thus be noted during a flotation process, namely a pulp phase and a froth phase.

Flotation of the coal particles is caused by the wetting of the coal surface by the oil (collector), which forms a layer around the hydrophobic coal particles. The hydrophobic oil-coated particles attach themselves to the air bubbles and float to the surface. A stable froth is needed on the surface, otherwise the bubbles will break up after reaching the surface and particles will drop back into the pulp. This necessitates the addition of a frother that also imparts some surface wettability characteristics. The mineral particles that are mostly present as clays are not affected by this addition and stay suspended in the water (Hindmarch et al., 1951-52).

Laskowski (1998) explains the proposed mechanism of froth flotation. As the bubbles move through the pulp they crowd together nearing the froth zone. Drainage of entrained particles and water occurs due to thick pulp layers that surround the air bubbles. As the bubbles move upwards in the froth zone, the pulp layers surrounding the bubbles decrease in thickness and the amount of entrained particles and water decrease as well. The layer surrounding the bubble becomes so thin that drainage (of water and entrained particles) becomes minimal at the top of the froth zone.

Three types of surfaces can be distinguished on coal, i.e.:

- A naturally non-wettable (in water) hydrophobic surface.
- Polar hydrophilic surfaces, and
- Surfaces that are heteropolar. Coal falls into this group since it has a hydrophobic carbon skeletal and hydrophilic functional groups (Hindmarch and Waters, 1951 - 52).

Factors that influence floatability of coal include the following:

- Coal rank

exinite. Bujnowska also found that the reactive coal macerals do not necessarily float first, but that the initial froth consists mainly of vitrinite and inertinite. It was also found that the inertinite flotation yield are the highest, followed by vitrinite and exinite.

For high rank coals, the order of flotation is: vitrinite > inertinite > exinite.
For medium rank coals, it was found that vitrinite has a higher floatability than the other macerals (Sarkar et al 1984).

From the above it is clear that macerals can be separated with a surface property method like flotation. However, this may be difficult if included minerals and macerals are present (without possible liberation).

Laas (1986) found that the vitrinite rich coals are more susceptible to oxidation due to their more aliphatic structure, and this has a negative effect on flotation. The inertinite rich coals are more aromatic in structure.

2.7.3 Surface functional groups

The presence of functional groups on the coal surface depresses the floatability of the coal, since the surface functional groups are hydrophilic (Beafore, 1979). The increase in surface functional groups is caused by oxidation of the coal, which causes the coal to be less floatable (Sun, 1954). Similar observations were made by Zimmerman (1964).

Water molecules are adsorbed on the coal surface (Bujnowska, 1985) causing a more hydrophilic character on the coal and rendering it less floatable. The concentration of COOH (carboxylic) and phenolic (OH) functional groups increases during oxidation and impart a negative surface charge on the coal (Fuerstenau, 1982).

2.7.4 Oxidation of organic (coal) surface

Coal that is mined near the surface or has been stored for long periods of time will have undergone physical and chemical changes (oxidation) due to weathering (Beafore et al, 1979, Sun 1954).The flotation of oxidised coal is influenced by the following factors:

(i) An increase of the amount of fine coal, which is due to higher brittleness of oxidized coal.

(ii) Higher surface area that develops due to increased amount of fines.

(iii) Lowered pulp pH.

(iv) Free cations in the coal pulp.

(v) Lowered surface hydrophobicity.

(Beafore et al 1979, Fuerstenau et al, 1987).

Sun (1954) stated that the low floatability of oxidised coal is caused by an increase in the non-floatable components (oxygen containing components and coal ash content) together with a decrease in floatable components (carbon and hydrogen containing parts) of the coal.

The changes that are observed in the coal structure due to surface oxidation are illustrated in Figure 2.5 (after van der Westhuizen, 1990):

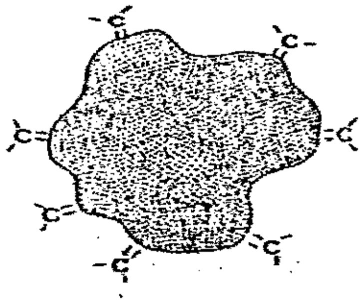


Figure 2.5.1: Unoxidised coal

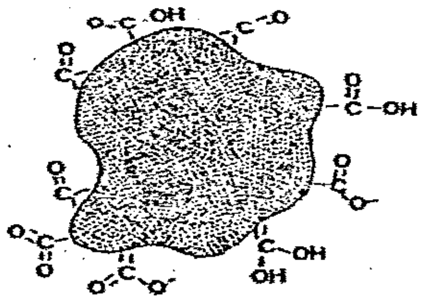


Figure 2.5.2: Oxidised coal

2.7.5 Slime coating and entrainment

Slime is defined as ultra fine particles that remain indefinitely in suspension. The presence of slime during flotation leads to excessive use of reagents, a decrease in recovery and an increase in the amount of frother that is used. Slime coating is ascribed to the electrostatic attraction between particles of opposite charge. The clays present in the coal sample have a dual electrical charge, which causes them to bond to the oppositely charged (negatively) coal surface (Bunt, 1997).

To minimise this slime coating, Jowett et al., (1965) adsorbed negatively charged ions onto the clay surface to create an electrostatic repulsion force between the clay and the coal.

Entrainment is caused by fine particles that are transported to the froth/water interface without being attached or bound to air bubbles, and which contaminate the floated coal (as reported by Bunt, 1997). The minerals moves to the froth zone due to capillary forces between the air bubbles and are captured in the stable froth.

2.7.6 Particle size

Panapoulos et al (1986) found that there is a relationship between maximum recovery and particle size. The maximum flotation yield is obtained at a particle size of between 100 - 200 µm, whereas the floatability decreases to zero at a particle size of 1 mm. Zimmerman (1964) found that the best flotation results could be obtained at particle sizes of 250 and 105 µm (this is confirmed by Tsai, 1982). This recovery can be attributed to the presence of bigger and heavier coal particles in the solid phase, which leads to break-up of air bubbles and intrusion of large quantities of water between the air bubbles (Sablik et al 1983).

Panapoulos et al (1986) and Horsfall et al (1986), however, showed an increase in floatability with <75 µm coal particles (as a result of increased mineral liberation at lower particle sizes). This was confirmed by Brown et al (1953 - 54) and Woodburn et al (1984).

2.7.7 Pulp temperature

Bailey (1953) found that the floatability of four British coals increased at a pulp temperature between 25 °C and 30 °C. At lower pulp temperature (below 25 °C) the floatability of the coal decreased, and no influence was noted at pulp temperatures above 30°C.

2.7.8 Pulp density

McCandless et al (1978) found that for flotation of particle size between 590 µm to 70 µm, a 5 % pulp density is required. Horseley (1951 - 52), on the other hand, suggested that the pulp density should be 10 - 15 %. Horsfall (1986) floated coal particles (<50 µm) at a pulp density of 5 %. The pulp density also determines the amount of flotation reagents that are added (Brown et al, 1953, 54).

The parameters discussed in sections 2.8.1 to 2.8.8 summarise the coal parameters that influence flotation. The parameters associated with the reagents are discussed in the following sections.

2.8 Reagents

Reagents that are used in flotation include collectors, frothers, depressants and promoters. These will be discussed in detail. Fuerstenau (1976) and Miller

(1977) found that lower rank coal needs four times more reagents for effective flotation than higher rank coals.

2.8.1 Collectors

Collectors added to coal flotation can be cationic, anionic or neutral reagents, and form strong bonds between high rank and unoxidised vitrinite coals (high aromatic structures). The neutral reagents do not create hydrophobicity on the coal surface, but enhance the natural hydrophobicity (floatability) of the coal.

An effective collector must have the ability to attach to the coal surface, should also increase the coal surface hydrophobicity (Fuerstenau, 1976; Hindmarch et al, 1951 - 52, Nimerick et al, 1980). Adding collector to the coal pulp can thus increase the floatability of low rank coals.

Different kinds of oils can be used as collectors for flotation (Fuerstenau 1976). An example of this is the use of non-polar collectors (oil) together with a frother recommended by Bujnowska (1985) for coal flotation.

Brown (1962) found that there is a relationship between the coal structure and the structure of the collector. An example of this is the use of aromatic collectors for the flotation of high rank coal (higher aromaticity). The use of aliphatic hydrocarbons are recommended for the flotation of lower rank coals, which has a more aliphatic structure.

The effect of reagents (called bridging liquids) on the oil agglomeration process will also be discussed in the following paragraphs, since oil agglomeration is similar to flotation a coal surface based beneficiation process.

Van Nierop (1988) found that the addition of collector during the flotation of coal resulted in increased recoveries due to the enhancement of the coal surface hydrophobicity by the hydrophobic oil. It was also found that collectors containing mainly aliphatic bonds resulted in lower coal recoveries than aromatic collectors. This effect is ascribed to the aliphatic groups being unable to wet the aromatic surfaces (inertinite macerals) of the coal.

Labuschagne (1986) found that paraffinic straight chain reagents like hexane lowered the rate of agglomeration but resulted in increased ash removal (increased selectivity). This was confirmed by Van Heerden (1987).

Labuschagne (1986) found that unsaturated hydrocarbons result in higher rates of agglomeration than saturated hydrocarbons. This is ascribed to delocalisation of pi-electrons in the unsaturated bonds compared to the σ-bonds in the saturated carbons.

Van Heerden (1987) found that benzene resulted in the highest rate of agglomeration due to the availability of pi-electrons. Van Nierop (1988) concluded that the use of aromatic hydrocarbons as collectors increased the coal surface wettability due to pi-electron overlapping. An example of the pi-overlapping between an aromatic collector and a coal surface is illustrated in Figure 2.6.

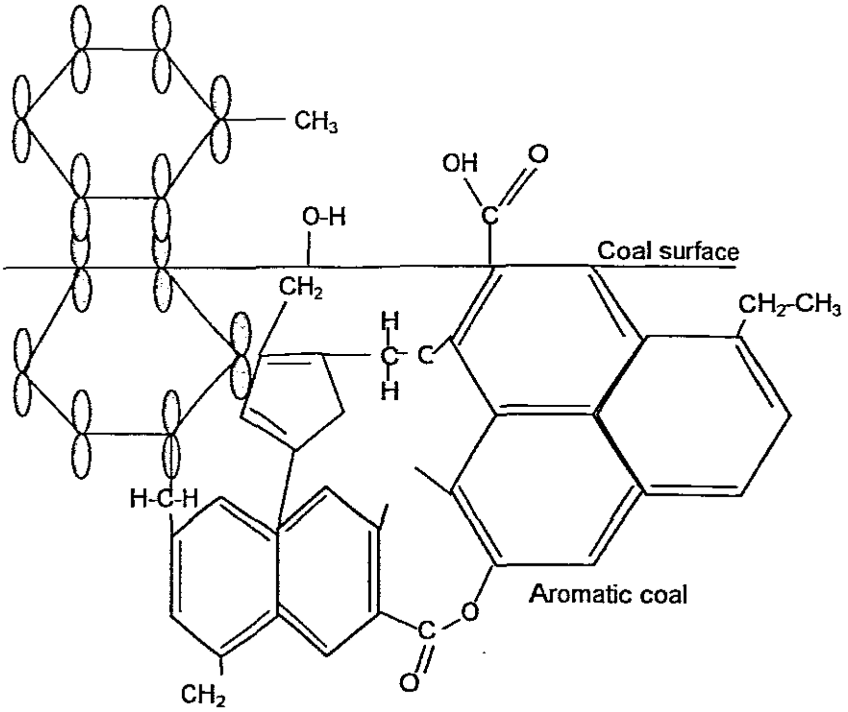


Figure 2.6: Pi- electron overlapping between collector and aromatic coal (Van Nierop, 1988)

Alkyl substitution on the aromatic benzene ring was found to lower the rate of agglomeration (Van Heerden, 1987), and is ascribed to steric hindrances that may occur or the decrease in the amount of aromatic rings per unit of reagent (Van Heerden, 1987).

Labuschagne found that molecules with electron deficiency (as in the case of the benzene ring) decrease the rate of agglomeration in comparison to electron donor substituents.

Findings by a number of researchers on collectors also indicated that:

1. Carboxylic acids have low selectivity although the C10 –to C16 fatty acids were shown to be efficient coal collectors (Klassen, 1958)
2. Aromatic collectors are less effective collectors than the corresponding aliphatic components (Klassen, 1958)

3. Unsaturated hydrocarbon collectors are less effective than saturated hydrocarbons, this is contradictory to what Van Heerden (1987) found.
4. Branched hydrocarbons are more effective collectors than the straight chain hydrocarbons (as cited by Fickling, 1985)

The concentration of the collector that is needed for flotation is determined by the rank of coal. For example: bituminous coal requires very little collector to float, whereas low rank bituminous coal requires little to very much collector before flotation is accomplished (Fuerstenau 1976, Miller 1977, Rogers et al, 1956). The collector does not create surface hydrophobicity, but increases the hydrophobicity of the already hydrophobic coal surfaces (Nimerick et al, 1980).

The collector dosage (concentration) plays an important role in flotation, which can be seen from Figure 2.7. It is clear that low collector dosages result in poor froth development during froth flotation of coal. At lower collector dosage, the collision frequency between the coal surface and the dispersed oil is lower, whereas the probability of collision between the coal particles and oil increase at higher collector dosages.

Collectors are usually non-ionisable compounds that are mostly insoluble in water, and only a thin layer on the coal surface is needed to increase the coal surface hydrophobicity (Wills, 1981).

The collector should have a relatively low viscosity to ensure uniform covering of the coal surface which is a prerequisite for coal flotation. Horsley (1951 - 52) found that the collector properties of paraffin can be increased by adding an emulsifying agent. Emulsification also seems to lower the dosage of reagents required (Staszcsuk, 1983).

Figure 2.7 shows that as the collector dosage is decreased in a coal flotation system, the froth stability (measured as froth developing time) also decreases.

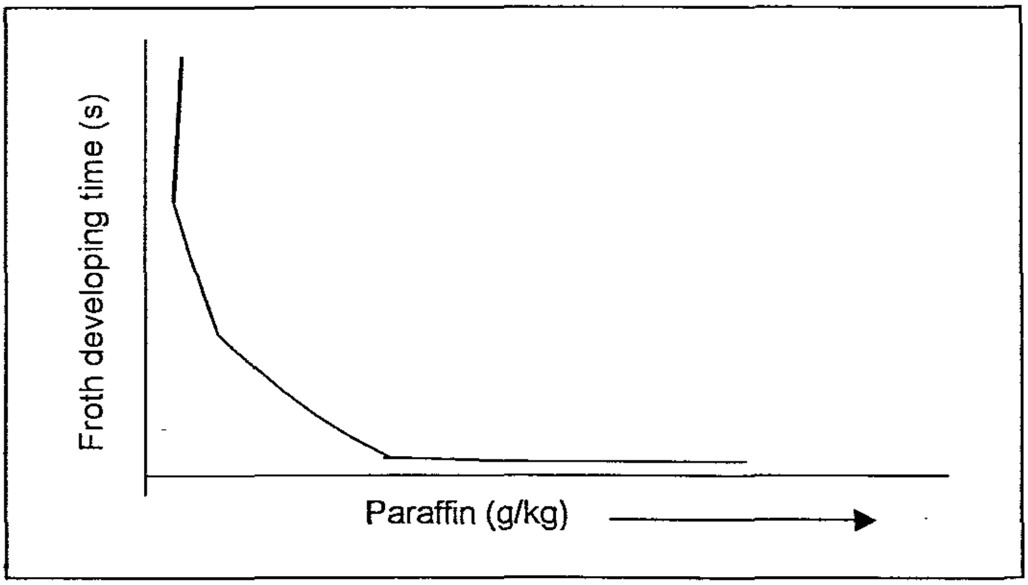


Figure 2.7: **The effect of paraffin addition on froth developing time (Woodburn, 1984)**

Osborne (1988) stated that there is a linear relationship between the viscosity of the oil (collector) and the recovery and ash content of the concentrate. As the viscosity of the collector is increased, the recovery of coal during flotation decreases.

Van Nierop (1988) found that the viscosity of the collector plays a role only at very low (less than 0,5 cP), or very high (above 5 cP) values. At low viscosities (e.g. hexane) the collector disperses into very fine droplets and covers the coal surface as a very thin layer. The attachment of the oil to the particles is very weak and is easily broken by the turbulence within the float cell. Collectors with high viscosities do not disperse properly and the coal surface is only partially coated, resulting in poor recoveries.

Normally, collectors are added in small quantities to the pulp to obtain a monolayer of collector on the coal surface. An increased amount of collector can decrease the selectivity (separation between coal and mineral particles) of the collector (Elashevich et al 1969, Willis 1981).

The most popular types of coal collectors are emulsions of oils such as diesel, kerosene or paraffinic oils. One way of relating various oils used as collectors are to compare their relative viscosities (Osborne, 1988).

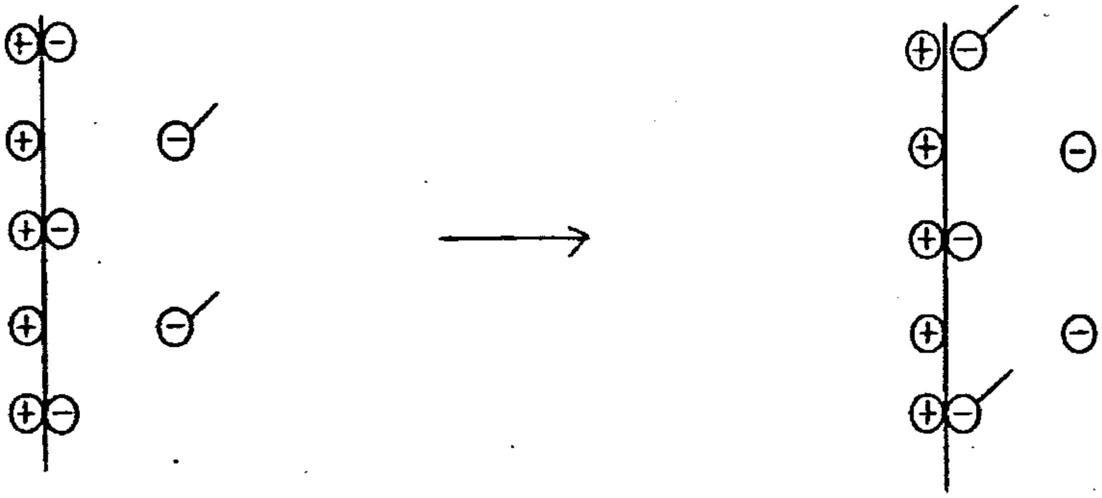
Recent improvements in coal flotation involve the addition of ionic or non-ionic additives (Osborne, 1988).

Sun (1954) showed that long chain amines are effective as collector for oxidised coal.

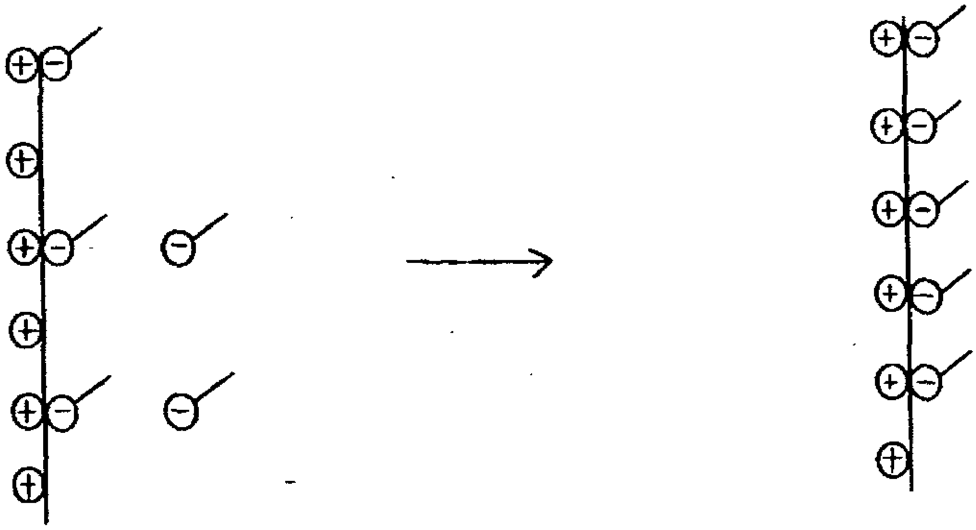
2.8.1.1 Adsorption on Coal Surface

Adsorption on a coal sample takes place through one of the following mechanisms:

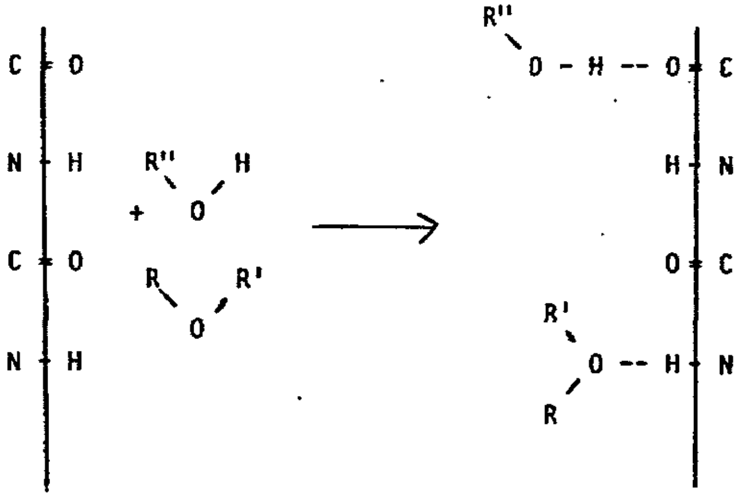
Ion exchange - the replacement of adsorbed ions (Law 1966, Rupprecht 1972, Wakamutsu 1968, Rosen 1975).



Adsorption of ions from a solution on opposite charge points that are free from counter ions (Law 1966, Rupprecht 1972, Rosen 1975).



3 Hydrogen bonding - adsorption through hydrogen bonding between the substrate and adsorbate (Bairomov 1972, Law 1966, Snyder 1968).



4 Hydrophobic bonds.

5 Adsorption through polarisation of π electrons.

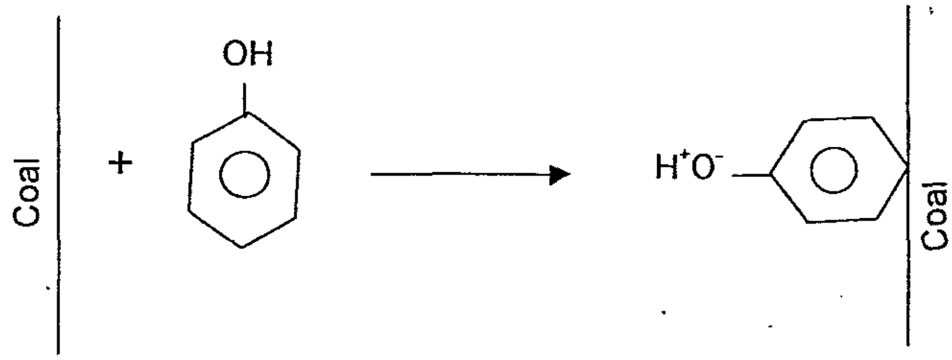
6 Adsorption through polarization.

Adsorption is influenced by the following:

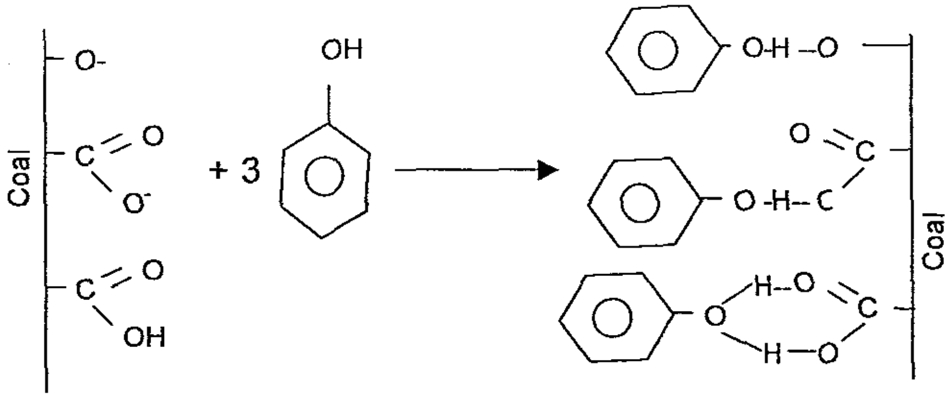
1 The nature of the structural group.
2 The molecular structure of the surfactant.
3 The pH of the water phase.

By using similar meganisms for adsorption of conditioners on coal Matthyser (1984) explains agglomeration results obtained with different conditioners as follows:

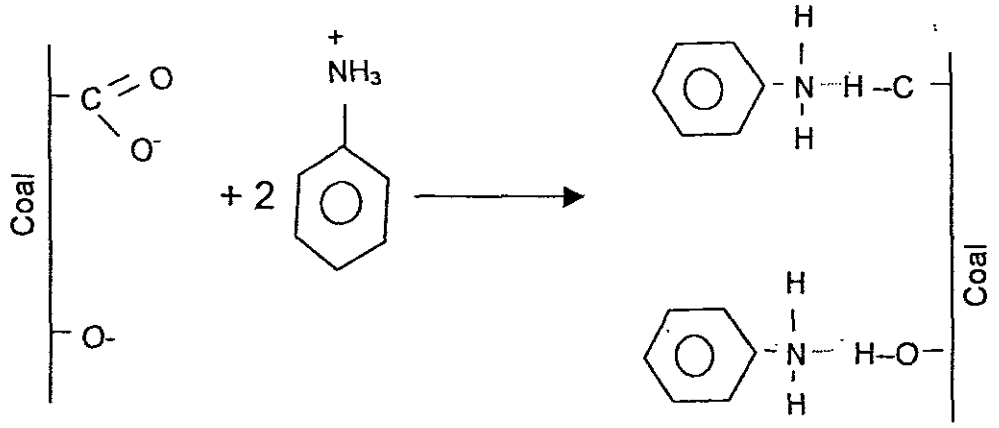
1 Hydrophobic bonds between the phenyl group and hydrophobic coal surface increase the negative surface charge of the coal. This result to a decrease in agglomeration.



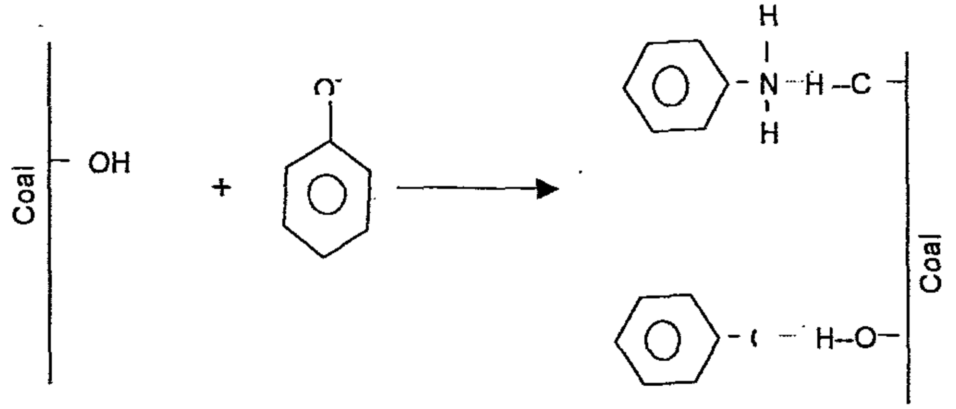
2 Hydrogen bonding between the carboxylic, phenolate of carboxylate ions and the hydroxyl group of the oil will decrease the surface charge due to the phenolate that is away from the coal surface



3 Hydrogen bonding between the carboxylate and phenolate ion and protonated oil decreases the negative charge on the coal surface and will enhance agglomeration.



Hydrogen bonding between neutral hydroxyl groups and hydroxyl from phenolic oil will lead to very little decrease in the negative charge on the coal surface.



Thomas (1951) found that the adsorption of organic molecules from a water and alcohol phase onto a coal surface decrease with decreasing in rank and increasing oxygen functional groups. Thomas (1951) also suggested that the adsorption take place on the non-polar part of the soluble organic molecule.

The effects of surface spreading and pore penetration were investigated by Moxon, Bensley, Keast-Jones and Nicol (1987). The study showed that during flotation with hydrocarbons ranging from C6 to C16 carbon chain length, the maximum yield of coal is obtained by using a C12 collector (dodecane). The flotation yield of shorter chain length hydrocarbons is lower due to penetration of the liquids into the pore structure of the coal, thereby lowering the surface concentration of the collector on the coal. The hydrocarbons with a higher chain length (above C12) have a negative effect on coal recovery during flotation, which is ascribed to the viscosity of these reagents, which prevents the liquid from spreading on the coal surface.

To interpret the interaction of between a reagent and a coal surface, factors like the nature of the reagent, the nature of the coal and the medium from which adsorption take place need to be considered. Due to the heterogeneity of coal (all the different maceral components), there are various adsorption mechanisms. Since coal is porous, it is recommended that adsorption changes as well as the slow kinetics be taken into account when investigating the interaction of molecules with coal surfaces.

2.8.2 Promoters

Promoters are reagents that do not float coal by themselves, but their addition improves the effectiveness of the collector and/or frother during flotation.

Promoters act as a bridge between the low rank (or oxidised) coal surface and the hydrocarbon collector that is used. This is illustrated in Figure 2.8.

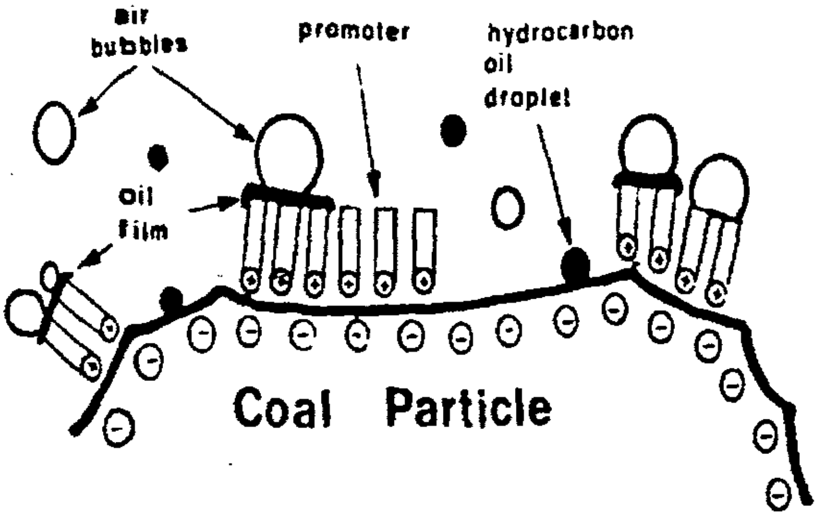


Figure2.8: An explanation of the function of a promoter (after Keys, 1986)

These surfactants includes amines (Mishra, 1978), alkanolamine-tall oil fatty acid condensates (Meyer et al. 1980), imidazolines (Hefner, 1981), alkyl phenol formaldehyde condensates (Gross, 1985), petroleum lignosulfonates (Fu et al. 1986), alkoxylated fatty acids or fatty acid esters (Keys, 1986), ethoxylated fatty acids (Sablik et al, 1979), hydroxyl alkylated polyamines (Hefner, 1981) and many more.

2.8.3 Depressants

Depressants are used to increase selectivity and lower the inorganic recovery during flotation (Allum et al, 1954). Any reagent that oxidises the coal surface (removes natural hydrophobicity) can be regarded as a potential depressant. An example of this is the use of long chain carboxylic acids (Fullard, 1986).

2.8.4 Frothers

The principal aim of a frother is to produce a stable froth during flotation (Allum et al, 1954). Frothers also influence the kinetics between coal particles and air bubbles (Leja, 1982).

Frothers lower the water surface tension, allowing small bubbles to form and preventing air bubbles from coalescing (Rubin et al, 1982).

Frothers are usually non-ionic surfactants that consist of a polar or ionic part (e.g. an OH group) that is attached to a short alkylchain or a phenylring (Fuerstenau 1982). Fuerstenau (1982) also determined that the relationship of non-polar to polar parts in the frother molecule is of such nature that the frother is soluble in water.

Another requirement for a frother is the ability of the non-polar part to attach to an air bubble while the polar part of the molecule is directed to the water; their polar groups repel one another and prevent the froth from coalescing (Figure 2.9).

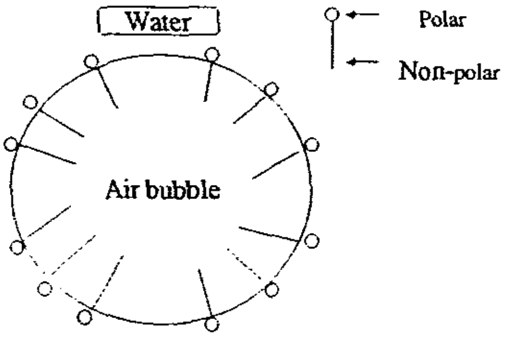


Figure 2.9: Froth (bubble) stabilisation as presented by Fullard (1986)

Stabilisation of the froth is important to floatation, and determines if the froth (mainly coal fraction) and pulp (mainly minerals) can be separated. During flotation the polar end of the frother is directed to the water and the non-polar end

to the air bubble. The froth is therefore stabilised due to the repulsion of the polar ends, which prevents coalescence of the air bubbles.
Pine oil and cresol were used in the earlier days as frothers but nowadays synthetic frothers like methyl-isobutyl carbinol (MIBC) are used (Ruben et al, 1982, Wills, 1981). MIBC is a short chain alcohol with limited collecting properties.

Now that an understanding of the reagents has been obtained, it is important to review the floatability characterisation techniques.

2.9 Methods of characterisation of reagent uptake and floatability

2.9.1 Contact Angles

The contact angle is defined as the angle formed between an air bubble or a liquid bubble and a solid surface (Fuerstenau, 1982) (Allum & Whelan ,1954). Contact angle is a measure of the degree to which the liquid or air bubble can displace water from the coal surface, and is also an indication of the wettability of the coal surface with a particular liquid. Coal that is naturally hydrophobic results in a large (above 90°) angle between the oil drop and the coal sample in a water medium (Brown, 1962).

There is interaction between the surface of the solid and the molecules of the liquid. The work that is done, the work of adhesion, is given by:

$$W_{SL} = \gamma_s + \gamma_L - \gamma_{SL} \text{ --- } (1)$$

Where γ_s and γ_L are the surface tension of the solid (S) and the liquid (L), and γ_{SL} is the interfacial surface tension.

From the above an equation can be derived to measure the contract angle, i.e.:

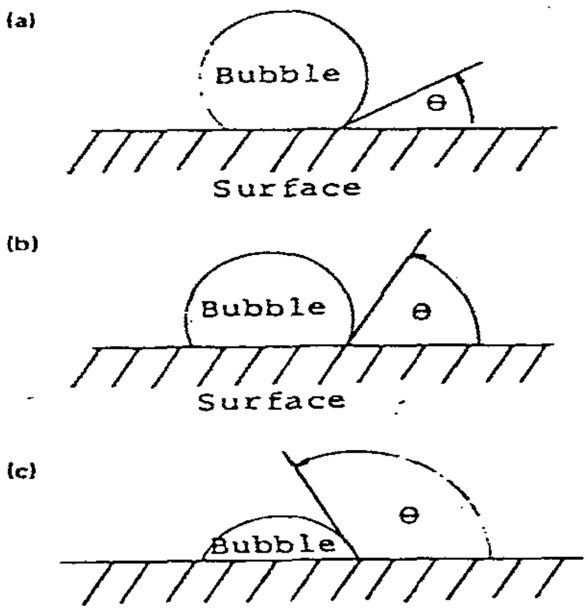
$$\gamma_{SL} = \gamma_S - \gamma_L \ * \cos\theta \qquad \text{--} \quad (2)$$

where θ is the contact angle (bailey & Whelan, 1953).

An increase in contact angle leads to an increase in the wettability of the coal/solid surface, since the collector has to absorb on the solid surface for effective flotation. As the contact angle increases, the floatability of the solid (in this case coal) also theoretically increases (Beafore, et.al. 1979).

In Figure 2.10, where the bubble represents an oil droplet on a coal surface. θ Is the contact angle between the coal surface and the tangent to the oil bubble at the point of attachment. The measurement is taken in a plane perpendicular to the coal surface (Van Nierop, 1988).

Gutierrez-Rodrigues et al (1984) investigated the contact angles of coals of different rank and concluded that contact angle measurements are not accurate (cannot be measured) on coals with a fixed carbon content of less than 61%. They also concluded that the amount of oxygen present as hydroxyl functional groups on the coal influences the hydrophobicity of the coal (the more hydroxyl groups, the less hydrophobicity).



(a) In this example, the contact angle is small and the adhesion of the bubble is therefore low.

(b) Here the contact angle is large and there is therefore good adhesion between the bubble and the surface.

(c) In this example, the contact angle is even larger than in (b)

Figure 2.10: Changes in contact angles on coal

Due to the heterogeneity of coal, contact angle measurements are not accurate and only provide information regarding the part under investigation and not the complete sample (Fuerstenau, 1987).

Hysteresis occurs when external forces acts on the applied force and result in inaccurate analysis. During contact angle measurement factors like surface roughness, adsorption and contaminated surfaces cause hysteresis (Leja, 1982). Another common hysteresis that occurs during contact angle measurements is the effect of gravity on the drop size formed on the planar solid surface. If the solid plane is inclined, the bubble might tilt to one side (similar to being "top heavy").

Laskowski (1974) cites that flotation is a typically non-equilibrium process, and that the interactions in the agitated, aerated pulp are not representative of the contact angle measurements at equilibrium.

For the reasons mentioned above, contact angle measurements should be applied with caution.

2.10 Zeta Potential

Zeta potential determinations are used to measure the surface potential of particles suspended in a solution. Indirectly zeta potential measurements can be used to determine the adsorption mechanisms in mineral/water or coal/water systems (Brookes et al, 1984).

For most solids in an aqueous system, the surface potential is negative since positive ions are more soluble than negative ions. This results in more negative ions being present at the separation level (Adarjan 1968, Labuschagne, 1982).

An increase in hydroxyl and carboxylic functional groups on the coal surface increases the negative zeta potential (Woodburn et al, 1983). Pethukov (1982) concluded that the higher the surface charge of the coal, the more hydrophilic the surface of the coal, due to the enhanced localisation of electron density of the chemical compound used as the flotation reagent on the coal surface.

The charge on the coal surface depends on the pH. As the pH of the solution decreases, the hydronium ions are adsorbed on the coal surface and the coal surface acquires a positive charge. With an increase in pH, the hydronium ions are replaced with hydroxyl ions and the coal surface obtains a negative charge (Campbell & Sun, 1970).

Brown (1962) and Fuerstenau (1982) obtained the maximum floatability through froth flotation at the point of zero charge (PZC). This is ascribed to the non-charged coal particle that is unable to bond to water. The hydrophobicity of coal is therefore a maximum at the PZC. (Nimerick et al 1980, Rubin et al 1982).

2.11 Flotation release analysis

Flotation results are often compared to washability data. However, the accuracy of washability analysis on fine coal (< 0.5mm) is questionable. Moreover, comparing a density-based washability analysis to a surface property-based flotation process can lead to totally erroneous conclusions (Forrest et al, 1994).

Dell (1953) proposed a technique called release analyses to obtain the optimum carbon yield (provided recovery by entrainment was not a possibility) for a particular coal. The analysis involves repeated flotation of timed incremented froth flotation products. Operating conditions are varied in order to obtain flotation products, and the results is used to construct a single flotation (ideal) release curve. As the name indicates, the analysis shows the release of the carbon available for flotation together with expected optimum recovery and ash content.

Dell (1964) later introduced a modified release analysis technique, that was much simpler and less time consuming. In this approach, the sample was initially separated into floatable and non-floatable components by repeated stages of cleaning. The floatable material was then separated into components having various degrees of floatability by collecting froth products as a function of increasing aeration rate and agitation. The resulting products and the overall tailings were used to construct the release curve. A comparison of the two methods for a copper ore floated under a variety of conditions showed strikingly similar results. This comparison seemed to indicate that the release curve was a function of the material, and substantially independent of such factors like reagents, pulp density, pH and operator bias (as cited by Bunt 1997)

Another technique, known as tree analysis (Nicol and Bensley, 1983), was found to be relatively insensitive to a variety of collector and frother combinations. In this procedure, a coal sample is initially floated in a batch flotation cell using some arbitrary reagent dosage. The tailings and concentrate from this cell are then separately refloated. This procedure is repeated such that the testing branches out in the manner of a tree.

Pratten et al (1989) evaluated the different methods of analysing the response of coal to flotation and concluded that release analysis is an improvement on batch scale flotation tests but contradictory to the findings by Dell, found that the yield/ash curve is dependant on collector dosage. They also found that the tree analysis was more tedious than the release analysis. Both techniques were however preferred to washability analysis and batch flotation to determine the flotation performance of a given coal type.

2.12 Surface extraction

Surface extraction determinations are used to determine the reagents that are needed to float a particular coal sample. The procedure involves the extraction of aliphatic (soluble hydrocarbon) groups on the coal using a mild solvent. This indicates that the degree of oxidation on the coal surface, which has a negative influence on the floatability of coal, decreases the amount of aliphatic bonds that can be extracted.

The extracted aliphatic filtrate solutions are measured on an UV-Vis spectrophotometer at a wavelength of 400 nanometre (nm). Spitzer (1986) related the absorbency obtained for the extracted aliphatic groups and the recoveries obtained during froth flotation to different degrees of oxidation.

Figure 2.11 indicates that when absorbency values of greater than 0,5 are obtained, only a frother is needed for flotation. If the absorbency value is less than 1,5 but greater than 0,1, then a collector is needed in addition to the frother.

If absorbency values of less than 0,1 are obtained, the coal will need additives (e.g. surfactants) for froth flotation (Spitzer 1986). However, these conclusions will probably differ for Southern Hemisphere coal, which is of a different type to Northern Hemisphere coal.

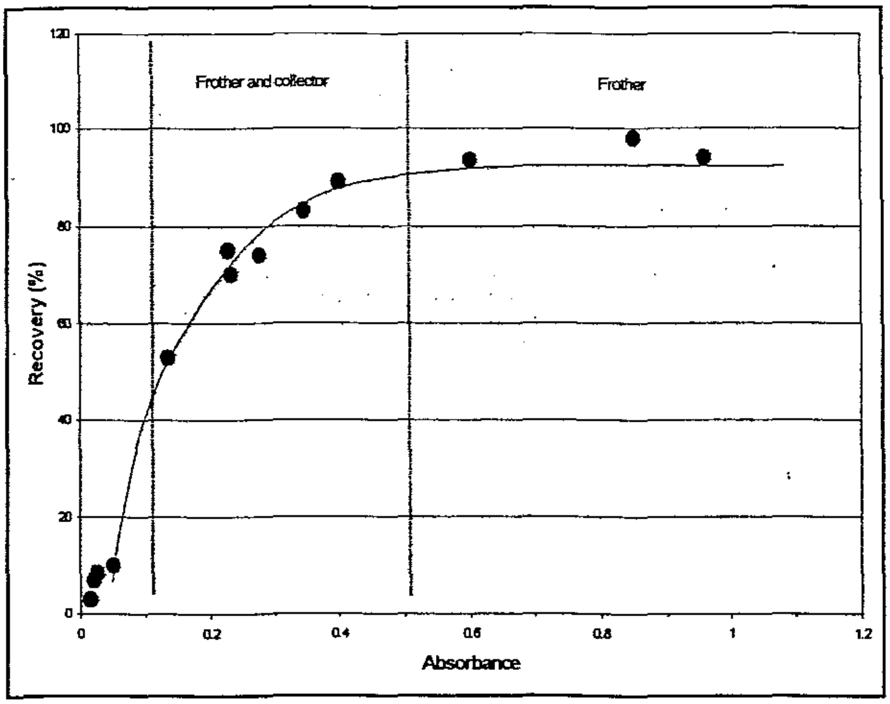


Figure 2.11 Flotation recovery (frother only) vs absorbance @ 400nm of Pittston-moss coal (After Spitzer, 1986)

Now that a general overview of the coal and reagent literature has been given it is necessary to discuss the methods for evaluating results on a statistical basis and the validity of statistical models.

2.13 Statistical analysis of results

Statistics are applied in experimental investigation as a tool to determine the validity, repeatability and usefulness obtained for the results. A number of approaches can be used for such investigations, and some of them will be discussed in this section.

Screening studies (for example a range of collectors) can be analysed statistically to minimise the amount of experiments in order to obtain the maximum amount of information – back-upped by statistical results. This method is less time consuming than evaluating each variable (dosages, pH, etc.) individually, or doing random (trial and error) experiments. The method used for the screening study is called a factorial design program (also called an experimental program). Such a program has the following benefits:

1 More information from each experiment than in unplanned approaches,
2 An organised approach toward the collection and analysis of information
3 More credibility in the conclusions
4 Interactions between experimental variables are shown.

Experimental design programs is often used in screening studies that are aimed at discovering which of a large number of possible variables affects the response (for flotation, the response will be recovery, ash content, calorific value, etc.). From the statistical computer packages available, the information can be used to fit the data to build linear models (a mathematical equation).

Mechanistic studies is aimed at developing a mechanistic model that leads to the correct functional form of the response, and can explain why the response is affected by the variables in the manner observed. Mechanistic models are typically formulated in terms of differential equations, with parameters that are usually non-linear.

Empirical studies are another method aimed at producing an empirical model that relates the effects of the different variables on the response, and can result in linear, quadratic or cubic response surfaces.

2.13.1 Response surface methodology

Response surface methodology consists of a group of techniques used in the empirical study of relationships between one or more measured responses and a series of measurable variable. This technique is used to evaluate the effect that a given set of variables has on a certain response, the expected response given that the input values are known.

Response surface methodology is a method of constructing a model (mathematical relationship) to determine how a number of experimental variables, such as collector dosage, air rate, pulp density, etc., affects a response such as recovery, and in particular to find experimentally combination of conditions that provides the highest response. An example of the use of response surface designs is found in Bunt (1997).

However, it should be noted that statistics serves only as confirmation and formalisation of results and do not improve understanding.

2.14 Chapter summary

There is currently no structured method that predicts reagents suitable for flotation of fine coal. It is therefore one of the principle aims of this study to derive such a method and to evaluate the effect of coal and reagent characteristics on flotation performance.

The methodology that is used to determine the characteristics of the coal is also not employed by all coal characterisation laboratories. It is therefore important to evaluate the currently used methodology and to publish the outcome to the benefit of the coal industry in South Africa.

The methodology that will be examined includes coal and reagent characterisation.

Coal characterisation analysis that will be used consists of:

1) Maceral content to determine the effect of the difference in coal structure.
2) Proximate analysis to evaluate the difference in carbon content, volatile content and ash content.
3) Float-sink analysis to determine the floatability of the coal sample as well as the expected yield at a given density.
4) Oxygen-containing functional groups to determine the type of oxygen groups present on the coal surface.
5) Surface extraction of aliphatic coal surface groups to determine the degree of oxidation and the kind of reagents necessary to obtain froth flotation.
6) Flotation release analysis to determine the flotation performance of a coal using a standardised collector and frother

Reagent screening methodology includes

1 Contact angle measurements on demineralised coal tablets to assess the influence of the reagent on only the carbon fraction and,

2 Contact angle measurement on density separated coal to evaluate the influence of minerals on selectivity for the coal.

Prior to froth flotation testing it is necessary to complete the above detailed characterisation of the coal surface due to the deleterious effect of oxidation on froth flotation. Reagent screening is also of essence to screen suitable selective reagents and to minimise the amount of flotation tests.

2.15 Hypothesis:

It is expected that the characteristics for the different coal samples will differ due to the different coal seams that are used as well as their origin. Ultimate and proximate analysis will provide the necessary information on the ash, moisture, carbon and oxygen contents. Surface oxygen group content determination, together with surface extraction values, will be evaluated to determine the hydrophobicity of the different coal samples. Contact angle measurement will serve as a screening for reagents on the demineralised coal samples to determine the most suitable collectors for flotation for each coal. The collectors will then be evaluated again by contact angle measurements on density separated coal to determine their selectivity for the coal rich particles from the bulk sample. Finally, release analysis with Dodecane (the optimum expected yield) will give a release curve that can be used to determine optimum recovery and ash contents for each coal by plotting flotation data onto the release curve. Actual flotation experiments will test the findings from the characterisation phase.

Chapter 3

Experimental Procedures

As discussed in previously (see section 1.3), the aim of this thesis is to develop a model for coal flotation that can be applied to the different coal types in South Africa. The model must be able to predict with a high degree of certainty what kind of reagent will be suitable for a certain coal type. This model will be developed using coal and reagent characterisation information that was obtained from the test work presented in this thesis.

3.1 Introduction

The experimental procedures followed in this thesis comprised numerous test work phases aimed at the development of a methodology to predict the reagents that are to be used for flotation of a certain coal type. The chapter begins by describing the coal sampling and characterisation procedures that were followed throughout the study, as well as the reagent screening procedures.

The coal characterisation procedures that were followed consisted of petrographic analysis, proximate analysis, washability studies, oxygen-containing functional group determination, surface extraction analysis and flotation release analysis.

The reagent screening procedures that were tested for validity included contact angle determination on both demineralised and density separated coal. The reagents were tested using a flotation procedure.

These procedures will next be discussed separately.

- Coal type
- Functional groups
- Oxidation.
- Slime coating and entrainment.
- Pulp density, particle size.
- pH of pulp.
- Conditioning.
- Reagents.
- Frother dosage.

(Leja 1982, Van Nierop 1986, Wheeler and Keys 1986). These will be reviewed below.

2.7.1 Coal rank

The hydrophobicity of coal is not only determined by the oxygen functional group content, but also by the rank of the coal (Fuerstenau, 1987, Bujnowska, 1985, Fuerstenau 1976, Fuerstenau et al 1983, 1987).

Only a slight correlation can be noticed between the fixed carbon and volatile matter content in the coal although both parameters are used as a measure of coal floatability (Fuerstenau 1982). Coal with a greater content of waxy hydrocarbons and volatile matter has an increased floatability (Fuerstenau 1982). An increase in percentage carbon (higher rank) results in a more closed microstructure that has fewer polar functional groups. This leads to a less water-wettable (more floatable) surface (Fuerstenau, 1982).

2.8.2 Coal Type

Bujnowska (1985) stated that the floatability of macerals groups in sub-bituminous coals and low rank coals is in the order of inertinite → vitrinite →

3.2 Coal characterisation

3.2.1 Characteristics of coal seams

This section of the review is aimed at understanding in particular the coal characteristics of the coal samples used in this study. These include highveld seam 3 and 4 (Twistdraai), Highveld seam 5 (Syferfontein seam 5 upper), Waterberg and Witbank seam 2 and seam 4 coal.

3.2.1.1 Preparation characteristics of the Highveld coal

This coalfield is growing rapidly in importance, although its coal is used mainly in a unbeneficiated state. The seams correlate with those of the adjacent Witbank coalfield, but whereas at Witbank, the number 2 seam is the most important, in the Highveld coalfield the major seam is the number 4 lower. Seam 1 is seldom developed and is always thin; the number 2 seam is generally about 2m thick with an ash content of about 14%. Highveld seam 3 coal occurs as an intermittent thin band.

The Highveld seam 4 coal is used for power generation and for conversion into liquid products via the gasification process at Sasol 2 and 3. The seam is on average almost 4m thick, with a raw CV of between 18 and 25 MJ/kg. In some areas, the number 4 seam contains a high grade fraction (> 27 MJ/kg) that can be washed out, and the field may therefore be the scene of major preparation developments in the future (Horsfall, 1982)

The number 5 seam seldom exceeds 2m in thickness, and can be less than 1m thick. It consists mainly of bright, coal sometimes with duller coal towards the top. It is restricted to the higher ground and can be mined where it occurs largely for blend-coking coal. In the outlying areas of the coalfield the rank of the coal is lower, with consequent loss of coking properties.

3.2.1.2 Preparation characteristics of the Waterberg coalfield

The Waterberg coalfield consists of narrow bands or coal bearing "zones" that alternate with dirt bands. These bands may be up to 100m thick. The raw ash content of the Run-of-mine (ROM) coal varies between 50 and 60%, due to the high contents of epigenetic and syngenetic minerals within the coal. Crushing to a particle size of 0.1mm or less is necessary to effect good liberation (Horsfall, 1982)

The Waterberg coal is vitrinite rich, unlike most other South African coals, and is used for power generation and liquefaction.

3.2.2 Sample preparation

Representative samples were obtained from Twistdraai colliery, Syferfontein seam 5 upper from Syferfontein colliery, Waterberg coal from Grootegeluk colliery, and seam 2 and seam 4 Witbank coal from Rietspruit colliery.

The samples were dried and crushed to 95% below 2mm using a Retsch jaw crusher. The samples were next split into five representative 1 kg samples (the representiveness of the samples was confirmed using the ash content of each sample) using a 20 slot ¼" riffler. The samples were stored in a Perspex nitrogen container to prevent oxidation.

The bulk of the coal samples were stored under water to prevent the coal from excessive oxidation.

3.2.2.1 Particle size distribution

A 1kg sample of coal was placed in a rod mill together with 613 g of water to obtain a slurry density of 62%. The following rods were used in the mill: two rods with a diameter of 35mm and mass of 2450g each, six rods with a diameter of 25mm and a mass of 1215g each and six rods with a diameter of 20mm and a mass of 795g each. The sample was milled for 30, 60, 90 and 120 minutes respectively to determine the time of milling to obtain a particle size distribution of 95% below 150 μm. A Retsch crystalsiser was used to determine the particle size distribution of each milled sample.

The same procedure was used for all five coal samples used in this investigation.

3.2.3 Ash-by-size analysis

Prior to doing the analysis the screens were inspected for wear and tear to ensure proper separation of the different coal particle sizes.

A milled coal sample was hand screened (wet) using new SABS approved screens of sizes 150 μm, 106 μm, 75 μm, and 45 μm. The fractions were vacuum filtered and dried in an oven at 80 °C for six hours. The samples were weighed and the yield percentage and ash content was determined for each size fraction.

This procedure was repeated for each coal sample.

3.2.4 Petrographic analysis

The prepared crushed coal sample is mounted together with epoxy resin and allowed to harden. After setting the block is ground and polished to examine the sample under the microscope. Due to the differences in reflectance of the coal macerals, the sample can be classed into the different coal maceral groups present on the sample.

Maceral analysis was conducted at the CSIR's Enertech division in Pretoria. The analysis was carried out under oil-immersion using 25X, 32X and 50X oil-immersion objectives. An automatic point counter was used at traverse spacings of 0.4mm, and intervals between the traverses of 0.5mm. At least 500 points (excluding the binding resin) were counted and registered on a point counter. The ore microscope was fitted with a 100W quartz –halogen lamp.

3.2.5 Proximate analysis

The moisture content, fixed carbon content, volatile content and ash content of each coal sample were determined at the SCI (Sasol Chemical Industries) laboratories.

The method entails thermal analysis by heating the known mass of coal sample in an inert (usually nitrogen) atmosphere up to 100°C and determining the mass loss as moisture. The sample is further heated in an inert atmosphere and the mass loss that occurs up to about 500°C is attributed to volatiles. The mass loss upon further heating up to 900°C is attributed to fixed carbon. At this stage, the inert atmosphere is changed to air and the sample is kept at 900°C until no further mass loss occurs. The remaining mass indicates the ash content of the sample.

3.2.6 Density separation (sink-float analysis)

Density separation was carried out as described in section 3.2.2.1 to determine the washability characteristics of each coal sample that was used in this study (95% below 150 μm).

In this procedure, about 5 g of coal was added to a glass tube and 80 cm^3 of a bromoform and toluene mixture (at a specified density) was added to the coal. The densities that were used ranged between 1.4 g/cm^3 and 2.0 g/cm^3. The coal dense liquid mixture was mixed and then centrifuged using a Beckman centrifuge at 2400 rpm for 20 min. The fractions obtained were separated from one another, filtered and thoroughly washed with acetone to remove the density liquid. The samples were then dried in an oven at 80°C for a period of six hours, after which the fractions were weighed and analysed for ash content.

3.2.7 Oxygen-containing functional group determination

The oxygen-containing functional group determination was conducted on each coal sample using the procedures of Blom et al. (1957). The calculations that were used to determine the percentage oxygen as carboxylic, hydroxyl and total acid and hydroxylic acid groups are given in appendix B2.

3.2.7.1 Carboxylic acid groups

The carboxylic group content was determined using an ion exchange principle with the aid of calcium acetate, and the concentration of the acetic acid formed was determined titrimetically against standardised sodium hydroxide.

Reaction equation:

$RCOOH + \frac{1}{2} Ca(OOCCH_3)2 \rightarrow RCOO (\frac{1}{2}Ca) + CH_3COOH$

Method:

a) About 1g of coal was added to 50cm^3 of a 1 mol/dm^3 HCl solution and stirred for a period of 18 hours in order to hydrolyse all of the carboxylic salts to the corresponding acid form. Dissolution of the carbonates present in the mineral fraction also occurs (the presence of carbonates interfere with the sodium hydroxide titration value). Excess water was removed from the sample by vacuum filtration and the acid was removed by soaking the coal in distilled water until a pH of 7.6 was obtained. The sample was again filtered to remove the excess water and dried in an oven at 80°C for six hours. A correction was made for the reduction in ash content that followed the removal of the carbonate minerals.

b) Approximately 300 mg of the dried coal, 10 cm^3 of a 0.5 mol/dm^3 calcium acetate solution and 50 cm^3 deionised (CO_2-free) water were added to a flask, which was sealed under nitrogen and stirred for 18 hours. After filtration, the sample was washed with aliquots of deionised (CO_2-free) water and the filtrate titrated against a standardised 0.02 mol/dm^3 sodium hydroxide solution using phenolphthalein as indicator until a transition from colourless to pink was observed.

3.2.7.2 Hydroxyl groups

The total percentage hydroxyl groups were determined by acetylation using acetic acid anhydride. The ester that formed was saponified using barium hydroxide prior, and the reaction product was then acidified using phosphoric acid. The acetic acid that formed was distilled off and the concentration was determined titrimetically against a standardised sodium hydroxide solution.

Reaction:

1) $ROH + \frac{1}{2}(CH_3CO)_2O \rightarrow CH_3COOR + \frac{1}{2} H_2O$

2) $CH_3COOR + \frac{1}{2} Ba(OH)_2 \rightarrow ROH + \frac{1}{2} Ba(OOC.CH_3)_2$

3) $\frac{1}{2} Ba(OOC.CH_3)_2 + \frac{1}{3} H_3PO_4 \rightarrow 1/6\ Ba_3(PO_4)_2 + CH_3COOH$

Method:

a) The same procedure as in paragraph 3.2.6.1a was followed

b) Approximately 1.5g of the dried coal as described in paragraph 3.2.7.1a was added to a 1:2 mixture of acetic acid anhydride and pyridine, and boiled under reflux for 24 hours. The mixture was cooled, filtered and washed with distilled water in order to remove all of the acid. The product was then dried in an oven at 80°C (under nitrogen atmosphere) for 6 hours. 500mg of the coal was accurately weighed and added to 2g of barium hydroxide and 40cm^3 of distilled water. The reaction mixture was boiled under reflux for a period of 5 hours. Following this, the reaction mixture was acidified with 2 cm^3 ortho-phosphoric acid, and 25cm^3 of distillate recovered and titrated against a standard 0.02 mol/dm^3 sodium hydroxide solution using phenolphthalein as indicator. 25 cm^3 of distilled water was added to the reaction mixture and the distillation/titration procedure repeated. The distillation procedure was repeated until constant titration values were obtained.

3.2.7.3 Total acid and hydroxylic acid groups

The method concerns the reaction between excess barium hydroxide and the organic acid groups present in the coal sample. The decrease in barium hydroxide concentration was determined titrimetically against a standardised hydrochloric acid solution.

Reactions:

1) $ROH + RCOOH + n\,Ba(OH)_2 \rightarrow \frac{1}{2}(RCOO)_2Ba + 2H_2O + \frac{1}{2}(RO)_2Ba + (n\text{-}1)Ba(OH)_2$

2) $(n\text{-}1)Ba(OH)_2 + 2(n\text{-}1)HCl \rightarrow (n\text{-}1)BaCl_2 + 2(N\text{-}1)H_2O$

Method:

a) The method described in section 3.2.7.1a was followed.

b) 1g of the dried coal was accurately weighed and added to a solution containing 2g of barium hydroxide dissolved in 40cm^3 distilled (CO_2-free) water. The reaction mixture was stirred for 24 hours under a nitrogen atmosphere, filtered and the coal residue washed with small aliquots of distilled (CO_2-free) water to remove all of the excess barium hydroxide present. The filtrate was titrated against a standardised 0.5 mol/dm^3 hydrochloric acid solution using bromothymol blue as indicator.

3.2.8 Surface extraction

1g of dry coal was accurately weighed into a flask and 20cm^3 of a 1:1 chloroform and ethyl acetate mixture was added. The flask was closed and stirred for 10 minutes, filtered, and the filtrate was used to determine the absorbency of light by the extracted aliphatic groups at a wavelength of 400nm.

3.2.9 Flotation release analysis

Flotation release analysis was conducted on the coal sample described earlier in section 3.2.2.1. The procedure involved the separation of combustibles (coal) from the non-combustibles in a rougher flotation step, followed by a second and third cleaner step to improve separation. Isomerised paraffin was used as a collector together with MIBC as frother.

A mechanical Leeds flotation cell was used. A detailed description is given in section 3.4.1.

The 3 ℓ Leeds cell was initially filled to a volume of 2 ℓ using tap water, and the impeller speed set to 1200rpm. 150g of coal solids (dry basis) was added to the cell, which was filled to 3 ℓ with additional tap water. The distance between the pulp-froth interface and the overflow weir (i.e. froth depth) was approximately 1cm. The desired quantity of oily collector (6 ℓ/t isomerised paraffin) was added to the suspended pulp using a micro-syringe, ensuring that the syringe tip was below the pulp surface. After the pulp had been conditioned with collector for 5 minutes, frother (40ppm MIBC) was added using a micro-syringe and the pulp was further conditioned for a period of 30 seconds.

The air rate was then set to the desired level (3ℓ/min), and the concentrate recovered. More reagents were added to the cell once the froth appeared barren and unstable, and flotation continued. Once all of the floatable material had been collected, the tailings were drained from the cell into a bucket and the residual pulp constituted the rougher tailings sample.

A cleaner flotation step was then conducted, whereby the bulk rougher concentrate was added back to the empty cell and water added to the cell operating level. The operating procedure mentioned above was repeated. The concentrate recovered in this flotation step constituted the cleaner concentrate, and the residual pulp that was drained from the cell the cleaner tails.

The final re-cleaner flotation step was conducted, again by following the above-mentioned procedure with the exception of reagent addition. The final concentrate was collected in six fractions (one every 20 seconds). The residual pulp remaining in the cell constituted the re-cleaner tails.

The final cleaner concentrate samples and tailings were filtered, dried and weighed in order to determine the cumulative yield over the duration of the float. Ash analysis was also performed on these samples so that cumulative concentrate ash contents and recoveries could be determined.

3.3 Reagents

3.3.1 Selection of reagents as collectors

The selection of the reagents that were used in this study was based on reagents used by previous researchers. The reagents were:

Aniline: Matthyser (1984), increased flotation

P-Cresol:: Swart (1987), poor agglomeration

Nitrobenzene: Swart (1987), decreased agglomeration

Tetralin: Swart (1987), agglomeration

Toluene: Swart (1987), agglomeration

Hexane: Van Nierop, Van Heerden, selective for flotation, decrease agglomeration rate

Hexene: Van Heerden, increased agglomeration rate

Benzene: Van Heerden, increased agglomeration rate

Oleic acid: Keys 1986, increased flotation response

Dodecane: Moxom et al 1987, optimum recovery of coal

Decane: influence of carbon chain length

Dodecene: Unsaturated hydrocarbon effect

Iso-decanol: Influence of isomerism and alcohol

The characteristics of the above selected reagents are shown in Table 3.1. Analytical grade reagents with a purity of >98% were used at all times.

Table 3.1: Properties of reagents used as collectors

Reagent	Viscosity (cPs)	Density (g/cm^3)	Surface tension (mN/m)	Manufacturer	Structure
Aniline	4.57	1.022	43.4	Merck	$C_6H_5NH_2$
O-cresol	8.32	1.027	37.76	Unilab	C_7H_8O
M-Cresol	13.4	1.033	37	Unilab	C_7H_8O
P-Cresol	14.5	1.018	35.82	Unilab	C_7H_8O
Oleic acid	25.6	0.89	33.18	Sigma-Aldrich	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
Nitro-benzene	3.36	1.204	35.94	Sigma-Aldrich	$C_6H_5NO_2$
Benzene	0.648	0.877	28.4	Sigma-Aldrich	C_6H_6
Tetralin	3.71	0.970	34.8	Sigma-Aldrich	$C_{10}H_{12}$
Toluene	0.59	0.867	28.4	Riedel de Haen	$C_6H_5CH_3$
Dodecane	1.35	0.749	25.4	Sigma Aldrich	$C_{12}H_{26}$
Dodecene	3.16	0.758	25.27	Sigma-Aldrich	$C_{12}H_{24}$
Iso-decanol	13.4	0.829	26.63	Merck	$(CH_3)_2(CH_2)_8OH$
N-decane	2.65	0.73	23.69	Sigma Aldrich	$C_{10}H_{22}$
Hexane	0.326	0.661	18.4	Sigma-Aldrich	C_6H_{14}
Hexene	2.1	0.6731	18.28	Sigma Aldrich	C_6H_{12}

3.4 Contact angle measurement

Contact angle measurements were conducted to determine the contact (if any) between the coal sample and a reagent (collector). The method involves measurement of the angle (θ) between the coal and the liquid droplet.

The coal samples described in section 3.2.2.1 were demineralised chemically in order to minimise the influence of the minerals on the surface properties of the coal. 10g of dry coal was placed in a polythene bottle together with 500 cm^3 of a 1:1 mixture of hydrofluoric acid and hydrochloric acid (5 mole concentration of each). The mixture was stirred over a period of 48 hours using a magnetic stirrer. The mixture was then filtered using a Buchner device and the coal fraction was soaked in distilled water. Filtration and soaking were repeated until all traces of acid were removed. The coal was finally filtered and dried in an oven over a period of 6 hours.

The dried coal was pressed into a coal tablet using a vacuum press at pressure of 300g/cm^2. The sessile drop testing procedure was followed as described below.

A compressed coal tablet placed onto a glass rod was put into a 50cm^3 container and 30 cm^3 of tap water was added. A droplet (3 µl) of collector was brought into contact with the coal surface with the aid of a 5µl micro syringe. A schematic of the set-up is shown in Figure 3.1. The contact angle (θ) was measured on both sides of the droplet using a contact angle meter. All measurements were conducted four times and the average obtained.

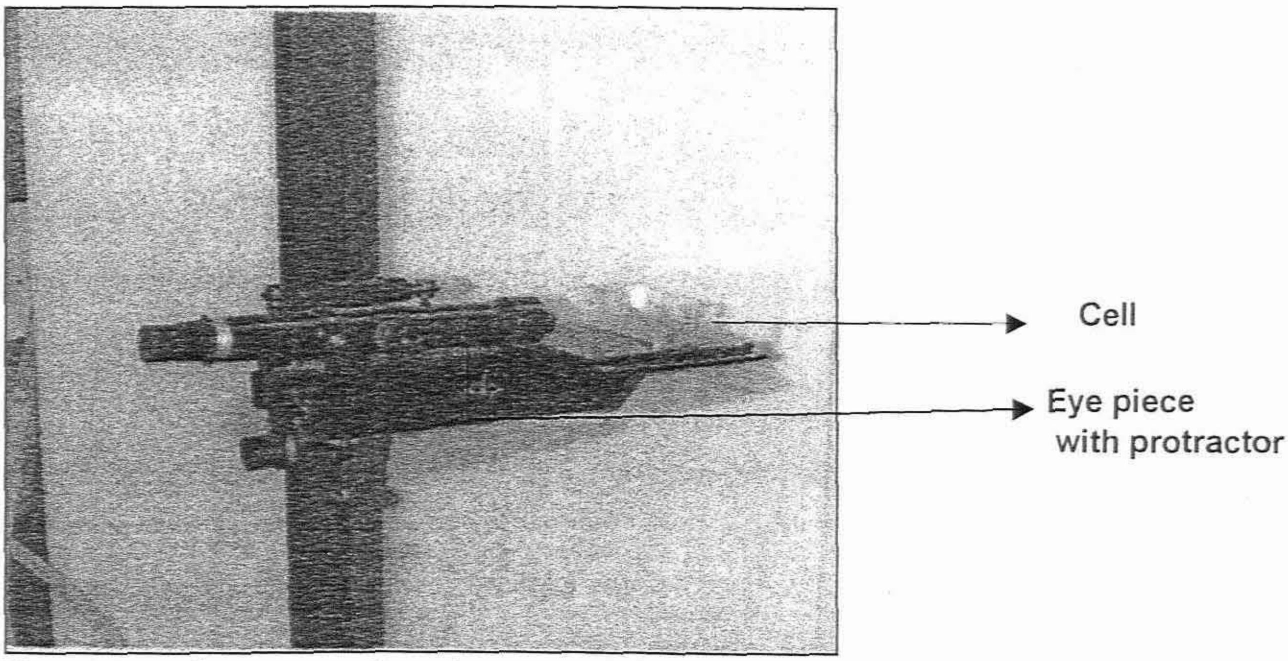


Figure 3.1: Contact angle meter

The collectors were also tested for selectivity on each coal sample by pressing coal tablets from density separated (density of 1.5 g/cm^3) coal and measuring the contact angle between the coal and the collector. Four angles were measured and the average obtained.

The reagents were next used in flotation tests to validate the results obtained from the contact angle measurements.

3.5 Froth flotation

This section describes the froth flotation equipment used and the flotation procedure that was followed. The coal samples that were used for these tests are those described in section 3.2.2.1.

3.5.1 Leeds flotation cell

A schematic of the 3 ℓ capacity bottom-driven batch scale Leeds cell is shown in Figure 3.2. The cell was constructed from PVC. Air flow to the cell was controlled by means of a rotameter. The agitation speed was manually controlled by manipulation of a variable speed selector dial displaying agitation speed in rpm.

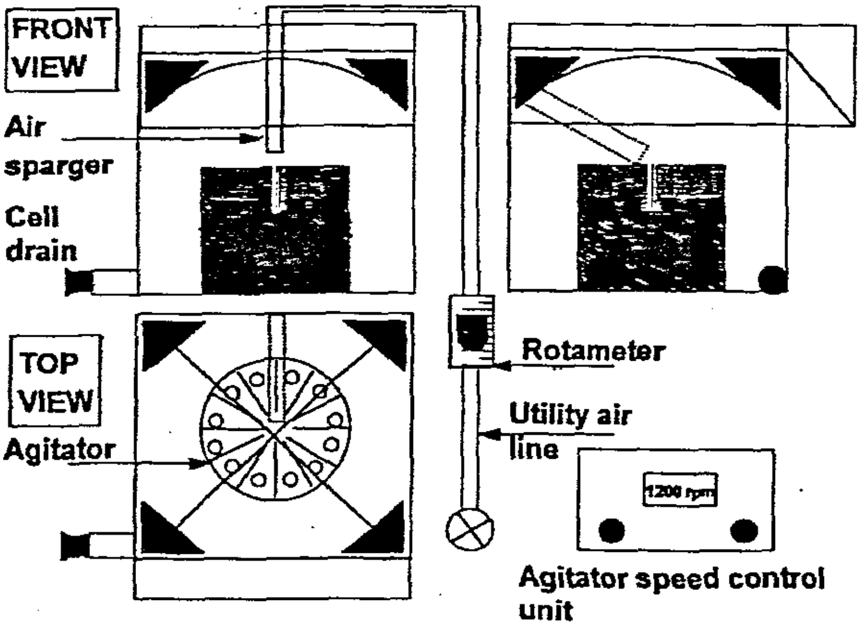


Figure3.2: Schematic of Leeds flotation cell

3.4.2 Flotation procedure

The 3 ℓ Leeds cell was filled to a volume of about 2 ℓ using tap water, and the impeller speed was set to 1200 rpm. 150g of dry coal as prepared in section 3.2.1.1 was added, and the cell was filled to 3 ℓ with additional tap water. The froth depth (distance between the pulp/froth interface and the overflow weir) was kept constant at 1 cm. A fixed dosage of 3 ℓ/t of collector was added to the pulp, ensuring that the tip of the syringe was below the pulp. A conditioning period of 5 minutes was allowed for proper coverage of the coal surface by the collector and 20 ppm (parts per million) frother (MIBC – methyl isobutyl carbinol) was added. After the frother had been allowed to disperse for a period of 30 seconds, the air was set to a level of 3 ℓ/min. The froth concentrate was collected over a period of 5 minutes for each flotation. The residual tailings that remained in the float cell were drained into a bucket by opening the drain valve. The concentrate and tail samples were filtered and dried in an oven overnight under nitrogen atmosphere.

Both samples were weighed and submitted for ash content analysis. The flotation tests were done in duplicate.

The procedures discussed above follow the general methodology used to evaluate a fine coal sample for the purpose of froth flotation. The application of some of these methods will be evaluated during the discussion of the results obtained in Chapter 4.

Chapter 4

Coal characterisation

Results and discussion

This chapter discusses first the results obtained from the determination of the milling time for each coal; and then the characterisation analysis of the coal, and concludes with a summary of these results.

4.1 Sample preparation

4.1.1 Milling time

The distribution of particles is measured as the percentage particles below 150μm. The results are shown in Table 4.1. In order to ensure that the particle size distribution (PSD) simulated the PSD required for flotation, it was necessary to construct a graph of recovery from milling versus time for each coal (see Figure 4.1).

From Table 4.1 it can be seen that the Twistdraai coal is milled to 95% below 150μm within 30 minutes. Syferfontein seam 5 upper coal takes 120 minutes to be milled to below 150μm, Waterberg coal is milled down within 60 minutes, Witbank seam 2 is also milled to less than 150μm within 60 minutes, and Witbank seam 4 coal takes 30 minutes to be milled down to 95% below 150μm.

From the results in Figure 4.1 it can be seen that the rate of attrition (as measured by the percentage passing 150μm) was slowest for Syferfontein seam 5 upper coal. This is followed by Waterberg coal then Witbank seam 2 and lastly Twistdraai and Witbank seam 4 coals which have identical slopes.

Table 4.1: Results from PSD analysis (Crystalsizer) at different times of milling

<table>
<tr><th colspan="6">Twistdraai – Particle size distribution, %</th></tr>
<tr><th>Particle size (µm)</th><th>120 min</th><th>90 min</th><th>60 min</th><th>30 min</th><th>0 min</th></tr>
<tr><td>-45</td><td>99.5</td><td>98</td><td>97.3</td><td>85.1</td><td></td></tr>
<tr><td>45</td><td>0.5</td><td>1.9</td><td>2.4</td><td>9.5</td><td></td></tr>
<tr><td>75</td><td>0</td><td>0.1</td><td>0.3</td><td>2.9</td><td></td></tr>
<tr><td>106</td><td>0</td><td>0</td><td>0</td><td>1.7</td><td>85.69</td></tr>
<tr><td>150</td><td>0</td><td>0</td><td>0</td><td>0.8</td><td>14.31</td></tr>
<tr><td></td><td>100</td><td>100</td><td>100</td><td>100</td><td></td></tr>
<tr><th colspan="6">SyferfonteinSeam 5 upper – Particle size distribution, %</th></tr>
<tr><td>-45</td><td>66.4</td><td>64.3</td><td>58.4</td><td>38</td><td></td></tr>
<tr><td>45</td><td>10.9</td><td>11.7</td><td>9.5</td><td>6.1</td><td></td></tr>
<tr><td>75</td><td>7</td><td>8.3</td><td>7.4</td><td>5.7</td><td></td></tr>
<tr><td>106</td><td>6.8</td><td>9.4</td><td>9.3</td><td>9.2</td><td>83.02</td></tr>
<tr><td>150</td><td>8.9</td><td>6.3</td><td>15.4</td><td>41</td><td>16.89</td></tr>
<tr><td></td><td>100</td><td>100</td><td>100</td><td>100</td><td></td></tr>
<tr><th colspan="6">Waterberg – Particle size distribution, %</th></tr>
<tr><td>-45</td><td>99.9</td><td>91.1</td><td>79.4</td><td>48.8</td><td></td></tr>
<tr><td>45</td><td>0.1</td><td>7.1</td><td>11.3</td><td>6.3</td><td></td></tr>
<tr><td>75</td><td>0</td><td>1.6</td><td>6.2</td><td>5.4</td><td></td></tr>
<tr><td>106</td><td>0</td><td>0.2</td><td>2.6</td><td>9.1</td><td>78.99</td></tr>
<tr><td>150</td><td>0</td><td>0</td><td>0.5</td><td>30.4</td><td>21.01</td></tr>
<tr><td></td><td>100</td><td>100</td><td>100</td><td>100</td><td></td></tr>
<tr><th colspan="6">Witbank Seam 2 – Particle size distribution, %</th></tr>
<tr><td>-45</td><td>94.4</td><td>99.4</td><td>82.4</td><td>61.9</td><td></td></tr>
<tr><td>45</td><td>5.2</td><td>0.6</td><td>8.9</td><td>7.3</td><td></td></tr>
<tr><td>75</td><td>0.4</td><td>0</td><td>4.1</td><td>5.5</td><td></td></tr>
<tr><td>106</td><td>0</td><td>0</td><td>3.7</td><td>10.1</td><td>79.96</td></tr>
<tr><td>150</td><td>0</td><td>0</td><td>0.9</td><td>15.2</td><td>20.04</td></tr>
<tr><td></td><td>100</td><td>100</td><td>100</td><td>100</td><td></td></tr>
<tr><th colspan="6">WitbankSeam 4 – Particle size distribution, %</th></tr>
<tr><td>-45</td><td>99.6</td><td>98.7</td><td>97.2</td><td>84.4</td><td></td></tr>
<tr><td>45</td><td>0.4</td><td>1.2</td><td>2.5</td><td>8.8</td><td></td></tr>
<tr><td>75</td><td>0</td><td>0.1</td><td>0.3</td><td>3.1</td><td></td></tr>
<tr><td>106</td><td>0</td><td>0</td><td>0</td><td>2.7</td><td>84.29</td></tr>
<tr><td>150</td><td>0</td><td>0</td><td>0</td><td>1</td><td>15.79</td></tr>
<tr><td></td><td>100</td><td>100</td><td>100</td><td>100</td><td></td></tr>
</table>

The milling curves that were constructed (Figure 4.1) indicate that both Twistdraai and Witbank seam 4 coal need less than 30 minutes to be milled to below 150 µm, Witbank seam 2 coal needs about 50 minutes of milling, followed by Waterberg coal which needs 55 minutes of milling; and lastly Syferfontein seam 5 upper coal which needs 105 minutes of milling.

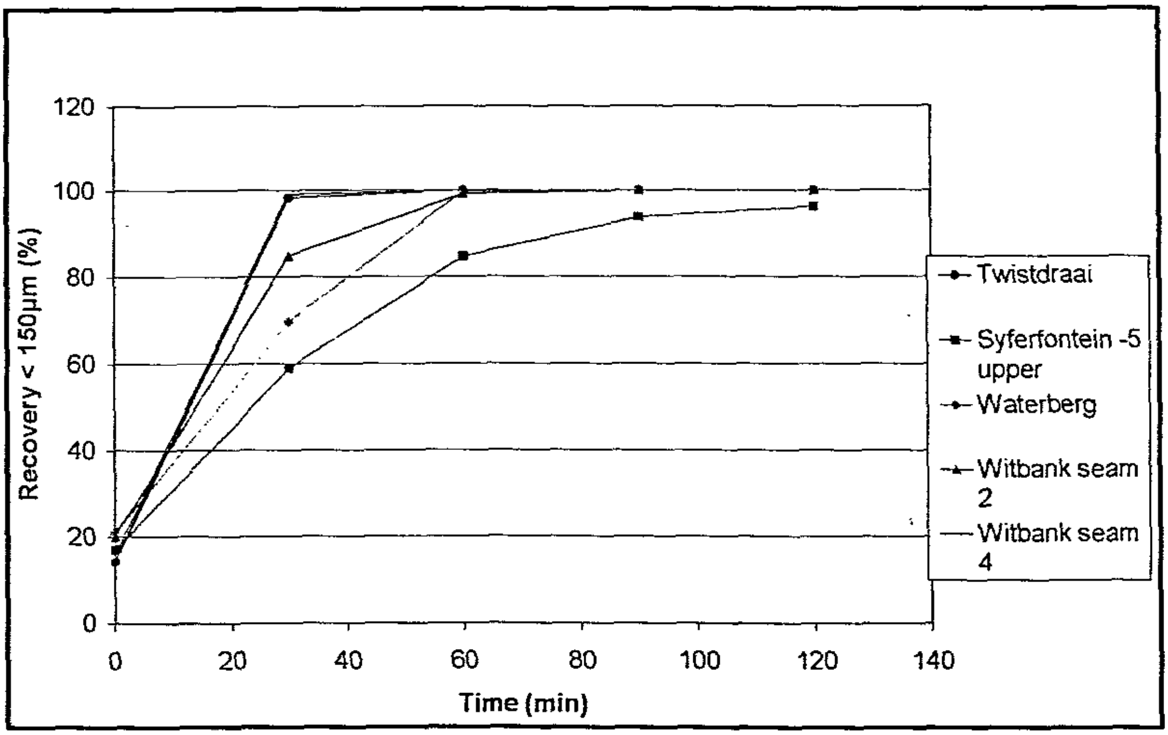


Figure 4.1: Time of milling vs. recovery of coal in the <150µm fraction

4.1.2 Mass size distribution results

The samples that were milled for the predetermined time to obtain a particle size of 95% below 150 µm were hand screened to determine the yield percentage and ash content of each fraction. The results are shown in Table 4.2.

From the yield-by-size and ash-by-size results in Table 4.2 it can be seen that the highest yield is found in the slimes fraction (< 45 µm), which also consists of the highest fractional ash content. Only a small portion (<5%) of the Witbank seam 4 sample has a particle size above 150µm, which still makes this coal amenable to froth flotation in terms of particle size. All the other milled coal samples contain less than 1% material above 150 µm.

The calculated feed ash contents of the coal samples that were used vary between 12.65% for Syferfontein and 32.2% for Twistdraai coal.

Table 4.2: Fractional mass size distribution results obtained for the different coal samples (as-received basis)

Particle size (µm)	Twistdraai		Syferfontein 5 Upper		Waterberg	
	Yield %	Ash %	Yield %	Ash %	Yield %	Ash %
-45	64.75	36.15	46.07	19.06	50.89	32.18
45	20.59	26.24	17.13	11.7	15.03	24.29
75	12.29	23.43	25.82	5.6	21.71	27.02
106	2.33	17.97	10.67	3.8	11.72	32.25
150	0.03	21.8	0.31	5.8	0.66	30.4
Feed (calculated)		32.12		12.65		29.87

Particle size (µm)	Witbank seam 2		Witbank seam 4	
	Yield %	Ash %	Yield %	Ash %
-45	52.41	17.55	49.24	35.03
45	17.68	15.31	11.38	28.32
75	24.84	13.74	16.10	26.64
106	5.03	13.79	18.72	26.41
150	0.04	19.6	4.56	25.8
Feed (calculated)		16.02		30.88

4.1.3 Feed ash content

The feed ash content of the samples are compared on different methods of analysis in Table 4.3

Table 4.3: Comparison of ash content in coal feed samples using different methods of analysis

	Standard method	Petrographic	Proximate
Twistdraai	27.81	28.8	28.2
Syferfontein seam 5 upper	14.22	13.9	13.3
Waterberg	28.78	28.8	29.4
Witbank seam 2	15.8	16.1	16.6
Witbank seam 4	32.53	33.8	33.8

It can be seen that the ash content of the samples is in the same range, no matter what method is used. These values are actual ash content values as determined, and should not be confused with the calculated ash content reported in Table 4.2. Calculated ash content values serve only as a back-calculation to check the validity of the results and if a homogeneous sample was used.

4.2 Coal characterisation

4.2.1 Petrographic analysis

The results of the petrographic analyses on the five coal samples are shown in Table 4.4.

Table 4.4: Petrographic analysis results for five different coal samples (as-received basis)

Sample	**Vitrinite Total (%)**	**Liptinite (%)**	**Inertinite Total (%)**	**Visible. Minerals (calc) (%)**	**Ash Content (%)**
Twistdraai	42	3	38	17	28.8
Syferfontein seam 5 upper	88	2	3	7	13.9
Waterberg	68	3	12	17	28.8
Witbank seam 2	24	3	65	8	16.1
Witbank seam 4	26	3	51	20	33.8

From Table 4.4 it can be seen that Twistdraai coal, Syferfontein seam 5 upper coal and Waterberg coal are high in vitrinite maceral content. Witbank seam 2 and seam 4 coal are rich in inertinite content. The inertinite rich coal samples have a higher aromatic structure than the vitrinite coal samples.

The Twistdraai and Waterberg coal samples have high calculated mineral contents (17%,) which also relate to the equivalent ash content of these two samples (28.8%). Witbank seam 4, having the highest calculated mineral content, also has the highest ash content of 33.8%.

Due to the particle size of the sample being very fine, it was decided not to do the vitrinite reflectance of the coal samples since the procedure requires a large enough surface to obtain reflectance. Reflectance can be measured but is not recommended.

It is also evident that the ash contents obtained by petrographic analysis differ from the ash contents calculated in Table 4.2. This is particularly true for Twistdraai coal, which consists of a calculated feed ash of 32.12% compared to 28.8% obtained by petrographic analysis. This is probably due to the ash content of the +150μm fraction, which was measured using TGA (thermogravimetric analysis) due to the sample being less than 1g. The same is observed for Witbank seam 4 coal, with a calculated ash content of 30.88% and a petrographically determined ash content of 33.8%. Again, this discrepancy is attributed to a different method of determining the ash content.

4.2.2 Proximate analysis

The proximate analysis results for the five different coal samples are shown in Table 4.5.

Table 4.5: Proximate analysis results obtained for five different coal samples

Sample	Moisture (%)	Volatiles (%)	Fixed C (%)	Ash content (%)
Twistdraai	6.8	25.2	39.8	28.2
Syferfontein seam 5 upper	3.8	32.7	50.2	13.3
Waterberg	1.8	30.1	38.7	29.4
Witbank seam 2	2.4	27.6	53.4	16.6
Witbank seam 4	2	24.3	39.9	33.8

Syferfontein coal has the highest volatile matter content (32.7%) followed by Waterberg (30.1%), Witbank seam 2 (27.6%), Twistdraai (25.2%) and Witbank seam 4 with 25.2% fraction of volatile matter.

The fixed carbon content decreases in the order of Witbank seam 2 (53.4%), Syferfontein seam 5 upper (50.2%), Witbank seam 4 (39.9%), Twistdraai (39.8%) and lastly with the lowest fixed carbon content is Waterberg coal (38.7%).

It is noted that the ash contents of the five coal samples vary between 13.3% and 33.8%. This compares favourably to earlier results given in Table 4.3.

Based on the fixed carbon content, it is expected that Witbank seam 2 coal will be the easiest to float, since this coal has the highest fixed carbon content which indicates higher hydrophobicity. The Witbank seam 2 coal will probably have a more aromatic structure, as will be confirmed by the petrographic analysis results.

4.2.3 Float- sink analysis results

The results of the float-sink analysis of the composite milled coal samples are depicted in Figure 4.2. A detailed table of the float-sink results can be found in Appendix A1.

Figure 4.2 shows that the ash content of the different coal samples decreases as the recovery decreases with each density separation. This is an indication of the degree of liberation within the samples. In general, the ash content reaches a minimum value for an ash content of below 5%, indicating that the mineral matter within the coal sample is liberated in terms of relative density properties.

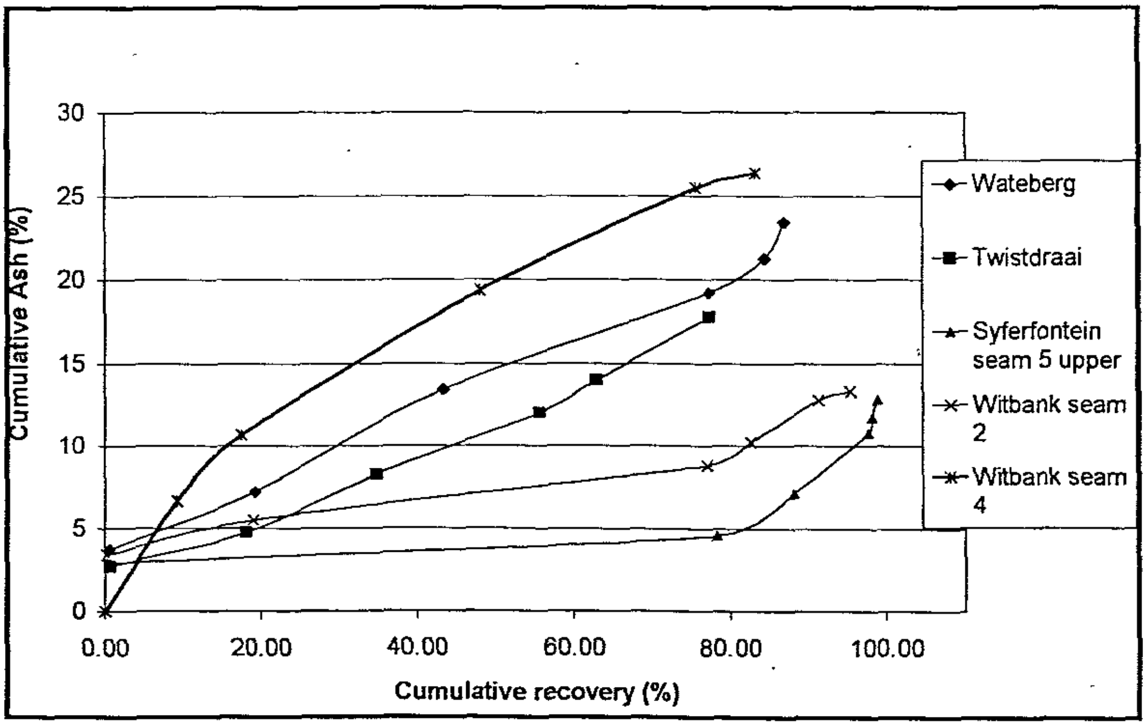


Figure 4.2: Float- sink data for different coal samples

The best flotation performance will therefore be obtained with Syferfontein coal, which has the lowest ash content and higher product yields than for the rest of the coal samples at a higher density.

The expected trend of flotation is in the order of Syferfontein seam 5 upper, Witbank seam 2, Twistdraai, Waterberg and Witbank seam 4. This is due to the amount of minerals that needs to be removed (higher for Witbank seam 4 than for Syferfontein seam 5 upper coal).

4.2.4 Oxygen-containing functional groups

The functional group content determined for the different coal flotation feed samples is summarised in Table 4.6

It can be seen that Witbank seam 4 coal contains a high percentage of carboxylic oxygen. Since the carboxylic oxygen content has a negative impact on flotation, it can be expected that the Witbank seam 4 coal will be difficult to float. It is further predicted that Witbank seam 2 will float easily. This is due to the fact that the carboxylic groups on the coal surface are linked to the water content on the coal surface (the hydrated layer formed by oxidation) and render the coal surface hydrophilic.

Table 4.6: Oxygen-containing functional group determination for different coal samples

Coal sample	% O as carboxylic acid groups	% O as total acidic groups	% O as phenolic groups
Twistdraai	0.90	0.99	0.167
Syferfontein seam 5 upper	0.84	1.64	0.139
Waterberg	1.02	1.08	0.168
Witbank seam 2	0.64	1.50	0.177
Witbank seam 4	1.36	1.31	0.146

Twistdraai coal, as well as Waterberg and Witbank seam 2 coal, has a high percentage of total acidic groups. Syferfontein seam 5 upper has the lowest percentage of total acidic groups. The total acidic oxygen content may increase the flotation yield due to the more acidic H^+ groups associated with the coal surface, which generally has a negative zeta potential. The coal surface will have a near zero charge, which is the point at which the coal will obtain its maximal hydrophobicity and be more susceptible to flotation.

Syferfontein seam 5 upper coal has the highest phenolic group content. This is an indication of the coal rank, since the phenolic group content increases with carbon content of the coal.

Fuerstenau et al (1983) found that the flotation behaviour of coal is characterised by the surface functional groups (especially the phenolic and carboxylic oxygen groups) more than by total oxygen content.

In summary, it is expected that the trend of flotation for the different coal samples will be as follows: Witbank seam 2> Syferfontein seam 5 upper>Twistdraai> Waterberg, >Witbank seam 4. This prediction is based on the carboxylic acid content of the coal, which has the biggest effect on flotation as was discussed in section 2.7.5.

4.2.5 Surface extraction

The results obtained for the extraction of aliphatic groups on the coal surface are given in Table 4.7.

Table 4.7 Surface extraction results for five SA coal samples measured at 400nm

Coal	**Absorbency at 400nm (cm^{-1})**	**Standard deviation (3 measurements)**
Twistdraai	0.162	0.003
Syferfontein seam 5 upper	0.182	0.01
Waterberg	0.541	0.003
Witbank seam 2	0.388	0.03
Witbank seam 4	0.418	0.003

It can be seen that Waterberg coal has the highest absorbency value at 400nm. The absorbency value (0.541) indicates the degree of oxidation of the coal, since the aliphatic groups on the coal surface (which decreases with coal surface oxidation) are extracted.

This indicates that the Waterberg coal sample should be the easiest to float, followed by Witbank seam 2 (absorbency of 0.418), Witbank seam 4 (absorbency of 0.388), Syferfontein seam 5 upper (absorbency of 0.182), and lastly Twistdraai coal with an absorbency value of 0.162.

A graph by Spitzer (1986) on Pittston moss coal recovery versus absorbency is used to predict the reagent requirements for flotation of a particular coal. From the Spitzer graph (shown in Figure 2.11), it may be predicted that all the coal samples will need a collector and frother for flotation with the exception of Waterberg coal, which according to the Spitzer graph, needs only a frother to float.

The surface extraction of aliphatic groups present on the coal surface will follow the trend of Waterberg > Witbank seam 2 > Witbank seam 4 > Syferfontein seam 5 upper > Twistdraai. The results that are obtained from the surface extraction analysis indicate that the surfaces of the coal samples is largely oxidised.

It is expected that the flotation of the coal samples overall, except perhaps for Waterberg and Witbank seam 4 coa,l will be difficult due to surface oxidation.

4.2.6 Flotation release analysis

Release analysis was conducted in order to obtain an indication of the optimum flotation performance that could be achieved by froth flotation. The release analysis results for the coal samples are given in Appendix A2, and are graphically depicted in Figure 4.3.

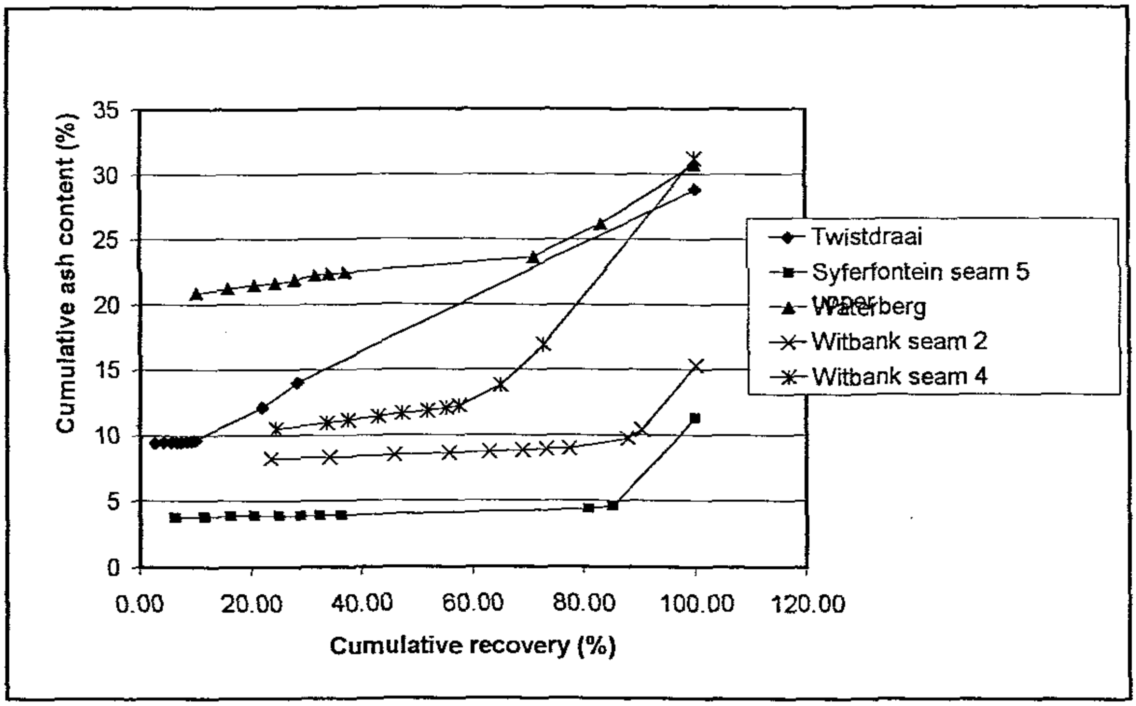


Figure 4.3: Flotation release analysis on five different SA coals

The shapes of the release analysis curves in Figure 4.3 are similar to those found in literature. The release analysis results obtained in this study will next be discussed for the five South African coals.

4.2.6.1 Twistdraai coal

From the release curve for the Twistdraai coal it is observed that the lowest ash content obtained was 9.42% at a product yield of only 2.64%. It is also observed that it is possible to obtain a product with an ash content of 14% at a product yield of 28.31% in a single stage of flotation.

4.2.6.2 Syferfontein seam 5 upper

The release curve obtained for Syferfontein seam 5 upper coal indicates that the lowest ash content that can be obtained during flotation is 3.78% at a product yield of 6.38%. From the curve it can be seen that a product ash content of 4.62% can be obtained at a product yield of 85.11%.

4.2.6.3 Waterberg

The release curve for Waterberg coal shows that a minimum ash content of 20.87% can be obtained at a product yield of 10.02%. In a single stage flotation step a product yield of 83.09% can be obtained at an ash content of 26.18%.

4.2.6.4 Witbank seam 2

From the release curve obtained for the Witbank seam 2 coal, it can be seen that a minimum ash content of 8.25% can be obtained at a product yield of 23.43%. From the curve it can also be seen that a product ash of 10.39% can be obtained at a product yield of 90.34% in a single stage flotation step.

4.2.6.5 Witbank seam 4

The release curve obtained for Witbank seam 4 coal indicates that an ash content of 10.48% is the minimum at a product yield of 24.52%. In a single stage flotation step a product yield of 72.92% is obtained at an ash content of 16.93%.

In summary, it is expected that the product yield during flotation for Twistdraai coal will be lower than for the other coal samples. Except for Twistdraai coal the expected optimum yield that can be obtained for the coal samples is above 70%.

4.2.7 Contact angle measurement

The contact angle measurements were conducted to identify suitable collectors for the flotation of the different coal samples. After initial contact angle measurements on demineralised coal, the collectors were evaluated for selectivity on density-separated coal samples. The results will thus be discussed in two separate sections. The characteristics of the reagents are listed in section 3.3.1, Table 3.1.

4.2.7.1 Contact angle determination on demineralised coal

After acid demineralisation the coals were subjected to contact angle determination to evaluate the selected reagents (collectors) on the "cleaner" carbon fraction. The results are shown in Table 4.8.

From Table 4.8, it is observed that aniline, o-cresol, m-cresol and p-cresol absorbed completely on the coal surface (180°). This is due to the fact that aniline, as well as the cresol products, consists of a substituted benzene structure.

The contact angle of oleic acid varied between the five different coal samples, with the highest contact angle obtained for Waterberg seam 4 coal (94°). The differences in contact angle between Syferfontein seam 5 upper, Waterberg, Witbank seam 2 and Witbank seam 4 coal are, however, not significant.

Table 4.8: Contact angle measurement results (degrees) obtained on demineralised coal

	TD	SYF	WB	WBS2	WBS4
Aniline	180	180	180	180	180
o-Cresol	180	180	180	180	180
m-Cresol	180	180	180	180	180
p-Cresol	180	180	180	180	180
Oleic Acid	67	90	86	92	94
Nitro-benzene	0	0	0	0	0
Benzene	0	0	0	0	0
Tetralin	56	60	60	70	60
Toluene	52	52	59	37	42
Dodecane	0	0	0	0	0
Dodecene	0	0	0	0	0
Iso-decanol	67	67	117	117	85
n-decane	0	0	0	0	0
Hexane	0	0	0	0	0
Hexene	0	0	0	0	0

TD: Twistdraai coal

SYF: Syferfontein seam 5 upper

WB: Waterberg

WBS2: Witbank seam 2

WBS4: Witbank seam 4

The contact angle results shows that nitro-benzene, benzene, dodecane, dodecene, n-decane, hexane and hexene did not adsorb on the coal surface (0°). The reason for this is that the benzenes (aromatic reagents) contain pi electrons that influence the wettability of the coal surface. It is predicted that these reagents will not be viable as collectors for fine coal flotation.

A possible reason why benzene does not adsorb on the coal surface is the low viscosity of the benzene (0.648 cps). As the benzene is substituted (e.g. o-cresol), the viscosity increases (8.32 cps) and the contact angle increases.

The nitrogen-containing benzene substitutes did not result in any contact angles that could be determined. This may be attributed to the nitrogen molecule's inability to donate pi electrons to the benzene structure.

The high contact angle or adsorption of the collector on the coal surface is not necessarily the optimum for that coa,l but might be an indication of how powerful the reagent will be during flotation. It may be that the reagent will also collect unwanted mineral matter (ash) during flotation due to the high contact angle (180 degrees) – oil wets the coal surface easily.

Another reason that the benzene reagent does not result in contact angles is ascribed to the fact that the coal surfaces seem to be oxidised, and therefore more hydrophilic, and this renders the coal more susceptible to water adsorption.

In summary, it seems that the substituted cresol reagents, oleic acid, toluene, tetralin and iso-decanol needs further investigation as collectors, due to the favourable contact angles that were obtained with these reagents. The results confirm that the coal surface is oxidized (with increased organic structure), and it is expected that oleic acid and iso-decanol will result in good flotation performance on the Witbank Seam 4 coal. Oleic acid is often used for mineral flotation, and consists also of a –COOH functional group that will bond with the –COOH groups on the coal surface.

The trend of flotation for this reagent is expected to be in the order of: Witbank seam 2> Syferfontein seam 5 upper>Twistdraai> Waterberg, >Witbank seam 4. Iso-decanol also has frothing properties, and will increase the effectiveness as a collector.

The effect of hysteresis in contact angle measurements (discussed in section 2.10) needs to be kept in mind when interpreting contact angle data. The actual testing of the reagents on flotation performance will better elucidate the applicability of this technique and the method that is used to determine contact angles on coal samples.

4.2.7.2 Contact angle results on density separated coal

The reagents were tested for selectivity between coal and minerals. The samples were therefore separated into a coal-rich fraction (ρ) <1.5g/cm^3, and a mineral or ash-rich fraction, density (ρ) >1.5 g/cm^3.

A high contact angle with the carbon-rich fraction, and a low or not determinable (zero) contact angle with the mineral-rich fraction, indicates that a reagent will be selective for flotation of a particular coal. From the results in Table 4.9, it can be seen that o-cresol, p-cresol, oleic acid and iso-decanol are selective for Twistdraai coal. O-cresol, m-cresol and p-cresol show selectivity for Waterberg coal, and oleic acid and iso-decanol for Syferfontein coal. Iso-decanol is also selective for Witbank seam 2 coal, and aniline for Witbank seam 4 coal.

Nitro-benzene, Tetralin and toluene show some selectivity for various coals, but the attractive forces between coal and reagent may not be strong enough for efficient separation. It appears that there is an interaction between nitrogen-containing groups and the mineral rich fractions.

An angle of zero indicates that the angle could not be determined as no attachment occurred between the coal and the reagent.

Table 4.9: Contact angle determination results on density separated coal samples

Reagent	TD		SYF		WB		WBS2		WBS4	
	ρ in g/cm^3		ρ in g/cm^3		ρ in g/cm^3		ρ in g/cm^3		ρ in g/cm^3	
	<1.5	>1.5	<1.5	>1.5	<1.5	>1.5	<1.5	>1.5	<1.5	>1.5
Aniline	180	73	180	83	70	53	180	101	99	0
O-cresol	125	0	180	95	90	0	180	100	87	58
M-Cresol	115	39	180	74	92	0	180	90	84	80
P-Cresol	180	0	180	99	90	0	180	101	95	95
Oleic acid	88	0	90	0	53	0	90	0	67	0
Nitrobenzene	69	0	0	0	40	0	0	0	46	0
Benzene	0	0	0	0	0	0	0	0	0	0
Tetralin	49	0	69	0	43	0	58	0	38	0
Toluene	54	0	53	0	44	0	57	0	0	0
Dodecane	0	0	0	0	0	0	0	0	0	0
Dodecene	45	0	0	0	45	0	0	0	0	0
Iso-decanol	90	0	90	0	63	0	103	0	57	0
N-decane	0	0	0	0	0	0	0	0	0	0
Hexane	0	0	0	0	0	0	0	0	0	0
Hexene	0	0	0	0	0	0	0	0	0	0

TD: Twistdraai coal
SYF: Syferfontein seam 5 upper
WB: Waterberg
WBS2: Witbank seam 2
WBS4: Witbank seam 4

From the above results it is expected that Twistdraai coal will result in low ash flotation products using oleic acid and iso-decanol, and higher yield products using o-cresol and p-cresol

It is predicted that selective flotation (low ash content) will be obtained for Syferfontein seam 5 upper coal by using oleic acid and iso-decanol as collectors.

Waterberg coal is expected to float selectively (lower ash content) by using o-cresol, m-cresol, p-cresol and oleic acid. The flotation yield that will be obtained by using oleic acid is not expected to be very good, due to a very low contact angle on the coal-rich fraction.

Table 4.10: Expected flotation trends as predicted by coal surface characterisation results

Analysis	Expected trend
Macerals	WBS2>WBS4>TD>WB>SF Inertinite rich coal floats first
Proximate	WBS2>SF>WBS4>TD>WB The fixed carbon content is an indication of the hydrophobicity of the coal
Carboxylic acid content	WBS4>WB>TD>SF>WBS2. Carboxylic acid content has a negative influence on flotation performance
Surface extraction	WB>WBS4>WBS2>SF>TD. Extraction of aliphatic groups indicates oxidation of the coal surface
Release curves	Low product yields are expected for Twistdraai coal, but the expected optimum yield for the other four samples are above 70%
Contact angle measurements	The expected trend of flotation for oleic acid could be in the order of: Witbank seam 2> Syferfontein seam 5 upper>Twistdraai> Waterberg, >Witbank seam 4. Iso-decanol also has frothing properties associated and will increase the effectiveness as a collector. It is expected that oleic acid will result in higher yield of product during flotation of Syferfontein seam 5 upper, Twistdraai and Witbank seam 2 coal. Lower flotation yields are expected for Waterberg and Witbank seam 4 coal. Iso-decanol with its associated frothing properties could result in higher flotation yield for Syferfontein seam 5 upper, Twistdraai and Witbank seam 2 coal.

Witbank seam 2 coal is expected to have the best flotation performance of all the coal samples due to the inertinite content but the flotation performance might be influenced by the higher content of hydroxylic oxygen surface functional groups. The best flotation performance is expected to be obtained using oleic acid and iso-decanol. Iso-decanol is expected to give higher flotation yield than oleic acid.

Witbank seam 4 is expected to be difficult to float, since this coal sample has the highest content of carboxylic acid functional groups. It is expected that aniline, oleic acid and iso-decanol will result in selective flotation of the coal but the expected yield from iso-decanol as collector will be lower than for aniline and oleic acid.

The validity of these predictions will next be tested and discussed in the following chapter.

Chapter 5

Froth flotation

Results and discussion

In this chapter the results obtained by froth flotation using a batch mechanical Leeds cell will be discussed. Single stage flotation tests were performed at fixed levels for air flow, collector and frother dosage, stirring speed (rpm) and flotation time, since these variables have an influence on flotation performance. The single stage flotation results will be discussed and compared with the coal characterisation analysis given in Chapter 4. The characteristics of the reagents that were used are given in Table 3.1. A short summary of the results on the release analysis will be given as an introduction to this chapter.

Introduction

Release analysis shows that the following results can be obtained in a single stage flotation step. A product yield of 72.92% can be obtained at an ash content of 16.93% for Seam 4 Witbank coal. A product ash of 10.39% can be obtained at a product yield of 90.34% in a single stage flotation step for Witbank seam 2 coal. In a single stage flotation step a product yield of 83.09% can be obtained at an ash content of 26.18% for Waterberg coal. Syferfontein seam 5 coal is expected to produce a product ash content of 4.62% at a product yield of 85.11%. It is possible to obtain a product with an ash content of 14% at a product yield of 28.31% in a single stage flotation for Twistdraai coal. The expected yield for Twistdraai is expected to be the lowest of all the coal samples.

The yields are those expected when using iso-paraffin as collector (C_{12} -paraffin). The reason for using iso-paraffin is that no recovery could be obtained by using dodecane, which is considered as the standard. Iso-paraffin is used commercially at the coal plants as a collector and from experience is known to result in good flotation performance. Iso-paraffin was not included in the test program initially and therefore was not evaluated as a collector.

5.1 Single stage froth flotation results.

5.1.1 Twistdraai coal

The froth flotation experiments were completed in duplicate under the following conditions:
Air flow: 3ℓ/min
Stirring rate: 1200rpm
Collector dosage: 3ℓ/t
Frother dosage: 20ppm
Flotation time: 5 min.

The average froth flotation results for the 5 coal samples as prepared in section 3.2.2. are shown in Tables 5.1-5.5, with a detailed table of results listed in Appendix A3.

From the results in Table 5.1 it can be observed that the highest yield (average yield of 78.33%) for Twistdraai coal was obtained with iso-decanol as collector, which confirms earlier discussion that the alcohol group on the structure enhances frothing properties in the collector. The ash content obtained at that yield is 14.58% from a feed ash content of 28.8%. The reason iso-decanol resulted in high yield products is due to its isomerised structure. The presence of the OH group in the molecular structure enhances the flotation of the coal as it increases frothing properties in the collector.

The lowest ash content (13.6%) was obtained by using dodecene as collector - this is ascribed to the presence of unsaturated carbon bonds. This confirms earlier findings by Van Heerden (1987) that unsaturated hydrocarbons resulted in higher agglomeration rates than saturated hydrocarbons. The flotation results that were obtained with the cresol substitutes indicate that o-cresol, m-cresol and p-cresol were not selective, as can be seen from the low product yields and the high ash contents.

Table 5.1: Froth flotation results obtained for Twistdraai coal

	Average		Standard deviation	
Reagent	**Yield %**	**Ash %**	**Yield %**	**Ash %**
Aniline	0	0	0	0
O-cresol	9.05	17.09	0.06	0.18
M-Cresol	13.87	17.33	0.99	0.64
P-Cresol	12.34	17.62	0.65	0.14
Oleic acid	35.43	16.07	5.80	0.86
Nitro- benzene	0	0	0	0
Benzene	0	0	0	0
Tetralin	16.47	14.43	0.007	0.10
Toluene	0	0	0	0
Dodecane	0	0	0	0
Dodecene	18.6	13.6	1.57	0.21
Iso-decanol	78.33	14.58	3.14	1.41
N-decane	0	0	0	0
Hexane	0	0	0	0
Hexene	0	0	0	0

The contact angle measurements (Table 4.8) results for dodecene were zero. This may be attributed to the fact that dodecene takes longer to adsorb on the coal surface than the time that was allowed for adsorption (30 sec) during contact angle measurements. However, dodecene did show some selectivity for the Twistdraai coal, although the contact angle was low (45°C –Table 4.9) on the coal-rich fraction. From contact angle measurements, it was expected that both p-cresol and iso-decanol to produce high yield products. However, the low yield and high ash content obtained with p-cresol confirms findings by Swart (1987) that p- cresol act as a conditioner/promoter for the minerals.

5.1.2 Syferfontein seam 5 upper

The flotation results obtained for Syferfontein seam 5 upper (Table 5.2) shows that the highest product yield (34.17% average) is obtained using oleic acid as collector. This is also the reagent that resulted in the lowest ash content (6.42%) for the product.

Table 5.2: Froth flotation results obtained for Syferfontein seam 5 coal

	Average		**Standard deviation**	
Reagent	**Yield %**	**Ash %**	**Yield %**	**Ash %**
Aniline	0	0	0	0
O-cresol	7.30	12.48	3.68	1.65
M-Cresol	11.42	11.71	5.11	1.36
P-Cresol	11.58	11.89	3.73	1.07
Oleic acid	34.17	6.42	5.38	1.17
Nitro- benzene	0	0	0	0
Benzene	0	0	0	0
Tetralin	0	0	0	0
Toluene	0	0	0	0
Dodecane	0	0	0	0
Dodecene	0	0	0	0
Iso-decanol	83.19	6.31	0.97	0.08
N-decane	0	0	0	0
Hexane	0	0	0	0
Hexene	0	0	0	0

The prediction made from contact angle measurements - that oleic acid and iso-decanol would be selective for Syferfontein seam 5 upper coal was confirmed for iso-decanol and oleic acid although a low product yield was obtained with oleic acid 34.17%).

The selectivity of the oleic acid on the coal samples may be due to its unsaturated, and confirms findings by Van der Linde (1980) that unsaturated fatty acid reagents are better collectors than saturated fatty acids. This is due to the pi-electron overlapping that occurs between unsaturated oils and hydrophobic coal surfaces.

5.1.3 Waterberg

From the flotation results (Table 5.3) obtained on Waterberg coal, it can be seen that the highest product yield (85.05%) is obtained when using iso-decanol as collector. The ash content of the product (22.21%) is high, indicating that iso-decanol is not selective for this particular coal. The product with the lowest ash content (12.76%) is obtained with dodecene at a product yield of 17.01%. It can also be observed that the substituted cresol collectors, oleic acid (as was predicted) and tetralin resulted in low yields (10 to 30%) and high ash content (13 to 20%).

Table 5.3: Froth flotation results obtained for Waterberg coal

	Average		**Standard deviation**	
Reagent	**Yield %**	**Ash %**	**Yield %**	**Ash %**
Aniline	0	0	0	0
O-cresol	18.27	19.51	1.06	2.29
M-Cresol	23.35	19.93	2.31	2.11
P-Cresol	23.58	20.13	3.41	1.64
Oleic acid	28.55	17.19	4.02	0.25
Nitro- benzene	0	0	0	0
Benzene	0	0	0	0
Tetralin	11.84	13.6	1.59	0.61
Toluene	0	0	0	0
Dodecane	0	0	0	0
Dodecene	17.01	12.76	1.99	0.502
Iso-decanol	85.05	22.21	2.31	3.96
N-decane	0	0	0	0
Hexane	0	0	0	0
Hexene	0	0	0	0

It was predicted from contact angle measurement results that the substituted cresol reagents would result in high yield selective products. No selectivity was obtained during the actual flotation. This confirms findings by Swart (1987) that cresol products positively condition the mineral fraction.

5.1.4 Witbank seam 2

The flotation results obtained for Witbank seam 2 coal are shown in Table 5.4. The product with the highest yield (87.77%) is obtained using iso-decanol as collector, with a relatively low (below 10 %) ash content of 9.85%. The product with the lowest ash content is obtained with tetralin as collector, but the yield is very low (21.1%). M-cresol and p-cresol resulted in products with a yield of 50% at an ash content of 10.07% and 10.11% respectively. Again, oleic acid resulted in a high product yield of 59.23%, but the ash content of the product (11.88%) indicates that the reagent is not selective.

Table 5.4: Froth flotation results obtained for Witbank seam 2 coal

	Average		**Standard deviation**	
Reagent	**Yield %**	**Ash %**	**Yield %**	**Ash %**
Aniline	0	0	0	0
O-cresol	37.42	10.82	2.72	2.25
M-Cresol	50	10.07	5.20	0
P-Cresol	50	10.11	3.37	0.16
Oleic acid	59.23	11.88	0.88	0.76
Nitro- benzene	0	0	0	0
Benzene	0	0	0	0
Tetralin	21.10	7.5	3.67	0.48
Toluene	0	0	0	0
Dodecane	0	0	0	0
Dodecene	39.87	8.62	6.64	1.30
Iso-decanol	87.77	9.85	2.02	0.27
N-decane	24.60	8.22	1.89	0.02
Hexane	0	0	0	0
Hexene	0	0	0	0

The predictions made from contact angle measurement results concluded that oleic acid and iso-decanol is selective for Witbank seam 2 coal. Tetralin again had a low contact angle for the coal-rich fraction and zero angle on the mineral-rich fraction (Table4.9). In this case, the predictions from contact angle measurements were confirmed.

5.1.5 Witbank seam 4

The flotation results for the Witbank seam 4 coal (Table 5.5) clearly show that iso-decanol results in the highest product yield of 79.07% at an ash content of 23.18%, again confirming the frothing properties of the collector. The lowest ash content that can be obtained is 14.31% at a product yield of 28.85% using p-cresol as collector.

Table 5.5: Froth flotation results obtained for Witbank seam 4 coal

	Average		**Standard deviation**	
Reagent	**Yield %**	**Ash %**	**Yield %**	**Ash %**
Aniline	0	0	0	0
O-cresol	19.2	15.60	0.97	0.77
M-Cresol	29.47	16.16	3.48	0.29
P-Cresol	28.85	14.31	2.82	2.49
Oleic acid	19.86	16.52	2.15	0.89
Nitro- benzene	0	0	0	0
Benzene	0	0	0	0
Tetralin	0	0	0	0
Toluene	0	0	0	0
Dodecane	0	0	0	0
Dodecene	0	0	0	0
Iso-decanol	79.07	23.18	3.04	1.65
N-decane	0	0	0	0
Hexane	0	0	0	0
Hexene	0	0	0	0

Although contact angle measurement results indicated that aniline would result in a flotation product with a good yield due to the large (99°) angle measured on the coal-fraction, zero yield was obtained with aniline. P-cresol had poor selectivity, and resulted in a low ash, low yield product. Iso-decanol resulted in a low contact angle on the carbon-fraction with no angle on the mineral-fraction. The selectivity during flotation is less than would be expected.

For Twistdraai, Syferfontein seam 5 upper and Waterberg coal, o-cresol, p-cresol and m-cresol show an increase in yield and ash content as the substitution moves from ortho to para position. This indicates that the vitrinite rich coals are susceptible to flotation by the aromatic collectors, though they are not selective on these coals.

No flotation product was obtained when using the straight chain paraffin and olefin reagents except for dodecene, which is able to float Twistdraai, Waterberg and Witbank seam 4 coal. The reason why the alkanes did not result in a contact angle is due to the short chain lengths (not enough hydrophobicity). Longer chain paraffin groups are more viable, resulting in contact angles with low rank coal. The benzene derivative reagents also seemed unable to float the coal except for tetralin, which floated Twistdraai, Waterberg and Witbank seam 2 coal.

The aromatic structure of tetralin due to the saturated ring structure attached to the benzene ring, may be the reason why this reagent floated vitrinite rich coals (Twistdraai and Waterberg) higher aromatic structure coal and inertinite rich (Witbank seam 2) less aromatic structure coal.

The fact that the coals do not consist entirely of one maceral may be another reason why some of the reagents floated both inertinite and vitrinite rich coals and why no definite trends between collector type and coal type could be observed.

5.2 Comparison of flotation and release analysis results

The results that were obtained for the flotation tests were plotted against the release analysis curves and are depicted in Figures 5.2.1 to 5.2.5. Iso paraffin (isomerised aliphatic C12 hydrocarbon chain) was used to construct the release curves since dodecane (the recommended reagent) did not result in flotation of the coal samples. The iso-paraffin was not incorporated in the initial test program and therefore has not been evaluated in the rest of the project.

5.2.1 Twistdraai coal

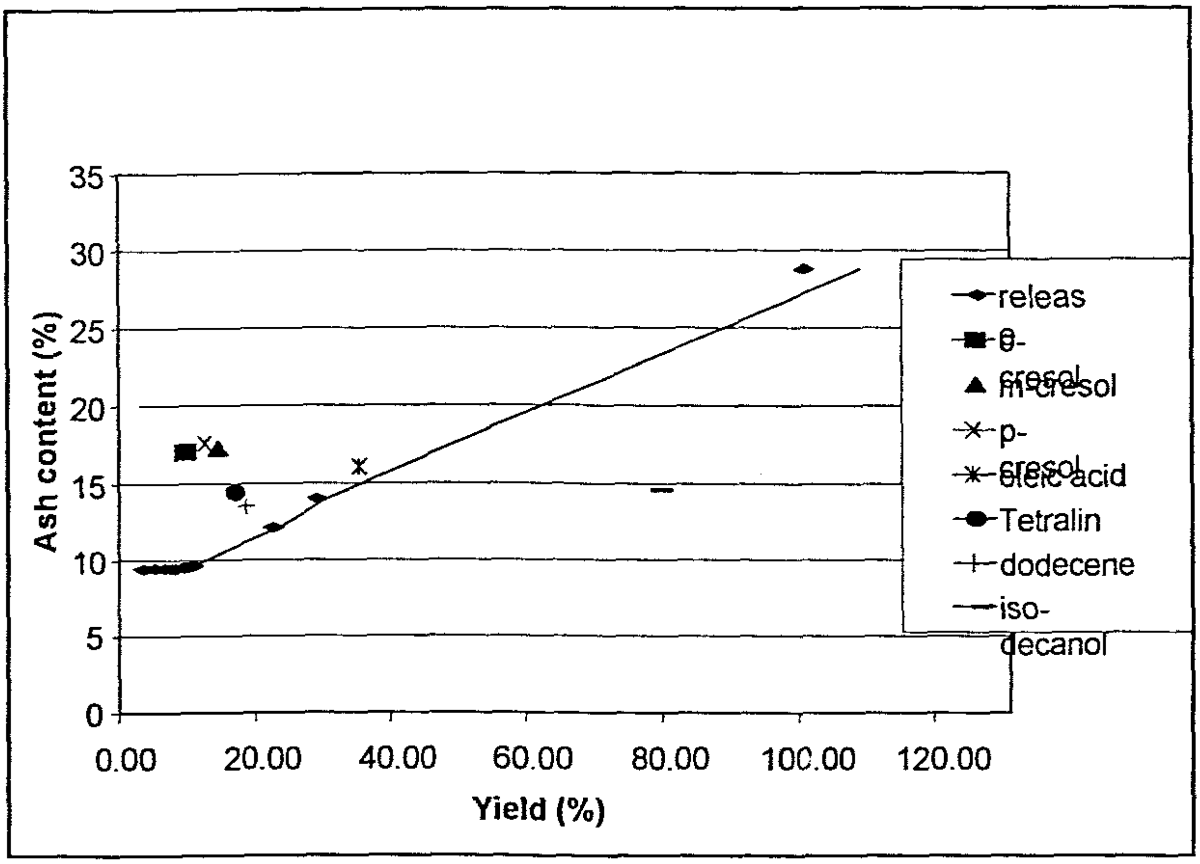


Figure 5.2.1: Comparison of release and flotation data points for Twistdraai coal

From the results in Figure 5.2.1 it can be seen that oleic acid resulted in a product that is closest to the release curve. Iso-decanol, on the other hand seems to be even a better collector for Twistdraai coal than the iso-paraffin that was used for the release curve. Dodecene and tetralin both resulted in data points close to the release curve.

5.2.2 Syferfontein seam 5 upper

The results obtained for the flotation data and release curve is shown in Figure 5.2.2.

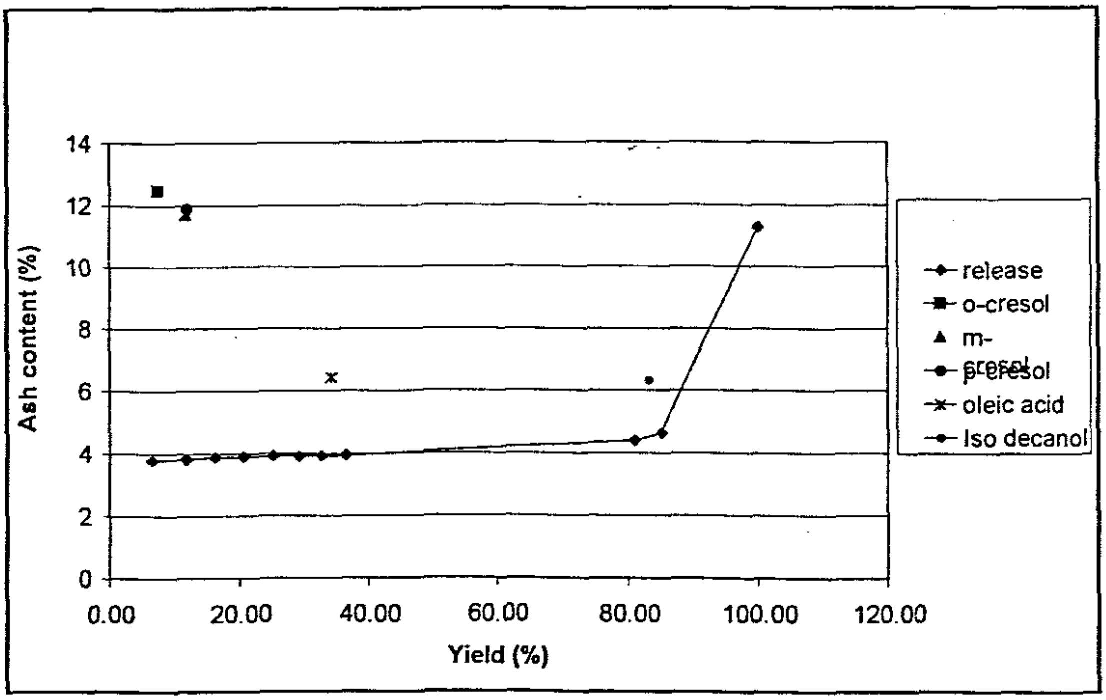


Figure 5.2.2: Comparison of release and flotation data points on Syferfontein seam 5 upper coal

It is clear that not one of the tested reagent data points is near the release curve, which was obtained using iso-paraffin as collector. The use of iso-decanol resulted in a flotation product that is the nearest to the flotation release curve.

5.2.3 Waterberg coal

From the results in Figure 5.2.3 it can be seen that the oleic acid data point is the nearest to the release curve optimum flotation data point (yield of 21.8% and ash content of 12.11%). This is followed by dodecene at a lower yield and ash content (18.6% and 13.6% respectively).

It can also be seen that the iso-decanol collector resulted in a product with a higher yield (85.05%) and higher ash content (22.21%). The data point lies beneath the release curve, and shows that the iso-decanol may be a more viable reagent for Waterberg than even the iso-paraffin that was used to construct the release curve.

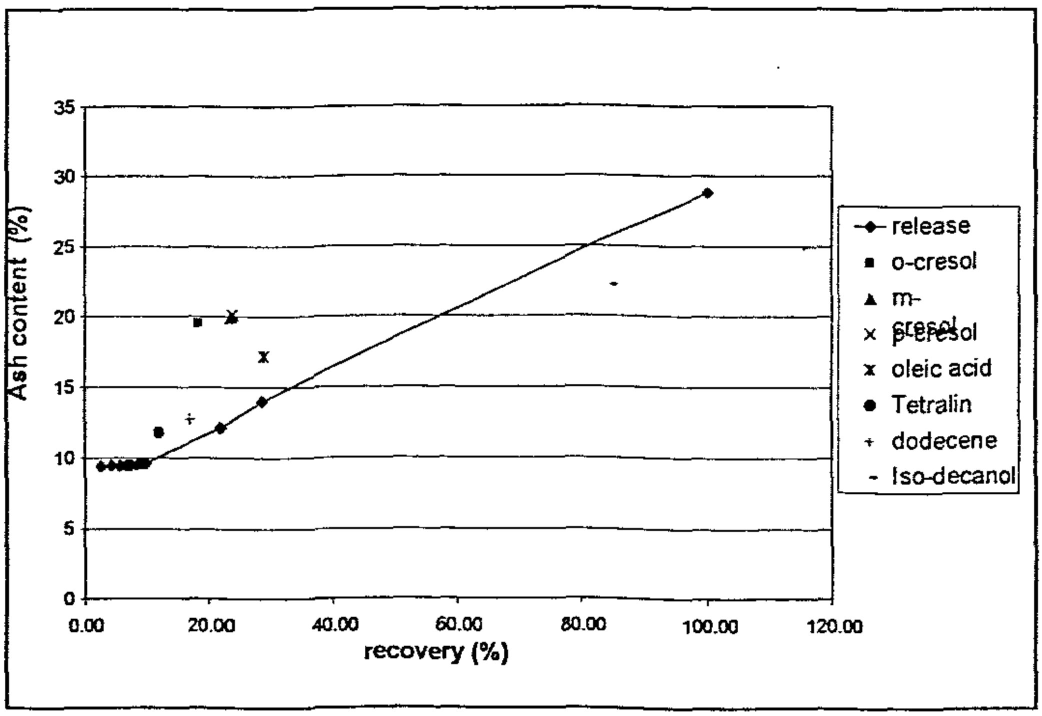


Figure 5.2.3: Release and flotation data on Waterberg coal

5.2.4 Witbank seam 2 coal

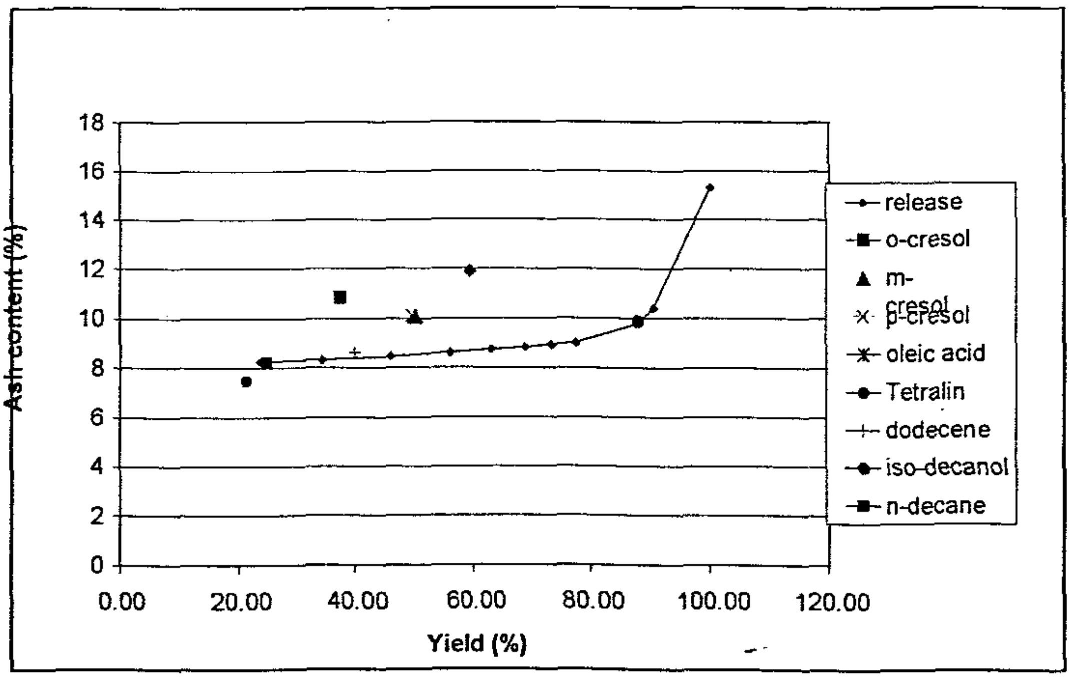


Figure 5.2.4: Comparison of release and flotation data for Witbank seam 2 coal

From the results in Figure 5.2.4 it can be observed that iso-decanol yielded a product similar to the one obtained by the release curve. The other reagents are also near to the curve indicating that the seam 2 coal is easy to float provided that the correct reagents are used.

This is in line with the prediction made from contact angle measurements (see section 4.2.7).

5.2.5 Witbank seam 4 coal

From the results in Figure 5.2.5 it can be seen that the data point obtained with iso-decanol is the closest to the release curve but the product has much higher ash content (23.18%). The rest of the reagents yield products with lower ash contents, but also at much lower product yields.

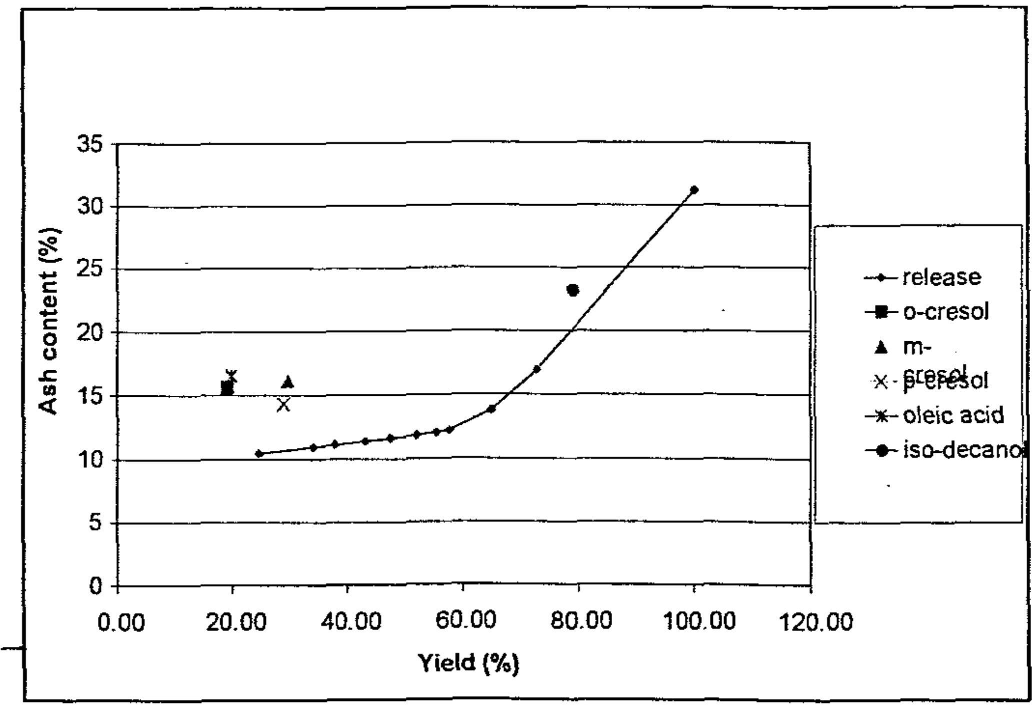


Figure 5.2.5: Comparison of release and flotation data points for Witbank seam 4 coal

In general, it seems as though the contact angle determinations based on selectivity can be linked to the selectivity. It seems like the smaller the angle on the coal-rich fraction, the better the selectivity. This may be attributed to the fact that less powerful reagents will pick up only coal particles during flotation. If a reagent is too powerful (high yield), the possibility of entrainment of minerals increases, as seems to be the case with iso-decanol.

In terms of the surface extraction values, there is no correlation with the flotation recovery or ash content of the float products. The absorption values that were obtained showed that Waterberg coal should be the easiest to float, needing the least reagents. This, however, did not seem to be the case. Witbank seam 2 coal was the easiest to float at an absorbency of 0.388. Syferfontein seam 5 was the most difficult to float, but had an absorbency value (0.182) larger than that of Twistdraai (0.162). The absorption technique was developed for Northern hemisphere coal and before it can be applied successfully to Southern hemisphere coal.

In summary, iso-decanol and dodecene produced flotation products that are near to the release curve, which represents the optimum flotation results obtained when using iso-paraffin as collector. Laskowski (1998) found that branched hydrocarbon chains are good frothers as can be seen from the use of iso-decanol with its frothing properties. Dodecene resulted in low ash products and iso-decanol in high yield products. The flotation data that was obtained with the release analysis for Waterberg coal showed that iso-paraffin should also be considered as a collector for this coal type.

The statistical significance of the data will be discussed in Chapter 6.

Chapter 6

Statistical Analysis of flotation data

Results and discussion

The information presented in the previous two chapters was evaluated statistically to confirm and provide statistical significance of the data. The fitting of the data is done in two section: firstly, to fit the coal characterisation results to the flotation yield and ash content; and secondly, to fit the characteristics of the reagents (and contact angle measurements) to the yield and ash content obtained by froth flotation.

Unfortunately no model could be fitted to the characteristics of the coal since the coal has only one value for a specific characteristic, eg. carbon content. The same observation was experienced with the individual characteristics of the reagents. Two linear fits were obtained to confirm the expected yield and ash content for the coal samples, and these will be discussed in the following sections.

It should be stressed that the use of the statistics is primarily to back up the experimental findings.

6.1 Fitting of coal data to yield response

The sum of the r^2 is used to determine the fitting of the data to a linear relationship. The results in Table 6.1 show that the r^2 is 0.9289, which indicates that 92,89% of the data (% flotation yield) fits a linear relationship.

The p-value has to be less than 0.05 for the data to be statistically significant. As can be seen from the results, the p-value is less than 0.0001 in all cases. A graph plotting the significance of the yield data against the type of coal is shown in Figure 6.1.

Table 6.1: Analysis of variance table (Response: Yield)

	Sum of		Mean	F	P
Source	**Squares**	**DF**	**Square**	**Value**	**Value**
Model	30477.14	11	2770.65	59.39	< 0.0001
Coal Type	5472.47	4	1368.12	29.33	< 0.0001
Reagent	24743.05	7	3534.72	75.77	< 0.0001
Residual	2332.41	50	46.65		
Lack of Fit	2023.14	19	106.48	10.67	< 0.0001
Pure Error	309.26	31	9.98		
Cor Total	32809.55	61			
R^2	0.9289				
Adj R^2	0.9133				

From the results in Figure 6.1, it can be seen that iso-decanol produced the highest yield on Witbank seam 2 coal. The reason for evaluating iso-decanol is that iso-decanol resulted in a data point for all the coal samples during flotation.

The results obtained from a one-plot graph of yield versus reagent for Witbank seam 2 coal is shown in Figure 6.2. It can be seen that iso-decanol produced a significantly higher yield than the other reagents. The reason is that no overlapping occurs between the data points obtained for iso-decanol and the other reagents. The significance is determined by the overlap of the Φ, which is the average of two duplicate values.

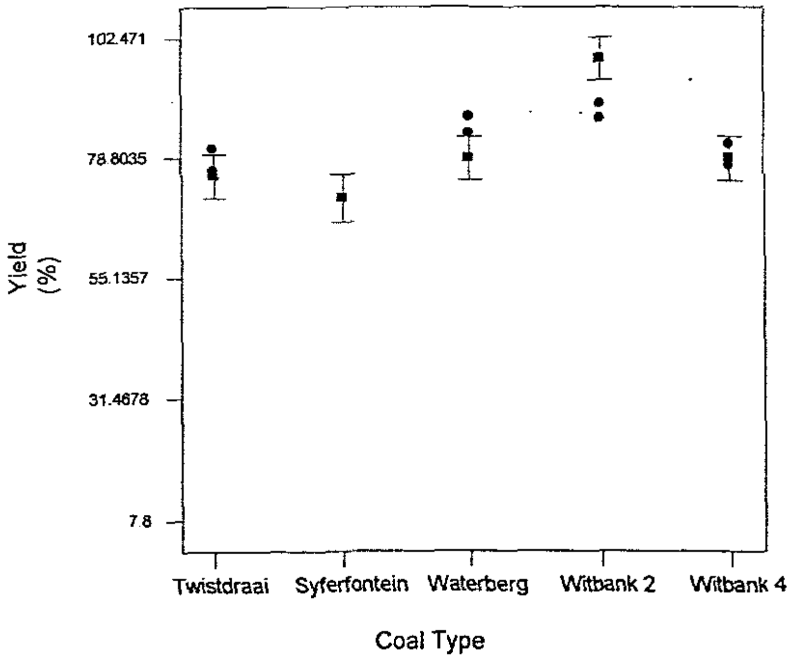


Figure 6.1: Significance of yield on coal type

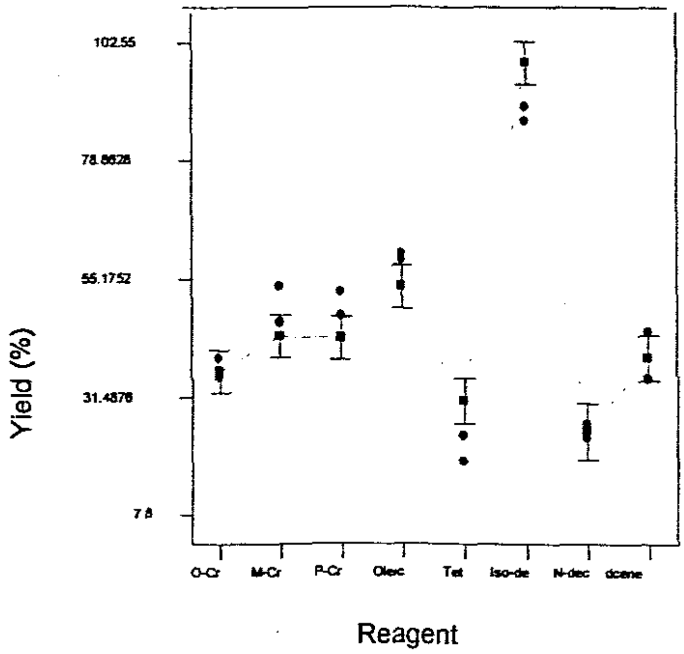


Figure 6.2: Significance of yield on reagent type

O-Cr: O-Cresol
M-Cr: M-Cresol
P-Cr: P-Cresol
Oleic: Oleic acid
Tet: Tetralin
Iso-de: Iso-decanol
N-dec: N-decane
D cene: Dodecene

6.2 Linear relationship for relating yield

The model that was derived from the statistical evaluation is as follows:

$$\text{Yield} = 28.25 - 5.05\,(A1) - 9.51\,(A2) - 1.68\,(A3) + 18\,(A4) - 9.48\,(B1) - 2.62(B2) - 2.98(B3) + 7.20(B4) - 15.54(B5) + 51.93(B6) - 21.65(B7)$$

6.3 Numeric values for coded factors

The numeric values for the coded factors are given in Table 6.2.

Table 6.2: Numeric values for coal and reagents

Twistdraai	1	0	0	0		
Syferfontein seam 5 upper	0	1	0	0		
Waterberg	0	0	1	0		
Witbank seam 2	0	0	0	1		
Witbank seam 4	-1	-1	-1	-1		
O-cresol	1	0	0	0	0	0
M-cresol	0	1	0	0	0	0
P-cresol	0	0	1	0	0	0
Oleic acid	0	0	0	1	0	0
Tetralin	0	0	0	0	1	0
Iso-decanol	0	0	0	0	0	1
N-decane	-1	-1	-1	-1	-1	-1

The numeric values for the coal and reagents (coded factors) are substituted into the linear equation (section 6.2) to determine the expected yield for a certain coal and reagent.

6.4 Fitting of coal data to ash content response

The ash content data points obtained for the flotation test work were evaluated against the coal type and type of reagent. The results are shown in Table 6.3

Table 6.3 Analysis of variance table

	Sum of		Mean	F	P
Source	**Squares**	**DF**	**Square**	**Value**	**Value**
Model	907.06	11	82.46	16.51	< 0.0001
Coal Type	651.65	4	162.91	32.61	< 0.0001
Reagent	171.73	7	24.53	4.91	0.0003
Residual	249.77	50	5.00		
Lack of Fit	195.00	19	10.26	5.81	< 0.0001
Pure Error	54.76	31	1.77		
Cor Total	1156.82	61			
R^2	0.7841				

It is observed that there is a definite relationship and that the R^2 value is good (0.78). The p-values are also below 0.05, which indicates that 95% of the data points fit to the proposed linear relationship.

The one-factor plot for the ash response in terms of the coal type is depicted in figure 6.3

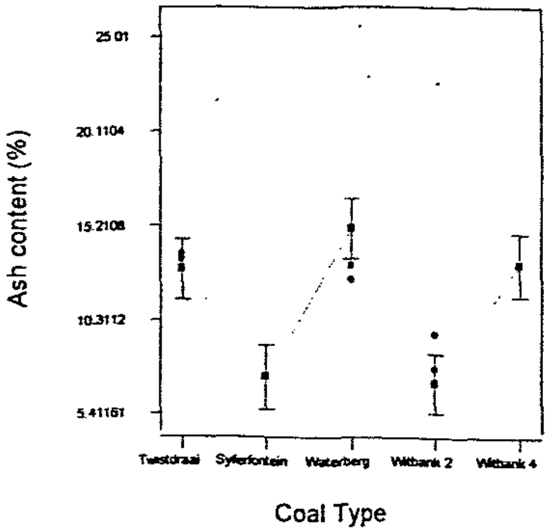


Figure 6.3: Significance of ash content on coal type

From the plot, it can be seen that there are significant differences in ash content between the different coal samples.

A plot of the ash content against the reagents (Figure 6.4) again showed that iso-decanol is the most significant collector, but there is some overlapping with the other reagents.

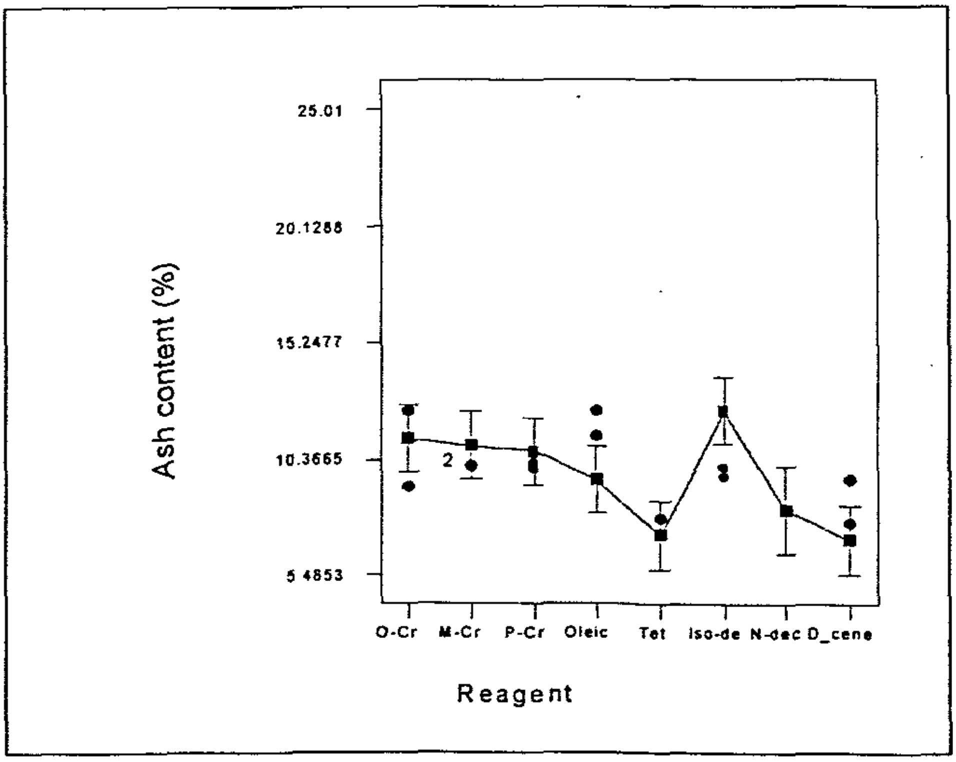


Figure 6.4: Significance of ash content on reagent type

6.4.1 Equation relating ash content

The relationship that fits the coal type and reagent type in terms of the ash content is as follows:

Ash content (%) = 13.75 + 1.86(A1) – 3.79(A2) + 3.95(A3) – 4.12(A4) + 1.58(B1) + 1.29(B2) + 1.06(B3) – 0.14(B4) – 2.47(B5) + 2.76(B6) – 1.42(B7)

6.5 Testing the validity of the linear relationships

Witbank seam 2 and m-cresol are used to test the validity of the model. The actual yield and ash content that was obtained is 50%, with 10.07% ash content.

Yield = 28.25 – 5.05(0) – 9.51(0) – 1.68(0) + 18(1) – 9.48(0) – 2.62(1) -2.98(0) + 7.20(0) – 15.54(0) + 51.93(0) – 21(0)
=43.6%

And for the ash content:

Ash content = 13.75 + 1.86(0) – 3.79(0) + 3.95(0) – 4.12(1) + 1.58(0) + 1.29(1) + 1.06(0) – 0.14(0) – 2.47(0) + 2.76(0) – 1.42(0)
= 10.9%

As can be seen, the results fit both the ash and yield relationships that are proposed.

It is not unusual to use coded factors for non-numerical entities. However, it is necessary to have a proper understanding of the use of coded factors within a relationship as used above before applying it.

Chapter 7

Conclusions and recommendations

The aim of this thesis was to develop a methodology to predict the performance of collectors for coal flotation that can be applied to the different coal types in South Africa. The prediction has to be statistically significant as to what kind of reagent will be suitable for a certain coal type. Since characterisation of a coal sample is very time-consuming; the aim of this project is also to conclude which parameter has the largest effect on coal flotation. It may be possible to measure only one or two influences to make a decision as to which reagent will be suitable for a specific coal.

7.1 Conclusions

From the coal characterisation data that was obtained, it can be concluded that the ash or mineral matter is distributed in the <45-µm fraction. The milled coal samples were well liberated, and this was evident from the release curves that obtained ash contents of 10% and less, and was confirmed by the float / sink analysis.

The petrographic results that were obtained for Witbank seam 2 indicated that the coal was mostly inertinite rich and resulted in the best flotation performance - as was predicted. The best yield and ash content that were obtained for Witbank seam 2 coal are 87.77% yield and 9.85% ash using iso-decanol as recommended collector at a collector dosage of 3 ℓ/t, and a frother dosage of 20 ppm using MIBC (methyl-iso-butyl-carbinol). The frothing properties of iso-decanol contribute to higher flotation yield.

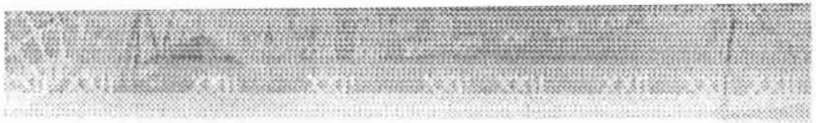
The petrographic analysis showed that the Syferfontein seam 5 coal is high in vitrinite content, but the flotation results obtained with the Syferfontein coal were lower than was expected. Iso-decanol proved to be the best collector for this coal. A product yield of 83.15% is obtained at an ash content of 6.31%. Twistdraai coal produced the best yield of 78.33% at a product ash of 14.58% when using iso-decanol as collector, and is also a vitrinite rich coal. Waterberg coal is also vitrinite rich, and iso-decanol produced the best product yield although dodecene was more selective as the collector.

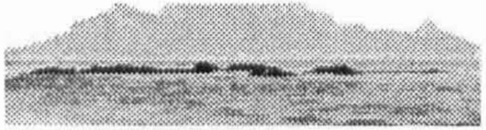
The results that were obtained for Witbank seam 4 coal indicate that the coal has a lower inertinite content than seam 2 coal and is only slightly more vitrinite rich. The ash content of the feed is considerably higher than for the seam 2 coal, and this may be the reason why the seam 4 flotation results were not as good. The findings by Bujnowska (1985) are confirmed in the sense that the inertinite rich coals float better than the vitrinite rich coals.

The fixed carbon content (highest for Witbank seam 2 coal) confirms the prediction that this coal will have the best flotation performance. This was also confirmed by the statistical results.

It was predicted from the surface functional group content analysis that Witbank seam 2 would be the easiest coal to float, due to the low carboxylic acid content. Witbank seam 4, on the other hand, has the highest carboxylic acid content and was therefore predicted to be the most difficult to float. It was seen from the flotation data that Syferfontein seam 5 upper coal was the most difficult to float, but indeed Syferfontein seam 2 was the easier coal to float.

Waterberg and Twistdraai coals were also high-vitrinite coals samples, and the flotation results obtained from these samples were also less promising than for Witbank seam 2 coal. Waterberg, Twistdraai and Witbank seam 4 coals were also low in fixed carbon content.





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Determination of the oxygen-containing functional groups showed that the Witbank seam 4 coal has the highest amount of total functional groups, which explains the poor flotation performance obtained for this coal.

The surface extraction results seem to be the highest for the Inertinite rich coals like Witbank seam 2 and seam 4. The extraction analyses do not show any trends in correlation with flotation data.

The contact angle measurements on the demineralised coal samples showed that aniline absorbed (180 °) on the surface of all the coal types studied but did not promote flotation. The reason for this is unknown. The cresol substitutes absorbed on all the coal fractions and resulted in flotation for all the coal types, which makes this reagent coal independent. The oleic acid floated all the coals, with the best result being obtained with Witbank seam 2 coal. The highest contact angle was obtained with Witbank seam 4 coal using oleic acid. In conclusion, it is evident that the contact angle values that were obtained do not show any correlation with the flotation data. However, if no contact angle could be measured, flotation will not occur.

Contact angle measurements on density separated coal showed that where no contact angle could be obtained on the mineral-rich fraction, the smaller the contact angle on the carbon-rich fraction the greater the selectivity. When the angle is above 100°C on the coal-rich fraction, the reagent is too powerful. This was particularly observed for iso-decanol as collector. The predicted flotation trend for oleic acid was achieved, and it seems that reagents with a contact angle of about 90° on the carbon rich fraction (with no angle on the mineral rich fraction) resulted in good yield and selective flotation performance.

The flotation data showed that all of the coal samples were amendable to froth flotation. The best results were obtained with the Witbank seam 2 coal, and the poorest flotation with Syferfontein seam 5 coal. Iso-decanol was found to be the best collector overall, which may be due to the frothing properties that are associated with it. The prediction that iso-decanol will result in selective flotation was found to be true.

The statistically confirmation of the flotation data provided a handy equation that could be used as a tool to predict yield and ash content for a specific coal, provided that it falls within the range applied to develop this empirical equation. The equation can be used to predict the yield and ash content that can be expected for a certain type of reagent, provided the reagents and coal are incorporated into the model. This may result in additional flotation test work to include additional reagents. The "model" equation may be used at the mine to vary between reagents as the coal requirements of the mine changes.

The parameters that showed correlation trends with the flotation data included carboxylic acid oxygen functional groups, contact angle measurements on density-separated coal, and release analysis. The order in which theseanalyses should be performed is not important.

7.2 Recommendations

Release analysis and oxygen-containing functional groups can be used for predictingthe performance of reagents for coal flotation.

Contact angle seems to be a good indication of the floatability on a coal sample, and can be used as a screening method, but it is recommended that flotation performance tests are conducted to validate these findings. In cases where the contact angles on the carbon fraction is 90°, but no contact angle can be obtained on the mineral fraction, are inconclusive and further work in this area is recommended.

Separating coal into samples containing different macerals could provide more information regarding the effects of different reagents on various coal types. The lack of a clear link between flotation performance, reagent, and coal type may be a result of the presence of a number of different macerals in each individual sample.

The effect of iso-paraffin as collector needs further investigation, since it seems from release analysis that this reagent resulted in the best flotation performance for most of the coal samples

It is also recommended that the selected reagent for flotation be used as collector for the release analysis and that the results be compared with those obtained using the standard dodecane collector.

The chemistry behind the interfacial chemistry needs further investigation, as iso-decanol (commercially used as third phase inhibitor during solvent extraction) can be used to float almost any coal, although its selectivity is not good. The interaction of mixed reagents also needs further investigation e.g. iso-decanol and dodecene to improve selectivity.

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Appendix A

Appendix A1:	Float - sink results
Appendix A2:	Detailed float release analysis
Appendix A3	Duplicate flotation results

Table A 1: Float and sink analysis for five different coal samples

Twistdraai						
Density (g/cm^3)	Mass (float) g	Mass (sink) g	Yield Float %	Ash Float %	Yield Float %	Ash Sink %
1.3	0.05	9.9	0.50	2.7	99.50	29.38
1.4	1.74	7.92	18.01	4.76	81.99	35.1
1.5	3.14	5.88	34.81	8.25	65.19	41.96
1.6	5.61	4.49	55.54	12	44.46	53.34
1.7	6.22	3.67	62.89	13.96	37.11	60.86
1.8	6.85	2.01	77.31	17.76	22.69	67.7
Syferfontein seam 5 upper						
1.3	0.03	9.9	0.30	2.9	99.70	13.28
1.4	7.76	2.15	78.30	4.57	21.70	43.34
1.5	16.74	2.29	87.97	7.12	12.03	56.8
1.6	8.1	0.2	97.59	10.78	2.41	64.7
1.7	9.75	0.19	98.09	11.73	1.91	70.4
1.8	9.72	0.12	98.78	12.83	1.22	72.8
Waterberg						
1.3	0.05	9.00	0.55	3.74	99.45	29.78
1.4	1.78	7.53	19.12	7.21	80.88	35.12
1.5	3.83	5.00	43.37	13.4	56.63	42.02
1.6	7.50	2.19	77.40	19.2	22.60	56.62
1.7	8.14	1.51	84.35	21.23	15.65	62.06
1.8	7.50	1.14	86.81	23.44	13.19	65.65
Witbank seam 2						
1.3	0.02	9.8	0.20	3.4	99.80	17.34
1.4	1.76	7.53	18.95	5.51	81.05	19.43
1.5	6.95	2.06	77.14	8.81	22.86	33.39
1.6	8.89	1.88	82.54	10.22	17.46	48.43
1.7	7.47	0.72	91.21	12.78	8.79	48.91
1.8	9.41	0.46	95.34	13.33	4.66	62.8
Witbank seam 4						
1.3	0	19.21	0.00	0	100.00	34.1
1.4	1.84	18.11	9.22	6.66	90.78	34.65
1.5	3.42	16.25	17.39	10.65	82.61	38.12
1.6	9.42	10.16	48.11	19.36	51.89	44.09
1.7	15.51	4.97	75.73	25.47	24.27	54.75
1.8	16.68	3.36	83.23	26.36	16.77	62.85

Table A2.1: Flotation release analysis results for Twistdraai coal

Sample	Yield(g)	Yield (%) Y	Ash(%) A	Y*A	Cum Yield (%)	Cum Ash (%)
C1	3.63	2.64	9.42	24.82	2.64	9.42
C2	2.2	1.60	9.55	15.25	4.23	9.47
C3	1.93	1.40	9.34	13.09	5.63	9.44
C4	1.37	0.99	9.65	9.60	6.63	9.47
C5	0.92	0.67	9.52	6.36	7.30	9.47
C6	1.46	1.06	9.79	10.38	8.36	9.51
C7	1.02	0.74	9.99	7.40	9.10	9.55
C8	0.95	0.69	10.41	7.18	9.79	9.61
Re-cl-tls	16.55	12.01	14.15	169.99	21.80	12.11
Cl-tls	8.97	6.51	20.32	132.31	28.31	14.00
R-tls	98.76	71.69	34.64	2483.63	100.00	28.80
Total	137.76					

Table A2.2: Flotation release analysis results for Syferfontein seam 5 upper coal

Sample	Yield(g)	Yield (%)	Ash (%)	Y*A	Cum Yield (%)	Cum Ash (%)
C1	8.84	6.38	3.78	24.11	6.38	3.78
C2	7.12	5.14	3.87	19.88	11.52	3.82
C3	6.29	4.54	3.97	18.02	16.06	3.86
C4	6.05	4.37	3.97	17.33	20.42	3.89
C5	6.3	4.55	3.98	18.09	24.97	3.90
C6	5.58	4.03	3.87	15.58	29.00	3.90
C7	4.91	3.54	4.01	14.21	32.54	3.91
C8	5.33	3.85	4.02	15.46	36.39	3.92
Re-cl-tls	61.66	44.50	4.76	211.81	80.88	4.38
Cl-tls	5.85	4.22	9.12	38.50	85.11	4.62
R-tls	20.64	14.89	49.3	734.32	100.00	11.27
Total	138.57					

Table A2.3: Flotation release analysis results for Waterberg coal

Sample	Yield(g)	Yield (%) Y	Ash (%) A	Y*A	Cum Yield (%)	Cum Ash (%)
C1	14.09	10.02	20.87	209.06	10.02	20.87
C2	7.75	5.51	21.9	120.66	15.53	21.24
C3	6.74	4.79	22.32	106.95	20.32	21.49
C4	5.36	3.81	22.45	85.55	24.13	21.64
C5	5.04	3.58	23.54	84.35	27.71	21.89
C6	5.32	3.78	24.9	94.18	31.49	22.25
C7	3.5	2.49	23.49	58.45	33.98	22.34
C8	4.09	2.91	23.49	68.30	36.89	22.43
Re-cl-tls	48.21	34.27	24.91	853.77	71.16	23.62
Cl-tls	16.78	11.93	41.4	493.88	83.09	26.18
R-tls	23.78	16.91	53.1	897.71	100.00	30.73
Total	140.66					

Table A 2.4: Flotation release analysis results for Witbank seam 2 coal

Sample	Yield(g)	Yield (%) Y	Ash (%) A	Y*A	Cum Yield	Cum Ash
C1	33.01	23.43	8.25	193.29	23.43	8.25
C2	15.24	10.82	8.5	91.94	34.25	8.33
C3	16.33	11.59	8.93	103.50	45.84	8.48
C4	13.85	9.83	9.27	91.13	55.67	8.62
C5	10.17	7.22	9.59	69.22	62.89	8.73
C6	8.48	6.02	9.79	58.92	68.90	8.82
C7	6.17	4.38	10.37	45.41	73.28	8.92
C8	5.77	4.10	10.32	42.26	77.38	8.99
Re-cl-tls	14.55	10.33	15.6	161.10	87.71	9.77
Cl-tls	3.71	2.63	31.16	82.05	90.34	10.39
R-tls	13.61	9.66	61.18	591.00	100.00	15.30
Total	140.89					

Table A 2.5: Flotation release analysis results for Witbank seam 4 coal

Sample	Yield(g)	Yield (%) Y	Ash (%) A	Y*A	Cum Yield	Cum Ash
C1	34.5	24.52	10.48	256.954	24.52	10.48
C2	13.09	9.30	12.23	113.7735	33.82	10.96
C3	5.32	3.78	12.66	47.86525	37.60	11.13
C4	7.57	5.38	13.22	71.12174	42.98	11.39
C5	6.12	4.35	13.72	59.67337	47.33	11.61
C6	6.26	4.45	14.17	63.04044	51.78	11.83
C7	4.89	3.48	15.08	52.40651	55.26	12.03
C8	3.24	2.30	16.16	37.21015	57.56	12.20
Re-cl-tls	10.55	7.50	26.04	195.2399	65.06	13.79
Cl-tls	11.06	7.86	42.87	336.9641	72.92	16.93
R-tls	38.11	27.08	69.59	1884.781	100.00	31.19
Total	140.71					

Table A3: Froth flotation results obtained for 5 different coal samples

		Flotation in duplicate				Average	
Coal type	Reagent	Yield %	Ash %	Yield %	Ash %	Yield %	Ash %
Twistdraai	Aniline	0	0	0	0	0	0
	O-cresol	9.09	17.21	9.01	16.96	9.05	17.09
	M-Cresol	13.16	17.78	14.57	16.87	13.87	17.33
	P-Cresol	11.87	17.72	12.8	17.52	12.34	17.62
	Oleic acid	39.53	16.67	31.32	15.46	35.43	16.07
	Nitro- benzene	0	0	0	0	0	0
	Benzene	0	0	0	0	0	0
	Tetralin	16.46	14.5	16.47	14.35	16.47	14.43
	Toluene	0	0	0	0	0	0
	Dodecane	0	0	0	0	0	0
	Dodecene	19.67	13.71	17.45	13.42	18.6	13.6
	Iso-decanol	76.11	15.58	80.55	13.58	78.33	14.58
	N-decane	0	0	0	0	0	0
	Hexane	0	0	0	0	0	0
	Hexene	0	0	0	0	0	0
Syferfontein 5 Upper	Aniline	0	0	0	0	0	0
	O-cresol	9.9	13.64	4.69	11.31	7.30	12.48
	M-Cresol	15.04	12.7	7.8	10.71	11.42	11.71
	P-Cresol	14.21	12.64	8.94	11.13	11.58	11.89
	Oleic acid	37.97	7.24	30.36	5.59	34.17	6.42
	Nitro- benzene	0	0	0	0	0	0
	Benzene	0	0	0	0	0	0
	Tetralin	0	0	0	0	0	0
	Toluene	0	0	0	0	0	0
	Dodecane	0	0	0	0	0	0
	Dodecene	0	0	0	0	0	0
	Iso-decanol	83.87	6.36	82.50	6.25	83.19	6.31
	N-decane	0	0	0	0	0	0
	Hexane	0	0	0	0	0	0
	Hexene	0	0	0	0	0	0

Table A3: Froth flotation results obtained for 5 different coal samples

Coal type	Reagent	Flotation in duplicate				Average	
		Yield-1 %	Ash 1- %	Yield-2%	Ash-2%	Yield %	Ash %
Waterberg	Aniline	0	0	0	0	0	0
	O-cresol	17.52	21.13	19.02	17.88	18.27	19.51
	M-Cresol	21.71	21.45	24.99	18.41	23.35	19.93
	P-Cresol	21.17	21.29	25.99	18.97	23.58	20.13
	Oleic acid	25.7	17.01	31.39	17.37	28.55	17.19
	Nitro-benzene	0	0	0	0	0	0
	Benzene	0	0	0	0	0	0
	Tetralin	10.71	14.03	12.96	13.17	11.84	13.6
	Toluene	0	0	0	0	0	0
	Dodecane	0	0	0	0	0	0
	Dodecene	15.6	13.11	18.42	12.4	17.01	12.76
	Iso-decanol	86.68	25.01	83.42	19.41	85.05	22.21
	N-decane	0	0	0	0	0	0
	Hexane	0	0	0	0	0	0
	Hexene	0	0	0	0	0	0
Witbank seam 2	Aniline	0	0	0	0	0	0
	O-cresol	39.34	9.23	35.5	12.41	37.42	10.82
	M-Cresol	46.32	10.07	53.68	10.07	50	10.07
	P-Cresol	47.62	9.99	52.38	10.22	50	10.11
	Oleic acid	59.85	11.34	58.6	12.41	59.23	11.88
	Nitro-benzene	0	0	0	0	0	0
	Benzene	0	0	0	0	0	0
	Tetralin	18.5	7.16	23.69	7.84	21.10	7.5
	Toluene	0	0	0	0	0	0
	Dodecane	0	0	0	0	0	0
	Dodecene	44.56	7.7	35.17	9.54	39.87	8.62
	Iso-decanol	89.2	9.66	86.34	10.04	87.77	9.85
	N-decane	25.93	8.23	23.26	8.2	24.60	8.22
	Hexane	0	0	0	0	0	0
	Hexene	0	0	0	0	0	0

Table A3: Froth flotation results obtained for 5 different coal samples

Coal type	Reagent	Flotation in duplicate				Average	
		Yield-1 %	Ash 1-%	Yield-2%	Ash-2%	Yield %	Ash %
Witbank	Aniline	0	0	0	0	0	0
seam 4	O-cresol	18.52	16.14	19.88	15.05	19.2	15.60
	M-Cresol	27.01	16.36	31.93	15.95	29.47	16.16
	P-Cresol	26.85	16.07	30.84	12.54	28.85	14.31
	Oleic acid	21.38	17.15	18.34	15.89	19.86	16.52
	Nitro-benzene	0	0	0	0	0	0
	Benzene	0	0	0	0	0	0
	Tetralin	0	0	0	0	0	0
	Toluene	0	0	0	0	0	0
	Dodecane	0	0	0	0	0	0
	Dodecene	0	0	0	0	0	0
	Iso-decanol	81.22	22.01	76.92	24.34	79.07	23.18
	N-decane	0	0	0	0	0	0
	Hexane	0	0	0	0	0	0
	Hexene	0	0	0	0	0	0

Appendix B

Calculations

B1 Ash content

Ash content (%) = $((C - A)/ (B - A)) \times 100$

Where A = Mass of empty crucible
B = Mass of crucible with coal
C = Mass of crucible with ash
Accurately weighed on a 4 decimal balance

B2 Oxygen containing functional groups

B2.1 Carboxylic acid content

% O as COOH =

$$(0.64 \times V) / ((m - (m ((Ash + 0.5)/100))))$$

Where V = Volume titrated
M = Mass of coal
Ash = Ash content of coal after acid treatment.

B2.2 Total acid group content

% O as total acid groups =

$$(1.6 \times V)/ m - (m ((Ash + 0.5)/100))) - \%\ O \text{ as } COOH$$

Where V = Volume titrated
M = Mass of coal
Ash = Ash content of coal after acid treatment.

B2.3 Phenolic group content

% O as OH =

$$((V \times 0.032)/(((m-0.00083) / 1) * (V (m ((Ash + 0.5) / 100)))))$$

Where V = Volume titrated
M = Mass of coal
Ash = Ash content of coal after acid treatment.