

1.A

THE ROLE OF HYDROCARBON OILS IN COAL FLOTATION :
AN INVESTIGATION INTO SOME PULP PHASE SUB-PROCESSES

By :

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ABSTRACT

Oil dispersion, oil adsorption (including selectivity), and the influence of oil on bubble creation and attachment were studied, in an attempt to explain observed differences in flotation behaviour with -500 μm unbeneficiated bituminous coal. Collectors were synthesis grade and commercial stocks of aromatic and aliphatic oils; MIBC was the frother.

Oil dispersions were analyzed using a Coulter Counter. All the oils were sufficiently dispersed for effective flotation, with aromatic oils being better dispersed. MIBC usually hindered oil dispersion.

The kinetics and extent of oil adsorption onto solids were monitored with a specially developed technique. Aromatic oils adsorbed extensively (90 %) on the coal but aliphatic oils adsorbed far less. Nevertheless this was sufficient to render coal particles floatable. All the oils were highly selective. MIBC did not promote oil adsorption.

Bubbles were electronically scaled and counted. Aromatic oils reduced bubble size markedly. Their spontaneous spreading at the air-water interface is associated with a net lowering of interfacial tensions. Aliphatic oils do not spread and consequently had little influence on bubble size. Bubble size is an important contributory factor to froth stability and oils which reduce sizes are better collectors. MIBC reduced bubble size (as expected): in combination with one commercial oil, sizes were reduced below those induced in the presence of either reagent in isolation.

Coal recovery was largely dependent on froth stability since oil dispersion and adsorption was adequate. The mode of conditioning was important at low reagent dosages; as was the mode of reagent addition. Oils should be predispersed prior to addition to the pulp to facilitate their distribution. MIBC, which is preferentially oil-soluble should be added to the pulp separately and as late as possible to ensure maximum frothing activity.

In the absence of extraneous surfactants, the pulp-phase behaviour of MIBC and oil is well understood and was invariably able to explain the observed flotation performance satisfactorily. Interfacial theory, which was reviewed in some detail, is currently inadequate for predictive purposes and empirical tests will remain necessary for the foreseeable future.

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CERTIFICATION BY SUPERVISOR

During the course of this study, the following paper has been published:

Franzidis, J-P. and Anderson, G.V.M., "A technique to study the adsorption of oily collectors onto coal and gangue minerals", *Adsorption Science and Technology*, 3, 1986, pp. 303-316.

In terms of Paragraph GP 8 of "General Rules for the Degree of Ph.D.", I, Dr. J-P. Franzidis, as supervisor of the candidate, G.V.M. Anderson, certify that I approve of the incorporation in this thesis of material that has been published.

.....

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NOMENCLATURE

(S.I. Units have been used)

a	=	Contact area
A	=	Surface area
c	=	Surfactant concentration
d	=	Diameter of contact area
D	=	Diffusion coefficient
F_s	=	Spreading coefficient
g	=	Gravitational constant
G	=	Gibbs free energy
G^s	=	Specific Gibbs surface free energy
h	=	Disjoining film thickness
k	=	Boltzmann constant
k_1, k_2	=	Rate constants
M	=	Mass of collector oil in the pulp water at time t
M_0	=	Mass of collector oil in the pulp water at time zero
M_e	=	Equilibrium mass of collector oil in the pulp
δ, δ_e	=	Normalized oil (collector) mass = M/M_0 or M/M_e
n	=	Number of droplets at time t
n_0	=	Number of droplets at time zero
N_i	=	Moles of reactant (adsorbate) i
P_o	=	Internal oil droplet (or bubble) pressure
P_e	=	Excess pressure within an oil droplet (or air bubble)
P_w	=	Pulp (water) pressure
R	=	Collision radius
R	=	Gas constant
r	=	Radius
r_i	=	Rate of disappearance of oil
S_f	=	Spreading force in a circular capillary
S	=	Solid surface area

T	=	Absolute temperature
t	=	Time
v	=	Velocity
V	=	Volume
W	=	Energy barrier to droplet-droplet coalescence/coagulation
α	=	Angle between phases in contact
$\gamma_i; \gamma$	=	Interfacial tension; Surface tension
γ_o, γ_{oa}	=	Oil surface tension
γ_s, γ_{sa}	=	Solid "surface tension"
γ_{sfa}	=	Surface tension of the solid with a thin hydrocarbon film
γ_{so}, γ_{co}	=	Solid-oil or coal-oil interfacial tension
γ_{sw}, γ_{cw}	=	Solid-water or coal-water interfacial tension
γ_{wl}	=	Water-non polar fluid interfacial tension
γ_{wo}, γ_{ow}	=	Water-oil interfacial tension
γ_{swo}	=	Line tension (3-phase "interfacial tension")
Γ_i	=	Adsorption density of surfactant (i) at a given interface
η	=	Phase viscosity
$\theta; \theta_e$	=	Contact angle; Equilibrium contact angle (aqueous phase)
θ_a, θ_o	=	Contact angle measured through air and oil respectively
μ	=	Population mean
μ_i	=	Surfactant thermodynamic chemical potential
π_d	=	Disjoining pressure
π	=	Adsorbed film pressure
ρ	=	Density
σ	=	Population standard deviation
φ	=	Phase volume fraction
χ	=	Interfacial potential
ψ	=	Distribution potential
ω	=	Fraction of interface covered by surfactant

SUMMARY

This study was prompted by the widely variable and often unpredictable flotation performance of many South African coals with conventional reagents (oil and MIBC). The influence of three pulp phase sub-processes on the (batch) flotation performance of a -500 μm fraction of an unbeneficiated South African bituminous coal was studied. This coal was from Greenside Colliery, which is located in South Africa's most important coal field, at Witbank. The sub-processes were : oil dispersion, adsorption of the oil onto coal (including its selectivity), and the influence of oil on bubble size. The sub-processes were studied at the same conditions and in the same vessel used for the flotation testwork wherever this was possible.

Hydrocarbon oils were used as collectors and MIBC as the frother. Two generic oil types, aromatic and aliphatic, were used. Both synthesis grade (essentially pure and definitely surfactant-free) and commercial stocks were tested. Boiling ranges typically fell between 180 and 250°C. The pure oils used were dodecane and hexyl benzene, and the commercial oils used were Shellsol AB, Shellsol K and Pegasol 3745.

Oil dispersion tests were carried out in a 3-litre laboratory batch flotation cell. The dispersions were analyzed using a Coulter Counter. All the oils were found to be sufficiently dispersed for effective flotation of the coal studied. However, aromatic oils were better dispersed than aliphatic oils at identical conditions. For all oils, the volume-mean droplet diameter was never bigger than 35 μm and in terms of number, droplets of the order of a few microns in diameter dominated the populations. Numbers of droplets ranged between 10^4 and 10^7 per millilitre of water, depending on the oil and the agitation conditions used. Oil dosages were 67 and 133 μl per litre of water. MIBC did not promote and usually hindered oil dispersion.

Oil droplet adsorption studies were conducted in a 500 ml turbine-agitated cylindrical, baffled vessel. The kinetics and extent of oil adsorption onto solids were monitored using a specially developed technique. This was successfully applied to both pure and commercial oil stocks. All the oils were found to adsorb to a significant extent (90 %)

on the surface of beneficiated (hydrophobic) coal. This remained true of aromatic oils with unbeneficiated coal but aliphatic oils adsorbed to much less of an extent. Nevertheless this was found to be sufficient to render the coal particles floatable. However, adsorption of aliphatic oils might be inadequate with more extensively oxidized, lower rank or higher ash coals. All the oils were highly selective towards hydrophobic carbonaceous material. MIBC did not promote oil adsorption.

Bubble sizing tests were carried out in the batch flotation cell. Bubbles were sized by drawing them into a glass capillary where they were electronically detected, scaled and counted. The presence of aromatic oils reduced bubble size markedly. This is associated with their spontaneous spreading at the air-water interface and thereby with a net lowering of interfacial tensions. Aliphatic oils do not spread and consequently had little influence on bubble size. One predominantly aliphatic commercial oil did reduce bubble size significantly, but only in the presence of MIBC. In this case, bubble sizes were considerably smaller than those induced by either reagent in isolation. This was attributed to a "complexing" of MIBC and some unknown surface-active oil constituent at the air-water interface. Such anomalous behaviour may only be associated with an oil possessing a substantial aromatic content as powerful (strongly polar or ionic) surfactants are not soluble in strictly aliphatic oils.

Flotation recovery was largely dependent on froth form and stability since other prerequisites were satisfied : oil dispersion was adequate and oil adsorption onto the unwashed coal sample was sufficient to induce floatability. With regard to particle-bubble attachment, thermodynamics prove that an air bubble will adhere to an oiled particle upon contact. As bubble size is an important contributory factor to froth form and stability, aromatic oils always significantly out-performed "pure" aliphatic oils as collectors. The commercial oil which possessed both aromatic and aliphatic constituents but was of predominantly aliphatic character was also a good collector since it reduced bubble size significantly in combination with MIBC.

The mode of conditioning was found to be important to recovery at low reagent dosages (which are those which would be favoured in the interests of economy); as was the mode of reagent addition. Mild conditioning, premature MIBC addition and direct addition of oil to the

pulp, especially in combination with rapid oil adsorption, contributed to reduced recovery and/or grade. It is suggested that oils be predispersed prior to addition to the pulp to facilitate their distribution. Because MIBC is preferentially soluble in oil it should be added independently of the oil and as late as possible to the pulp to ensure its maximum activity at the air-water interface (frothing). In this respect, MIBC dosage should be on the basis of its concentration in water.

In the absence of extraneous surfactants, the pulp-phase behaviour of the oils, MIBC and the collector/frother combination is well understood and predictable. This behaviour was invariably able to explain the observed flotation performance satisfactorily (without recourse to a specific froth phase study).

Interfacial phenomena control sub-process behaviour, so other frothers (surfactants) could induce different behaviour and this might be advantageously exploited. Other coals are expected to change the magnitude, but not the trends, in adsorption and froth stability effects. Interfacial theory was reviewed in some detail. This revealed that the theory, especially that concerning the action of surfactants, is currently inadequate for predictive purposes. It is of qualitative use only, when applied to the dynamic/non-equilibrium conditions typical of flotation. Empirical testwork and semi-empirical theory will remain necessary for the foreseeable future.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

1.1.1 General

Modern mechanized mining methods have increased the proportion of -0.5 mm fines in run-of-mine (r.o.m.) coal. In South Africa, the usual practice is either to discard these fines or to re-add them (unbeneficiated) to coarser product(s). In 1985 South Africa discarded at least 3.7 Mt of -0.5 mm bituminous coal fines, mostly from washing plants in the Witbank area (DMEA, 1987).

Because of the non-selectivity of mechanical mining methods and the increased mining of poorer and more friable seams, the increase in the quantity of r.o.m. fines produced is often accompanied by an increase in the ash-forming (gangue) content. A recent survey (DMEA, 1987) has shown that the bituminous slurry discards have ash contents of up to 40 % (though the distribution is not uni-modal so that a weighted average is misleading). The average calorific value of these discards was reported to be 23 MJ/kg.

In their naturally arising state the fines have little economic value and their mining costs must be covered by revenue from coarser washed products. If they are re-added to a coarser product, the coarse fraction usually requires overwashing in order to meet overall product specifications, as the ash content of the fines is often too high.

Beneficiation of the fines would have financial advantages in terms of income that could be earned versus the present cost of fines disposal. By increasing the ash content and decreasing the quantity of the final discard, fines beneficiation would also reduce the detrimental impact of the discards, particularly burning dumps, on the environment - an area sadly neglected in practice. Brookes and Bethell (1984) point out that the disposal of fines effectively represents a permanent loss

of a primary energy source since current methods of fines disposal are not conducive to future reclamation. As economic and environmental pressures mount so the need to treat fines discard will increase.

Unfortunately in South Africa fine coal treatment is fraught with technical difficulties which have resulted in a long-standing reluctance to treat -0.5 mm fines. In many coal producing countries the beneficiation of coal fines by flotation is firmly established. However flotation has not been very successful when applied to South African coal fines. Rather, it has produced widely varying and often unpredictable results.

Recently, spiral concentrators have been introduced on some washing plants to produce thermal quality coal from slurry discards. Spirals are only really effective with particles above 200 μm . Ultra-fine material cannot be beneficiated efficiently by this or other gravity-based methods. Processes dependent on surface properties become the only practical approaches.

Techniques relying on surface chemistry, such as flotation and oil agglomeration, are the only ones capable of effecting separation of very fine material; and they can also be extended to somewhat coarser sizes. Though oil agglomeration has produced good results, high oil consumption has made it less attractive than flotation, where the natural hydrophobicity of coal is enhanced by the use of small quantities of oily collectors (which are selective towards coal).

Aplan (1987) believes that inertia and the lack of a research and development program has hampered the development of coal flotation but that the pace of research in this area is beginning to quicken. Laskowski (1986) confirms that coal flotation has now become "a must", even for oxidized and low rank coals, and is being extensively studied.

Research into the reasons for the generally poor flotation performance of South African coals (in terms of recovery and grade) is in progress at a number of research institutions in South Africa. Several factors could be responsible, the more important being :

1. Poorly applied flotation technology.

Factors such as the quantity of reagents added, the manner of reagent addition (in terms of conditioning procedure and the use of staged addition), and cell operating parameters such as aeration rate, pulp agitation, froth height and pulp throughput are all known to affect flotation performance.

The influence of various parameters, both physical (pulp agitation, pulp density, aeration rate, etc.) and chemical (pH in particular) on the macrokinetics of coal flotation have been well documented. (e.g. Eveson et al, 1957; Bitter, 1966; Mackenzie and Matheson, 1963; Dell, 1968). The impact of factors such as feed size distribution, pulp conditioning and reagent addition sequences has also been studied. (e.g. Robinson, 1959; Firth et al, 1978; Bensley and Nicol, 1985; Laskowski, 1986).

These investigations were conducted by observing the rate and degree of concentrate production and the associated concentrate ash content, in micro-flotation or laboratory batch flotation cells. All were concerned with non-South African coals. Despite the existence of such operational knowledge, flotation still has varying success when applied to South African coal fines - which generally float poorly.

2. Poor physical liberation.

The dominant gangue in South African coals is syngenetic* clay which is very finely disseminated within the coal matrix. While the ash content of a coal may be unsatisfactorily high, its presence in terms of surface area is often very small, making significant beneficiation by flotation impossible. Increasing the liberation of such finely disseminated material requires considerable size reduction which can be prohibitively expensive.

3. Inappropriate reagent selection.

Two types of reagent are generally used in coal flotation: a collector to enhance the hydrophobicity of the coal and a frother to regulate the froth phase. With very hydrophobic coal it may be possible to use a frother only. Coal collectors are almost

* Deposited contemporaneously

exclusively oils; the type of oil and its associated impurities have an important influence on flotation performance. The choice of frother and the frother-oil joint action are also of considerable importance in determining flotation performance.

It is well known that South African coals are quite different in physico-chemical nature to North American and European coals, which are generally quite readily floated. It is therefore possible that different reagents could be required.

Since 1983, a comprehensive investigation of the flotation of South African coals has been under way in the Department of Chemical Engineering at the University of Cape Town (U.C.T.). Some of the earliest work undertaken was a study of the effects of several important physical parameters (aeration rate, impeller speed, reagent dosage levels, etc.) on the flotation performance of various South African coals (Fickling, 1986). Latterly, an in depth study of the liberation characteristics of Greenside Colliery No. 2 seam coal (from Witbank - the country's most important coal field) has been completed (Harris, 1987).

The work to date has provided useful insight into several flotation problems. As a result two small continuous pilot flotation plants were installed at the Landau and Kleinkopje Collieries near Witbank, and operated successfully for some time (Horsfall et al, 1986). If not for the slump in world coal prices, a full-scale plant would probably have been built.

However, in some cases the research raised new questions which in turn pointed to the need for more fundamental studies. For example, it was found that under identical operating conditions, with the same coal feeds, flotation results obtained with different hydrocarbon oil collectors were often markedly different. This may be seen in Figure 1.1, which shows the coal recovery obtained with an homologous series of pure hydrocarbon oily collectors ¹, as a function of the type and number of carbon atoms in the oil molecule.

Two coals were tested : an as-received sample of Kleinkopje thickener underflow and a -150 μm fraction of milled Grooteegeluk

¹ n-alkyl benzenes and n-alkanes

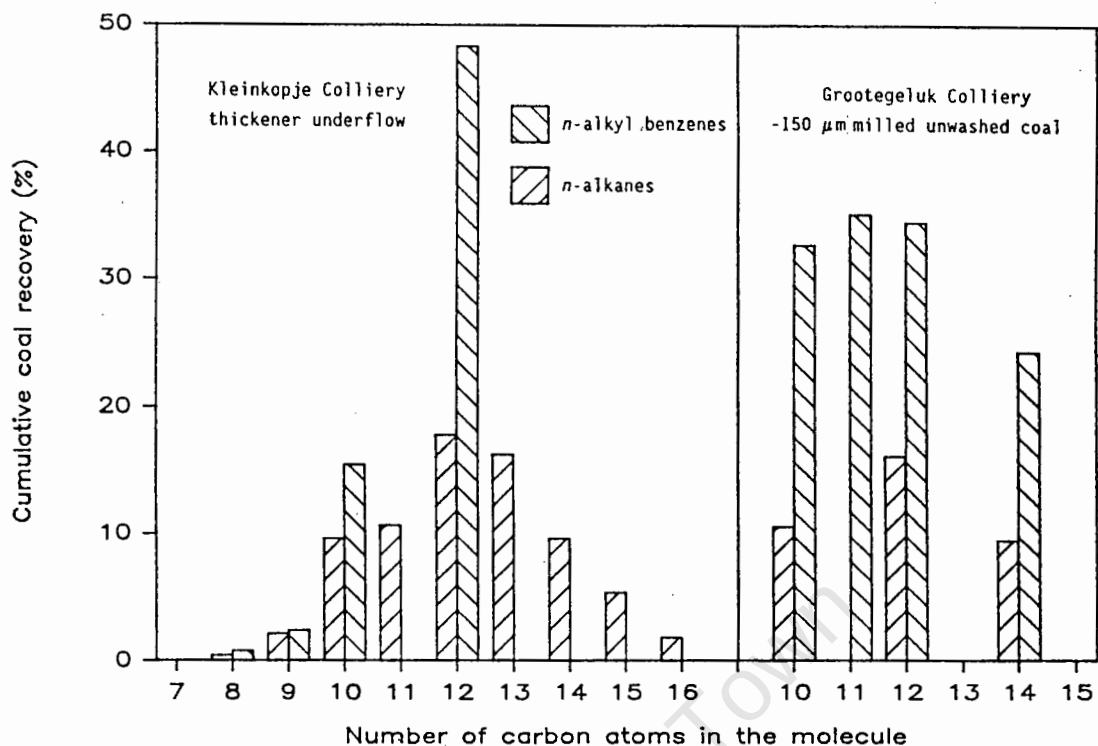


Figure 1.1 : Coal recoveries induced by the use of MIBC and pure hydrocarbon oils of increasing carbon number (molecular weight). Two generic oil types are shown, namely, aliphatic (n-alkanes) and aromatic (n-alkyl benzenes). Dosages were 600 g.t⁻¹ of coal for the oil and 6 μl.litre⁻¹ of water for the MIBC.

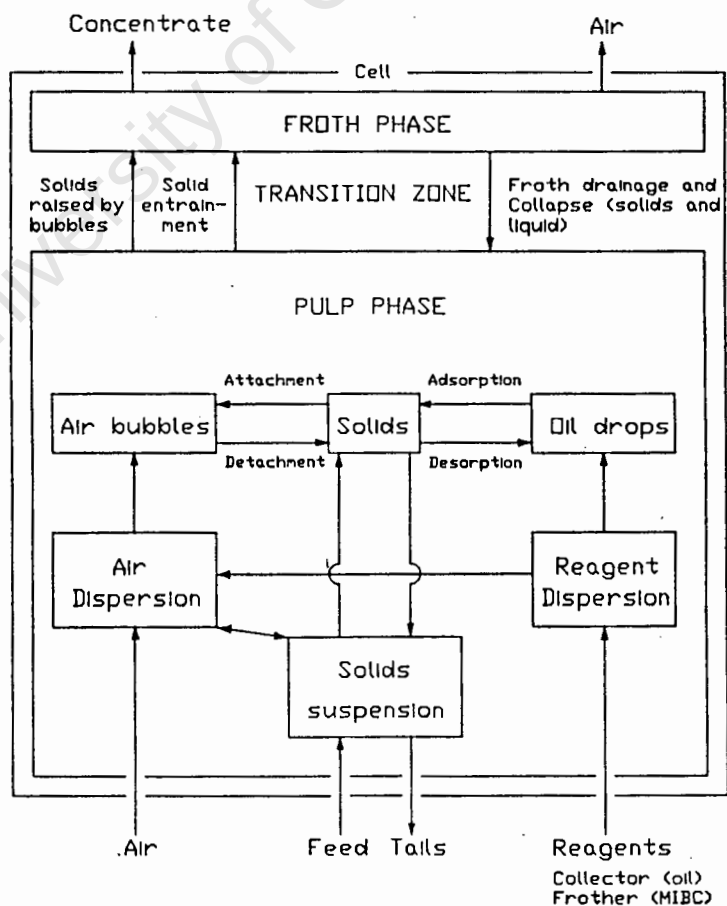


Figure 1.2 : Schematic diagram of the coal flotation process, including the sub-processes investigated in this thesis and their major inter-relationships.

unwashed (unbeneficiated) coal. The flotation performance of both coal samples was poor because of an inadequate frother dosage. Nevertheless, the trends in recovery are clear. For both coals, optimum flotation performance within a homologous series of pure oils generally occurred with about a 12-carbon molecule. More importantly, an enormous improvement in recovery was obtained when using aromatic oils instead of aliphatic oils of the same carbon number. This begs for a better understanding of the coal flotation process, and of the role of the hydrocarbon collectors within this process.

1.1.2 The flotation process with oily collectors

To try to understand the action of the oily collectors in coal flotation it is useful to consider the overall flotation process as being made up of a number of constituent (micro-scale) sub-processes or elementary steps. This is a well established approach (Mühle et al, 1982; Schulze, 1984; Al Taweel et al, 1986) in which the sub-processes are viewed as a sequence of events which integrally create the observed macro-scale flotation behaviour. The sub-processes are shown schematically in Figure 1.2, and include :

1. dispersion of the collectors in the pulp;
2. collision of collector droplets with and attachment to solid surfaces;
3. creation and dispersion of air bubbles;
4. collision of oiled solid particles with and attachment to rising air bubbles;
5. transport of air-solid aggregates (loaded bubbles) to the froth phase as well as the entrainment of unattached solids;
6. elutriation of entrained solid particles back into the pulp phase; and, finally,
7. removal of froth as concentrate.

Not all these sub-processes involve the oily reagents directly: the first four do while the last three are essentially transport steps.

An understanding of the first three steps, in conjunction with flotation testwork, should allow the success of bubble collision and attachment and of the subsequent transport steps to be readily gauged.

As indicated above, most of the previous work on oily flotation reagents and on coal flotation is based on an appraisal of macro-scale (overall) behaviour. The involvement of oily reagents in events occurring on a micro-scale during coal flotation is not well understood but its quantification would greatly assist in optimizing flotation performance. It would also allow more accurate modelling of the process with all the concomitant advantages in terms of plant design and control.

Researchers have made some attempts to correlate coal flotation performance with characteristics related to the collector oil, like oil viscosity (Glembotskii et al, 1970), oil boiling ranges (Whelan, 1953) and oil composition (Whelan, 1953). Success has been limited, probably because the properties of the oils should not be considered in isolation, as several of them in combination could affect the outcome of the overall process. Frequent use has been made of contact angle measurements (which are partly dependent on the nature of the coal surface) but again with limited success (Horsley and Smith, 1951; Brown et al, 1958). This is not surprising in view of the complexity of the flotation process as a whole.

Modelling the general flotation process accurately is a goal which is still eluding investigators despite the large amount of research undertaken in this area. Much of the research is empirically based. Anfruns and Kitchener (1976, p.626) emphasized that the sheer complexity of the flotation system makes a description of flotation in fundamental terms impossible and that semi-empirical models of the observed macro-kinetics are unavoidable. In a recent review McMichael (1985) found that semi-empirical models are still the most commonly used for all stages of the flotation process. More than a decade ago, Flint (1973) maintained that models were hampered by ignorance of collection and detachment processes occurring in the pulp. This ignorance still persists.

However researchers are increasingly aware of the necessity of establishing theoretical foundations for the flotation process. In the opinion of Schulze (1984), major hurdles still to be overcome are :

1. Difficulties in integrating the effects of the sub-processes into an overall model, especially in incorporating transitions between one sub-process and another.
2. Insufficient knowledge of the precise impact induced on a number of sub-processes (in terms of both process modification and process control) following reagent addition.

The collector oil quite evidently has a vital role to play in many of the sub-processes. Unfortunately, there is little documentation of the action of insoluble collectors in the elementary steps. On the other hand, the action of *soluble collectors* in certain of the sub-processes is fairly well understood. This is borne out by Schulze (1984), who reviewed current theoretical understanding of elementary flotation processes. Reagent insolubility and modifications to the theory which could be necessary to accommodate this received virtually no mention, indicating the lack of research in this area.

As an example, flotation research embodied in the literature is typically concerned with three phases (gas, solid and liquid). There are many references to 3-phase froths and 3-phase contact angles. There is a tacit assumption that characteristics of sub-processes involving insoluble collectors would be similar to those involving soluble collectors. This is, in some cases, patently untrue if only for steric (size) reasons. Soluble flotation reagents are present on a microscopic (molecular) scale. They congregate at various interfaces but are effectively in one or other of the phases and so do not interfere with the geometrical relationships between the phases. In contrast oil droplets have a definite size and cannot simply be regarded as forming part of an interface especially if they do not spread spontaneously at such an interface. Their presence in fact introduces an additional physically separate liquid phase with its own accompanying interfaces. It might therefore be more appropriate to consider 4-phase froths and 4-phase contact configurations. The additional phase is certain to introduce complications into the mechanisms prevalent in the

sub-processes, yet its influence in these respects has seldom been considered.

Compared with soluble collectors, insoluble collectors have fairly limited application in froth flotation, which might help to account for the relatively limited knowledge in this area.

1.2 OBJECTIVES OF THE RESEARCH

The elementary processes in flotation occur in or between two distinct regions, the pulp phase and the froth phase. Overall flotation performance is determined by the outcome of events occurring within both these phases. Events in the pulp phase must necessarily precede those in the froth phase. It is therefore reasonable to commence a study of the action of insoluble collectors with an investigation of their role in the pulp phase, especially as reviewers have indicated that knowledge in this respect is scant (Flint, 1973; Schulze, 1984). It may also be argued that the actions occurring within the pulp phase have a considerable influence on subsequent froth phase events.

The objectives of this research are to probe the action of hydrocarbon oils on the sub-processes within the pulp phase of the coal flotation process, and to determine whether this could explain the large differences obtained in (batch) flotation performance with a particular coal using these collector oils.

Williams (1965) used a similar approach to study the influence of insoluble reagents (oleic acid and mineral oil) on the flotation of fine hematite. Flotation recovery was used as an index to relate solids floatability to the elementary mechanisms of the process. His work was chiefly concerned with reagent dispersion and the influence of agitation time and intensity on this, though reagent sorption and spreading, air bubble contact angle and flocculation of the solids were investigated to a limited extent and related to flotation performance.

The flotation process is very complex. It is expected that many of the sub-processes will exert considerable direct influence on other sub-processes and will at times be impossible to isolate. However, for the purposes of this thesis, it is proposed that observed differences in

coal flotation performance are a result of the specific action of the oily collectors in one or more of the following pulp phase sub-processes :

1. Oil dispersion.
2. Collision of oil droplets with and attachment to solid particles (including the selectivity of the oils).
3. Creation and dispersion of air bubbles.
4. Oiled particle-air bubble collision and attachment.

The investigation of these sub-processes is also aimed at determining whether the action of the hydrocarbon oils in any one sub-process has a controlling influence on the overall process, and which processes can be ignored or tacitly assumed to occur.

1.3 SCOPE OF THE RESEARCH

In view of the limited documented research on the action of hydrocarbon oils in flotation sub-processes, and its absence with regard to South African coals, it was decided to adopt a fairly broadly based investigative approach. From a process engineering point of view, knowledge of the overall outcome of the action of the oil in each sub-process could provide sufficient understanding to manipulate the process so as to achieve successful coal beneficiation.

During the course of this work, and when reviewing the literature available, it became increasingly apparent that a better understanding of interfacial behaviour is essential to understanding and interpreting flotation behaviour. Nearly two decades ago Campbell and Sun (1970a) stated that it was of paramount importance to understand interfacial phenomena, especially solid electrostatic properties, in order to correctly apply and improve the flotation of coal. However interfacial behaviour in coal flotation is still poorly understood (Al Taweel et al, 1986). The inadequacy of this understanding is believed to be primarily responsible for problems associated with selectivity, reagent utilization and, in general, the lack of predictability in coal flotation (Taylor et al, 1981).

In addition, the current understanding of interfacial phenomena relevant to (coal) flotation is not well summarized all in one place: this is particularly true of an interpretation of the sub-process/interfacial behaviour of insoluble collectors (which is scarce in any event). The literature reviews in this thesis are aimed at redressing this situation. The current understanding of interfacial processes important in coal flotation, and the role of oily collectors, are therefore reviewed and discussed in some detail.

Wherever possible, the experimental investigations of each sub-process were undertaken in the 3-litre laboratory flotation cell which was used in the batch flotation tests. Physical parameters (vessel geometry, mixing characteristics, air induction, etc.) were therefore identical. Observations and deductions from the sub-process studies could then be applied directly to the observed flotation performance.

Coal from one colliery and from one seam was chosen for the major part of the testwork. Nine different hydrocarbon oils were used in various parts of the work: one of these oils was split into seven 10°C boiling range cuts for the purpose of this investigation.

First, the dispersion characteristics of the oil in water were evaluated in the cell, i.e. the sizes of the droplets produced were measured (using a Coulter Counter), at various degrees of agitation and in the presence and absence of MIBC frother. This was followed by an investigation of the adsorption of the oils onto pulp solids (coal and gangue minerals). Adsorption tests were conducted in a 500 ml turbine-agitated vessel. A new technique was developed for measuring the rates of disappearance of the oils from the pulp liquid as they became adsorbed onto solid particles. The influence of the contacting procedures, the degree of agitation, the size of the solid particles, the presence of MIBC and the type of coal surface (washed or unwashed) was investigated. This was followed by an investigation of the selectivity of the oils; and an attempt to model the adsorption kinetics. The effects of the oils and the oil-MIBC combination on bubble formation in the flotation cell was then studied; as was the effect of agitation intensity. The bubbles were electronically detected, scaled and counted using a recently developed bubble-sizing apparatus which sampled the bubble populations in the cell. Finally, batch flotation tests were undertaken with the various oils and MIBC, at several dosages

and using a number of different conditioning procedures. The observed flotation performance was interpreted in terms of the three pulp phase sub-processes studied.

This work is set out in the chapters which follow. However, information pertaining to the coals and the reagents used is common to all the sub-processes studied and is therefore set out below for ready reference.

1.3.1 Coals studied

An investigation of the sub-processes in coal flotation is complicated by the coal itself. Coal is a very complex substance with properties which vary widely with both seam and geographical location.

The rich physico-chemical nature of coal is a legacy of its origins in very varied plant matter which was itself deposited under widely varying conditions. Being a natural process, non-combustible mineral matter (gangue) like clays and sands was also deposited with the carbonaceous material.

The physico-chemical characteristics of both coal and gangue are therefore not readily defined. Their characteristics are altered further during coal processing by external factors like oxidation and process water chemistry. Variation of coal surface properties aggravates attempts to quantify sub-processes involving coal.

For these reasons a single coal was selected for use in this study. This coal was from the No. 2 seam of the Witbank coal field - which is South Africa's most important coal field - and was obtained from Greenside Colliery. The coal is bituminous.

Almost all of the research work described in this thesis was carried out on this coal. It was felt that once the action of the reagents in conjunction with one coal was better understood, the same procedures could be readily extended to other coals. Furthermore some of the sub-processes postulated to affect flotation performance, e.g. oil dispersion, do not involve the coal directly.

Three different samples from Greenside Colliery were used. These were :

1. Unwashed (r.o.m.) coal.
2. Washed coal: known in the South African industry as l.a.c.² (a blend coking coal with about 7 % ash). Two very similar though not identical samples of the washed coal were obtained from the colliery (at different times). Coal from the later sample was used in most of the testwork. When the original batch was used this is clearly stated.
3. Thickener underflow discard coal.

The unwashed and thickener underflow coal samples have very similar maceral and ash contents, while the washed coal, which obviously has a much lower ash content, has a somewhat different maceral make-up.

The petrographic and proximate analyses of these samples are presented in Tables 1.1 and 1.2 below. The analyses were performed by the Falcon Research Laboratory in Richmond, Johannesburg.

Table 1.1 : Petrographic analyses of the coal samples

	Vitrinite	Exinite	Inertinite	
			Reactive	Non-reactive
Unwashed (r.o.m.)	24.5 %	2.0 %	15.8 %	58.5 %
Washed	47.2	7.1	11.0	34.7
Thickener underflow	31.3	1.6	14.4	52.7

Table 1.2 : Proximate analyses of the coal samples

	Moisture	Ash	Volatiles	Fixed carbon
Unwashed (r.o.m.)	2.3 %	20.4 %	24.2 %	53.1 %
Washed	2.2	7.9	33.4	56.5
Thickener underflow	-	20.9	-	-

The unwashed (run-of-mine) sample was selected for use in most of the testwork. The advantage of unwashed material is that it is neither contaminated chemically, by exposure to washing plant water, flocculants and heavy media, nor physically, by treatments such as cycloning which would preferentially remove some size/density fractions. The behaviour of the collector oils would therefore not be influenced by unknown or unquantifiable factors.

Fines from the thickener underflow of any mine possessing a washing plant would have been subjected to such treatments, though this is the stream to which (possibly in its unthickened form) beneficiation by flotation would ultimately be directed. For comparative purposes a limited amount of experimental work was conducted with the thickener underflow coal sample.

It was sometimes useful to deal with a "pure" coal, in order to evaluate the "true" performance characteristics of the oil. In these cases the washed coal (l.a.c.) sample was used.

1.3.2 Collector oils selected

South African coals are known to require the addition of an oily collector to achieve reasonable flotation yields. This is true of bituminous coals in general (Fuerstenau et al, 1983). The hydrocarbon oils selected for investigation in this work are discussed below.

Hydrocarbon oils (typically fuel oils like diesel and kerosene) and MIBC (an aliphatic alcohol frother) are commonly used throughout the world for the flotation of coal, often with considerable success. Since reagent cost is the highest operating cost in coal flotation (Fuerstenau, 1985), it would be wise to assess the capabilities of commonly available comparatively cheap reagent stocks, like industrial oils, before considering the development of expensive reagents. This thesis is therefore primarily concerned with probing the action of traditional coal flotation reagents (oily collectors and MIBC frother) in the flotation process.

Oil types selected varied from aliphatic through to aromatic with blends of both types in between. Both single species oils and commercial oils were used. The former were essentially chemically pure (isomers

occured in very small amounts but there were no surface-active constituents). The latter were impure in terms of hydrocarbon species, and probably contained additional organic species with surface-active properties. Boiling points/ranges fell between 165 and 250°C, this range being widely used in the coal flotation industry.

The specific choice of collector oils was influenced in part by the fact that much flotation work had already been conducted (within the Chemical Engineering Department at U.C.T.) with many of the oils selected. Much of this work is recorded in a series of progress reports (Franzidis et al, 1986, 1987). A knowledge of the action of these oils in the various sub-processes would therefore help to provide insight for the differences in flotation performance observed in this other testwork.

Sources and some characteristics of the oils selected are listed in Table 1.3. Some typical surface and interfacial tensions of oils, which will be referred to in later chapters, are listed in Table 1.4.

Table 1.3 : Characteristics of the hydrocarbon oils used as coal collectors

Oil	Composition	Boiling range °C	s.g. @ 20°C	Source
<i>Oils used predominantly :</i>				
n-Dodecane	aliphatic	216	0.749	Pure (99%) reagent (Merck)
n-Hexyl benzene	aromatic	227	0.861	Pure (97%) reagent (EGA)
Shellsol AB	>95% aromatic*	185-225	0.900	Shell commercial oil
Pegasol 3745	≈20% aromatic*	180-250 (in 10°C cuts)	**	Mobil commercial oil
<i>Oils used occasionally :</i>				
n-Decane	aliphatic	174	0.730	Pure (98%) reagent (Merck)
n-Tetradecane	aliphatic	254	0.763	Pure (99%) reagent (Sigma)
n-Hexadecane	aliphatic	284-286	0.773	Pure (99%) reagent (Merck)
Shellsol A	>95% aromatic*	165-185	0.875	Shell commercial oil
Shellsol K	<0.5% aromatic*	190-225	0.785	Shell commercial oil

* all percentages v/v

** (s.g. : 0.785, 0.788, 0.795, 0.800, 0.806, 0.812, 0.818 @ 25°C)

Table 1.4 : Typical oil and water surface tensions and oil-water interfacial tensions.

Oil surface tension (pure and impure oils)	25-30 mN.m ⁻¹
Water surface tension	72
Oil-water interfacial tension (impure oil)	12-32
Oil-water interfacial tension (pure aliphatic)	50
Oil-water interfacial tension (pure aromatic)	35-38

The source of and the data for specific oils (from which these ranges were obtained) may be found in Appendix 1.

Chemically pure reagents of a similar boiling point and with chemical constitutions broadly representative of the commercial oils were used in order to preclude the influence of the contaminants of commercial oils, particularly those with surface-active characteristics. Dodecane was used to represent the aliphatic oils - Shellsol K being its commercial counterpart. Similarly, hexyl benzene (1-phenyl hexane) was used to represent the aromatic oils typified by the commercially produced Shellsol AB. Pegasol 3745 was selected as a typical commercial oil containing significant proportions of both aliphatics and aromatics.

On occasion oils of different boiling point (and viscosity) were tested in the research programme. The oils were selected from the same chemical "family", i.e. they were chemical homologues of the more commonly used oils. The pure aliphatics, decane, tetradecane and hexadecane were used in comparative studies with dodecane. Amongst the commercial oils, the Pegasol 3745 oil was split into 10°C cuts which were then used to study boiling range and viscosity effects - the premise being that the cuts were essentially chemically homologous.

1.3.3 Frother selected

The frother used virtually exclusively in all testwork was MIBC (Methyl IsoButyl Carbinol [4-methyl 2-pentanol]) supplied by Shell Chemicals. This frother has wide application in the flotation industry. Klimpel and Hansen (1987, p.85) stated that MIBC is the single most common commercial frother in coal flotation today.

Other frothers were not considered, as the object of the research was an investigation of the impact of collector oils. This is not to deny the very significant role of the frother in coal flotation : however, the study of additional frothers and their joint action with the collector oils selected would have been an insurmountable task in the time available.

1.3.4 Layout of the thesis

As the work falls logically into four different sections (dispersion, adsorption, bubble formation and flotation), a separate chapter is devoted to each part of the work. Each chapter includes a review of the relevant literature, details of experimental procedures and a discussion of the results. The chapters are therefore largely independent, though the chapter on batch flotation includes a general discussion in which the results and conclusions of previous sections are drawn together to explain and interpret the observed flotation results. Detailed experimental data are not included in this volume but are available in a separate Data Appendices volume (on request).

CHAPTER 2

ANALYSIS OF OIL DISPERSIONS

2.1 INTRODUCTION

In coal flotation, mechanical agitation is used to disperse the oily reagents. This dispersion results in the formation of a considerable number of oil droplets of widely varying size. The droplet population so formed will be referred to as a "dispersion" rather than an "emulsion" since many droplets are larger than the maximum size necessary to ensure a reasonably stable mixture, i.e. an emulsion. Stability against phase separation normally requires droplets to be of the order of $1\text{ }\mu\text{m}$ or less (Garrett, 1965; Groves and Freshwater, 1968; Mima and Kitamori, 1966).

Besides oil dispersion other roles of agitation are : to provide the energy for oil-coal particle collisions and the adsorption and spreading of the oil, so as to induce maximum floatability to the desired component (the coal); to maintain the solids in suspension; to disperse air; and to ensure particle-bubble contact. These roles, with the exception (usually) of air dispersion, are normally carried out in a separate conditioning stage, and/or in the first cell of the flotation bank.

The importance of insoluble collector dispersion to flotation has been recognized for some time (Klassen et al, 1958). Williams (1965) specifically studied the role of insoluble reagent dispersion in the flotation of fine hematite particles. Williams (1965) deduced that dispersion and sorption of insoluble reagents are rate determining steps if the reagent is added to the pulp in an undispersed state. If the oils are pre-dispersed prior to solids addition, then sorption is essentially independent of conditioning time. Laskowski and Miller (1984) believed that dispersion of hydrocarbon oil is of critical importance to the achievement of improved flotation performance. Klimpel and Hansen (1987, p.82) re-affirmed that adequate dispersion is vital for optimizing hydrocarbon collector performance in coal flotation.

Thorough oil dispersion is clearly important to the ultimate success of coal flotation. Yet Glembotskii et al (1970) reported that the degree of dispersion of non-polar oils in flotation is very seldom quantified, and an evaluation of the reasons underlying the flotation performance of these oils is consequently severely hampered. From a literature review it is apparent that there is still inadequate data on the dispersion of typical coal collector oils and its influence on flotation performance.

The primary objective of this testwork was to quantify the degree of dispersion of a number of different hydrocarbon oils under a variety of conditions similar to those used in the batch flotation experiments (Chapter 5). This was done using a Coulter Counter and the technique is described below. A knowledge of reagent droplet size distribution was desired in order to determine the extent to which this factor influenced batch flotation performance (by affecting surface coverage, selectivity, etc.). A review of some theory of surface and interfacial behaviour was also undertaken since this behaviour determines the dispersion characteristics of the oils.

The nature of a dispersion of oil and water is dependent on the respective phase volumes, phase viscosities, the manner of dispersion and the type of surfactants present in the system. However, if the phase volume of the oil is very small, as in flotation, then an oil in water (O/W) dispersion will always be formed. Under fixed agitation and dosage conditions, the number and size of the oil droplets formed depends on the type of oil and the type of surfactants present.

It was thought that the best way of quantifying and then comparing the oil dispersions would be by determining their mean and deviation. The experimental dispersion data obtained were therefore modelled in terms of existing and theoretically valid size distribution functions. Obviously droplet size distributions can only be measured in the absence of pulp solids : the presence of solid particles and their adsorption of the oil droplets will make measurement impossible. Thus, for example, the droplet size distribution can only be inferred in instances where a collector oil is added directly to a pulp. However, flotation experiments were carried out (Chapter 5) in which the oils were dispersed in water in a flotation cell prior to solids addition, in a similar manner to that used when measuring the dispersion. Since the oil

droplet size distributions for each oil type were known, direct comparison of the effect of oil dispersion on the respective flotation results was possible.

2.2 THEORY AND LITERATURE REVIEW

2.2.1 Introduction

Upon breakup of the oil phase during dispersion in water, an interface is formed between each oil droplet and the surrounding aqueous phase. This is not a distinct phase boundary but rather a diffuse film of definite thickness with properties which vary from that of the bulk phases on either side of it. Since interfacial phenomena will also play a vital role in the other sub-processes to be considered in this thesis, certain concepts are introduced and reviewed at this stage. Reference to these concepts is also made in subsequent chapters.

2.2.1.1 Surface tension, surface energy and interfacial tension

Surface tension in liquids is a result of the disparate energies of surface and bulk molecules. In the bulk the intermolecular cohesive forces which ensure that the liquid retains its nature and does not break up under the influence of the thermal movement of its constituent molecules are reasonably well balanced, since each molecule is surrounded by others. This is not the case of surface molecules which are incompletely surrounded so that the intermolecular forces are not as thoroughly resolved. Figure 2.1 illustrates this phenomenon.

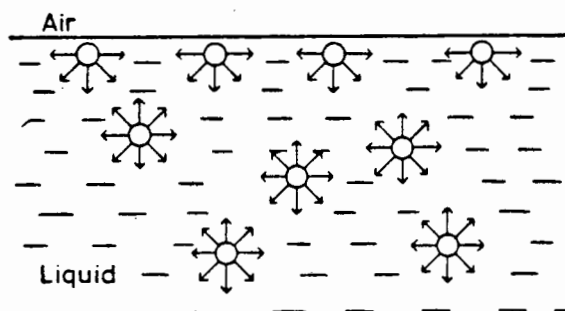


Figure 2.1 : Attractive forces between molecules at the surface and in the interior of a liquid. (From Shaw, 1985).

Surface molecules therefore represent an energetically higher state. In an effort to reduce the total energy of the system, surface molecules attempt to migrate into the bulk - the net result being a contraction of the surface to a minimum size; the force responsible being termed the surface tension, γ .

The change in total Gibbs free energy, G , of the system is given by :

$$\begin{aligned} dG &= -SdT + VdP + d(G^sA) + \sum \mu_i dn_i \\ dG &= -SdT + VdP + dG^sA + G^s dA + \sum \mu_i dn_i \end{aligned} \quad [2.1]$$

S , T , P , V , G^s , A , μ and n are entropy, absolute temperature, absolute pressure, volume, specific Gibbs surface energy, surface area, chemical potentials and moles of molecules respectively. G^s is assumed to be a non-equilibrium property since the equilibrium surface configuration may not be attained in some instances (elaborated below).

For a single condensed phase of constant composition and constant temperature and pressure Equation 2.1 becomes,

$$\begin{aligned} dG_{T,P,n} &= AdG^s + G^s dA \\ \left(\frac{\partial G}{\partial A} \right)_{T,P,n} &= G^s + A \left(\frac{\partial G^s}{\partial A} \right) \end{aligned} \quad [2.2]$$

where $\left(\frac{\partial G}{\partial A} \right)_{T,P,n}$ is defined as the surface tension, γ .
(Kruyt, 1952, p.116).

For a homogeneous liquid G^s is an intensive property dependent on the configuration of molecules at the surface and not on area, so from Equation 2.2,

$$\gamma = G^s \quad [2.3]$$

For solids the equivalence of surface tension and specific surface free energy as shown in Equation 2.3 does not hold since solid

surface immobility implies that the equilibrium arrangement of surface molecules is not usually attained (Adamson, 1960, p.235). Equation 2.2 must then be used.

Further complications in relating surface energies and surface tensions are introduced if the composition of the surface (solid, liquid or gas) varies from that of the bulk phase, i.e. if there is a surface excess or depletion of some component. This will be considered in Section 3.2.7.

Equation 2.2 indicates how surface tensions are evaluated by measuring the work needed to induce a reversible change in the surface area of the phase. This is quite simple to do with liquids but is impossible to do with solids.

Interfacial tension differs from surface tension (by convention) in that it is the force existing at the interface between two condensed phases, while surface tension is the force existing at the interface between a condensed phase and a gaseous phase (conventionally air). With liquids, the interfacial tension equals the difference between the surface tension of the two liquids when both are mutually saturated with one another. In addition to being invalid at non-equilibrium saturation levels, this relation also breaks down if the one liquid will not spread over the other, even to the extent of a monolayer. Examples of such systems are the higher order paraffins (alkanes) and water. Such paraffins, e.g. dodecane, are some of the oils studied in this thesis, so it is important to investigate spreading phenomena. Spreading is controlled by the balance of the cohesive and adhesive forces in action.

2.2.1.2 Cohesion and adhesion

The classical relation defining the work of adhesion of oil to water is known as the Dupré equation :

$$W_{ow} = \gamma_{oa} + \gamma_{wa} - \gamma_{ow} \quad [2.4]$$

where γ_{oa} and γ_{wa} are surface tensions while γ_{ow} is an interfacial tension. From Equation 2.4 it is evident that the work of cohesion within a single liquid is (for oil),

$$W_o = 2 \gamma_{oa} \quad [2.5]$$

One liquid will spread on the other if it adheres more strongly to the other than it coheres to itself. By combining Equations 2.4 and 2.5 spreading will occur if

$$\gamma_{oa} + \gamma_{wa} - \gamma_{ow} > 2 \gamma_{oa}$$

$$\text{or, } \gamma_{wa} - \gamma_{ow} - \gamma_{oa} > 0 \quad [2.6]$$

The left hand side of Inequality 2.6 is often referred to as the spreading coefficient, F_s . If this is positive the oil will spread and if not it will remain on the water surface as a lens and display a definite contact angle. Contact angles are discussed in detail in Section 3.2.6.

The concepts of adhesion and cohesion discussed above in relation to two liquid phases are also useful for describing the interfacial behaviour at solid surfaces, since a solid surface tension is not a phenomenon which can be physically interpreted or directly measured. Solid surface "tensions" are considered in more detail in Section 3.2.6.

2.2.1.3 The influence of surface active agents on interfacial tension

Surface active agents (surfactants) owe their properties to the existence of polar and non-polar portions within a single molecule. Such molecules tend to migrate to an interface since location here (i.e. adsorption or spreading) allows them to adopt their most energetically favourable orientation, with the polar portion of each molecule in the more polar bulk phase and the non-polar portion in the less polar or non-polar phase. This behaviour is depicted schematically in Figure 2.2 below. The theory of adsorption and its relation to surface free energy and surface and interfacial tensions is covered in Section 3.2.7.

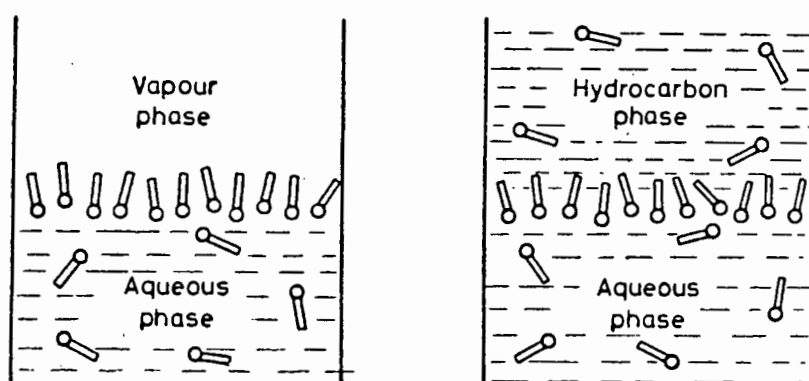


Figure 2.2 : Adsorption of surfactants as an orientated monolayer at air-water and oil-water interfaces. The circular portion represents the hydrophilic head group. (From Shaw, 1985).

The tendency of surfactants to migrate to the interface is in direct contrast to the tendency of bulk phase molecules to leave the surface, i.e. to contract the interfacial area. The effect of surfactant adsorption is consequently opposite - it tends to decrease interfacial tension. The continued migration of new surfactant molecules to the interface, in conjunction with the intermolecular repulsion between the orientated, packed surfactant molecules already at the interface, causes the interface to expand. The net result is that the interfacial film, containing the surfactant molecules, exerts its own pressure which counteracts the shrinking tendency of the pure phase interface. This is expressed in the relationship

$$\gamma_i = \gamma - \pi \quad [2.7]$$

where π is the surface film (or monolayer) pressure, and γ_i is interfacial tension.

The nature of the interfacial film and the density of surfactant packing is dependent on bulk phase surfactant concentration but is also strongly dependent on the nature of the surfactant molecule itself. Surfactants thus have varying influences on the behaviour of interface-related processes, e.g. the dispersion of oils. The effect of surfactants on oil dispersion will be considered in more detail in Section 2.2.4.

2.2.1.4 Capillary (excess) pressure within droplets (and bubbles)

The pressure within oil droplets is greater than that in the continuous aqueous medium as a result of the interfacial tension. This excess pressure (in relation to that outside the droplet) is important in that it influences droplet dispersion, droplet coalescence and the diffusion of oil molecules into the continuous medium. Very high excess pressures, which coincide with very small droplets (because of their high surface area to volume ratio), may enhance oil dissolution (solubility).

Quantification of excess pressure is undertaken below. Let it be assumed that oil is fed into the droplet via a minute capillary in order to increase its volume. In increasing the droplet surface area work must be done against the interfacial tension, i.e.

$$\text{Work} = \gamma_i \, dA$$

But the work in increasing droplet size can also be related to the excess internal pressure, P_e , and the change in droplet volume, i.e.

$$\text{Work} = P_e \, dV.$$

Hence, $\gamma_i \, dA = P_e \, dV$, and for spherical droplets,

$$\gamma_i \, 8\pi r \, dr = P_e \, 4\pi r^2 \, dr.$$

$$\text{Whence, } P_e = 2 \, \gamma_i / r \quad [2.8]$$

Excess pressure becomes significant if the droplet is very small. For an aliphatic oil with an interfacial tension of $50 \, \text{mN.m}^{-1}$ the excess pressure for a $1 \, \mu\text{m}$ (radius) droplet is $100 \, \text{kPa}$; for one of $1 \, \text{mm}$ radius it is only $0.1 \, \text{kPa}$.

Excess pressure is also evident in air bubbles and influences bubble-solid adhesion as well as froth phase behaviour, where gas diffusion through bubble lamellae reduces the number of bubbles without actual coalescence occurring (Davies and Rideal, 1961, p.10). For spherical bubbles in the pulp (i.e. air cavities), Equation 2.8 holds, but for bubbles in air two interfaces must be expanded (an internal and external interface) so,

$$\begin{aligned} \text{Work} &= 2 \gamma_i dA \\ \text{and, } P_e &= 4 \gamma_i / r \end{aligned} \quad [2.9]$$

2.2.2 The mechanism of droplet dispersion

The dynamic interplay of droplet breakage and droplet coalescence during agitation is responsible for the evolution of the droplet population.

Under the influence of turbulent currents the disperse phase (an oil droplet) is deformed within the dispersion medium (water) resulting in an increase in its surface area. The resulting instability (because of the higher energy state) causes the droplet (ellipsoid) to break into a number of smaller ones when its deformation becomes intolerable from a surface energy point of view. Glembotskii et al (1970) reported that disintegration of a stretched (ellipsoidal) droplet occurs at $L > 3.14 D$. As the droplet becomes smaller its internal pressure or "capillary pressure", $P = 2\gamma_i/r$, increases and the droplet becomes more resistant to a change in shape. Dispersion therefore becomes increasingly difficult to further.

Narsimhan et al (1984) have developed theoretical breakage functions for agitated liquid-liquid systems with a low dispersed phase fraction. Drop breakage is characterized by :

1. The rate of drop breakage, and,
2. The size distribution of the daughter droplets upon breakage of the parent drop.

The theoretical functions derived were tested on steady-state distributions produced in continuous flow experiments and were found to compare very well. Narsimhan et al (1984) also suggested that droplet breakage is not "thorough" and that "erosive" breakage, i.e. the loss of relatively small droplets from the parent drop, may be more common, particularly with small droplets.

2.2.3 Dispersion stability

Glembotskii et al (1970) stated that the free molecular forces on the surface of an oil droplet are uncompensated by the water medium, since the two are immiscible, and that this encourages droplet coalescence. The droplets evolved following agitation are referred to as primary droplets. If agitation ceases the droplet population may alter following the coalescence/coagulation of some of the primary droplets. The disappearance of primary (original) droplets following their contact during diffusion through the continuous medium may be predicted using the Smoluchowski equation :

$$1/n - 1/n_0 = Kt \quad [2.10a]$$

where n is the number of droplets at time t

n_0 is the number of droplets at time zero

K is a rate constant

t is time

In the simplest case, i.e. that of a mono-dispersion¹, Equation 2.10a becomes,

$$1/n - 1/n_0 = 4\pi DRt \quad [2.10b]$$

where R is the collision radius for the two droplets (twice the droplet radius to a good approximation).

D is the diffusion coefficient

The value of D is given by the Stokes-Einstein formula, i.e.

$$D = kT/6\pi\eta r$$

where η = viscosity of the phase

k = the Boltzmann constant

T = absolute temperature

r = radius of the primary droplets ($r = 0.5R$)

Dispersion stability may also be expressed in terms of a mean droplet volume and the number of droplets of this size necessary to constitute

¹ All the primary (original) droplets are of equal size.

the phase volume of the oil. Following the derivation of Davies and Rideal (1961, p.366),

Let V be the mean droplet volume, then,

$V = \varphi/n$, where φ is the phase volume of oil

From Equation 2.10b (which implies a consistent primary droplet size)² :

$$V = \varphi/n_0 + 4\pi DR\varphi t \quad [2.11]$$

Since the phase volume is independent of coalescence,

$$V_0 = \varphi/n_0$$

Hence

$$V = V_0 + 4\pi DR\varphi t \quad [2.12]$$

Equation 2.12 shows why phase volume and *continuous-phase* viscosity have such an important influence on the type of dispersion formed. However, Equation 2.12 usually predicts faster coalescence times than are normally observed since it does not account for interface stabilizing effects induced by surface active agents, i.e. not all collisions lead to aggregation. Davies and Rideal (1961, p.367) proposed that this shortcoming can be remedied by including an energy barrier term [analogous to an activation energy] in Equation 2.12 to give

$$V = V_0 + 4\pi DR\varphi t e^{-W/RT} \quad [2.13]$$

In other words the rate of droplet coalescence is governed by both diffusional and energetic factors. The effect of coalescence rates on the formation of an oil dispersion in the presence of a surfactant is considered in the following section. In coal flotation a typical surfactant would be the frother.

Rehfeld (1974) studied the stability of pure $n-C_6$ to $n-C_{17}$ alkanes and various alkyl benzene emulsions in water (all stabilized by sodium dodecyl sulphate) during centrifugation. The aromatic emulsions showed

² This is often a reasonable assumption in stabilized emulsions. For dispersions with a broad size range of primary droplets, Equation 2.10a may be used, though dispersion stability cannot then be predicted: the constant, K , must be empirically determined.

different behaviour to the alkanes. n-Decane and higher alkanes did not increase in droplet size when "creaming" (migrating to the surface of the continuous phase), i.e. no coalescence occurred. The aromatics did coalesce to some extent. He found emulsion stability to be inversely correlated to the spreading coefficient (LHS of Inequality 2.6) of the hydrocarbon on the aqueous solution. Those oils with the more positive coefficient spread more readily (decane and shorter chain alkanes and the aromatics) and produced the least stable emulsions.

2.2.4 The role of frother (surfactant) in oil dispersion

During initial dispersion and finally at steady-state conditions, two competing processes occur - phase breakage and phase coalescence. Emulsifying agents stabilize the new interface created by phase breakage, thus reducing the effect of coalescence. However the process of surfactant (emulsifier) migrating to the newly created interface takes time, and is dependent on the type of surfactant and its concentration in the bulk phase(s). Very small droplets, which tend to coalesce quickly because of high capillary pressures, i.e. high surface energies in relation to their masses, are hence short lived.

The stabilizing effect of surfactants is caused by electrostatic repulsion induced by the polar or ionic portion of the surfactant at the droplet surface, and the hydration of these head groups. The electrostatic properties of the surfactant and the orientated water film, with its resultant electrostatic characteristics, have the effect of repelling other similar interfacial films and hence of reducing coalescence. This hydrate cloud must be stripped off the surface of the droplets during collision if coagulation/coalescence is to occur. Electrostatic properties of oil droplets are discussed in the following section.

The interfacial film also has physical properties of its own which discourage coalescence. For example, the stabilizing layer formed by the hydrated surfactant molecules has a viscosity which is markedly greater than that of the bulk water because of its orientated, packed structure (Glembotskii et al, 1970; Davies and Rideal, 1961, p.369). The drainage rate of the aqueous film between two colliding droplets is consequently reduced.

It is evident from the above discussion that the stabilization of the oil-in-water dispersion is dependent on the charge/polarity of the adsorbed surfactant and the extent of its hydration. Its tendency to migrate to the oil-water interface is of considerable importance and is controlled by the structure of the surfactant. Some surfactants are more oil-soluble than water-soluble and will favour a water-in-oil dispersion, i.e. they will favour being solvated by oil molecules. The resulting high surface coverage of long-chain hydrocarbon molecules impedes water-water coalescence. Each $-\text{CH}_2-$ group at the interface of each water droplet presents a 72 J barrier to the bridging of the water between two closely approaching water droplets (Davies and Rideal, 1961, p.370).

The influence of the surfactant on the process of oil dispersion is thus clearly dependent on the nature of the surfactant. Its favoured behaviour can be ascertained from its hydrophile-lipophile balance (H.L.B.) value. Davies and Rideal (1961, p.372) showed that empirical H.L.B. values have a sound theoretical basis and can be related to the coalescence kinetics of the system.

Davies and Rideal (1961, p.372) gave the empirical formula for determining the H.L.B. value from the empirically determined "Group numbers" (*ibid*, p.374) of the constituent chemical groups of the surfactant, i.e.

$$\text{H.L.B.} = \Sigma (\text{hydrophilic group numbers}) - m(\text{lipophilic group number}) + 7 \quad [2.14]$$

where m is the number of lipophilic groups ($-\text{CH}_2-$, $-\text{CH}_3$ etc.)

For MIBC, with its single hydrophilic hydroxyl group, Equation 2.14 yields,

$$\begin{aligned} \text{H.L.B.} &= 1.9 - 6(0.475) + 7 \\ &= 6.05 \end{aligned}$$

A surfactant is preferentially soluble in water if its H.L.B. > 7 . Such values are typical of ionic surfactants, where the strong hydration of the ionic head and/or its charge makes solubility in oil very limited. The H.L.B. value calculated for MIBC indicates that it is preferentially soluble in oil and will therefore favour the formation of

a W/O dispersion. However the actual dispersion formed is dependent on a number of other factors such as the means employed for dispersion, phase volumes, etc. The H.L.B. value also gives no idea of the efficiency of the surfactant (the concentration required) or of its actual effectiveness in stabilizing a dispersion.

2.2.4.1 The influence of MIBC on oil dispersion

The influence of MIBC on mean oil droplet size can be deduced by consideration of the relative rates of O/W and W/O coalescence and their relation to the H.L.B. of MIBC. The rate of coalescence is governed by both diffusional and electrical phenomena as discussed in Section 2.2.3 above. From Equation 2.13 these rates can be written as :

$$\text{Rate of coalescence of O/W dispersion} = \frac{dV}{dt} = (4\phi kT/3\eta_w) e^{-W_1/RT}$$

$$\text{or, Rate 1} = C_1 e^{-W_1/RT} \quad [2.15]$$

$$\text{Rate of coalescence of W/O dispersion} = \frac{dV}{dt} = (4(1-\phi)kT/3\eta_o) e^{-W_2/RT}$$

$$\text{or, Rate 2} = C_2 e^{-W_2/RT} \quad [2.16]$$

In a system which excludes the influence of factors introduced by means of the mechanical agitation employed, i.e. in shaken systems, an O/W dispersion is preferentially formed if

$$\frac{\text{Rate 2}}{\text{Rate 1}} \gg 1$$

The rate equations (Equations 2.15 and 2.16) can be related to H.L.B. values (see Davies and Rideal, 1961, p.374) to give

$$\ln \frac{C_1 \text{ Rate 2}}{C_2 \text{ Rate 1}} = 2.2 \omega \text{ (H.L.B. - 7)}$$

$$= -2.09 \omega \quad \text{for MIBC} \quad [2.17]$$

where ω = fraction of the interface covered by surfactant.

From Equation 2.17 it is evident that increasing MIBC adsorption enhances Rate 1 in relation to Rate 2 and so tends to reduce the stability of the O/W dispersion. A water-in-oil dispersion is therefore favoured though the minute volume fraction of oil used in flotation makes this impossible. The expected effect of MIBC is therefore to increase the mean droplet size of the oil-in-water dispersion produced.

In addition to the presence of the added frother (MIBC) other more powerful surfactants may be present in a coal flotation system, arising as trace impurities in some commercial oily collectors, particularly any with a high aromatic content. The reason for the presence of these surfactants in commercial aromatic oils is simply that powerful surfactant impurities are normally ionic and hence insoluble in strictly non-polar oils (the alkanes). Davies and Rideal (1961, p.370) have shown that the presence of powerful ionic surfactants (oil emulsifiers and detergents) in combination with alcohol surfactants (of which MIBC is an example) may greatly enhance oil droplet stability and hence oil dispersion.

The reason for this behaviour is that the ionic surfactants can pack at the interface only up to the point where the repulsion between their ionic head groups prevents further adsorption. These surfactants effectively determine oil droplet surface charge and therefore the electrostatic component of inter-droplet repulsion force. Non-ionic surfactants like MIBC however can still pack between the ionic head groups, since inter-surfactant repulsion is far less pronounced. The presence of these surfactants enhances hydration of the oil surfaces and so boosts the hydration component of inter-droplet repulsion forces. The combined presence of the two surfactant types in the interfacial film can therefore considerably reduce interfacial tension, and oil droplet coalescence rates, and reverse the W/O emulsifying tendencies of (say) MIBC. Non-ionic surfactants, like MIBC, are also resistant to the effects of the presence of counter ions which occur in aqueous solutions (see Section 2.2.5 below).

2.2.4.2 Adsorption of non-electrolytes at the oil-water interface

Non-electrolytes such as MIBC adsorb at the interface in direct proportion to their bulk concentration provided this is very low³, i.e.

$$n = \beta c \quad [2.18]$$

where n = number of surfactant molecules adsorbing per unit interfacial area

β = a proportionality constant

c = the bulk concentration of the surfactant.

At higher concentrations non-electrolyte adsorption obeys the Langmuir isotherm (Davies and Rideal, 1961, p.184), i.e.

$$n = \frac{\beta' (c/\alpha)}{1 + c/\alpha} \quad [2.19]$$

where β' and α are constants (for any one temperature).

Inspection of Equation 2.19 shows that it tends to Equation 2.18 (with $\beta = \beta'/\alpha$) as surfactant concentration, c , becomes very small. At dosages of frother normally employed in flotation, concentrations in water are very low so Equation 2.18 will be valid.

2.2.4.3 MIBC solubilities in water and oil

MIBC solubility in water (c_w) is 1.7 % (Kirk-Othmer, Vol.1, p.719). Its solubility in oil can be calculated from its H.L.B. value using the following derived equation (Davies and Rideal, 1961, p.377)

$$(\text{H.L.B.} - 7) = 0.36 \ln \frac{c_w}{c_o} \quad [2.20]$$

whence : $c_w = 0.0714 c_o$

so that $c_o = 24 \%$ (where c_o is the bulk concentration of MIBC in a non-polar oil)

³ The relationship between the extent of adsorption of a species and its concentration in the bulk (at any given temperature) is termed an adsorption isotherm.

2.2.5 Electrostatic properties of oil droplets

An appreciation of the electrostatic properties of oil droplets is important since these properties influence droplet coagulation and coalescence and hence the degree of dispersion attainable under set conditions. These properties also have a very significant influence on oil-coal adsorption which is the subject of Chapter 3. Since the electrostatic properties are influenced by the nature of the oil, knowledge of these influences could help interpret the flotation behaviour induced by particular oils. Most of the discussion on the theory behind oil-water interfacial electrostatics, which is the subject of this section, is also relevant to coal-oil, coal-air, coal-water and air-water interfacial electrostatics and will be referred to in later chapters.

Surface charge develops as a result of :

1. Ionization of ionogenic compounds at the surface.
2. Specific adsorption of ionic surface active agents.
3. Migration of ions across the interface.

The charge arising at the droplet surface is dependent on the nature of the oil itself, the type of surfactant present and the pH of the water since OH^- and H_3O^+ are often potential determining ions (Burkin and Bramley, 1961; Ralston, 1983). Potential determining ions are those capable of migrating freely between the two phases in contact. For oils containing oxygen functional groups, OH^- and H_3O^+ ions will be potential determining since they can interact with the ionization equilibria established by such groups in water. However their interaction with pure hydrocarbon oils cannot be the same, yet pH is known to affect the potential of such oils (Douglas, 1943; Wen, 1977 as reported by Ng, 1982). An explanation is offered below.

The charge developed at the oil surface is normally negative in aqueous solution since cations are more strongly hydrated than anions : the former, e.g. H_3O^+ , tend to migrate into the bulk aqueous phase while the latter exhibit a smaller tendency to do so. The result is a net gain in negative charge at the interface (Shaw, 1985, p.149). In this manner pH will affect surface charge.

Relative solubilities of ions in oil and water, as well as specific adsorption of charged surfactants, also contribute to the charge differential between oil and water. The contribution of surfactant ions to the surface charge should not be important in this testwork since only MIBC, which is a non-ionic surfactant and hence does not contribute to surface charge, was used. However aromatic type commercial oils may well contain ionic surfactant impurities which will affect surface charge.

The surface charge is generally elucidated by electrokinetic measurements, i.e. by the behaviour of the droplet under the influence of an electric field. Electrokinetic techniques measure the zeta potential (see Section 3.2.2.2) which gives a clear indication of the nature of the charge (in the absence of surfactant ions) though the magnitude of the oil surface charge may be much larger (2 to 4 times; Mackenzie, 1969) especially in solutions with a high dielectric constant.

2.2.5.1 The electrical double layer

Charges at the oil surface are balanced by the formation of an electrical layer of counter ions within the oil (if this is possible) and in the water. The resultant double layer(s) develop(s) because the

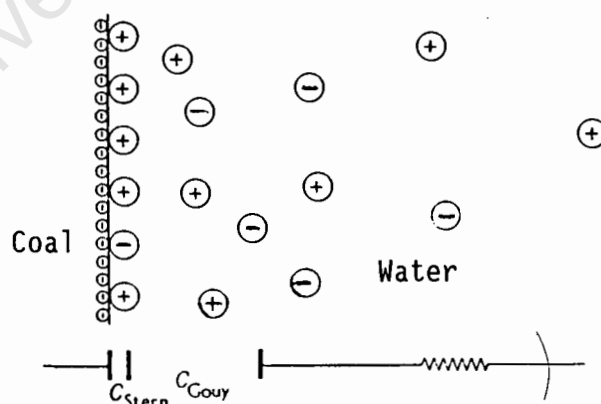


Figure 2.3 : Simple schematic representation of ions constituting the electrical double layer in the aqueous phase. (Modified from Davies and Rideal, 1961).

surface charge attracts counter ions to the liquid region near the surface while co-ions are repelled. Electroneutrality is maintained over the double layer as a whole. A schematic representation of the distribution of ions is shown in Figure 2.3.

Within a liquid phase, the double layer can be considered to consist of two regions. The inner (Stern) layer consists of rigidly held ions either directly adsorbed (de-solvated, at least in the direction of the interface) or electrostatically adsorbed and separated from the interface by solvating liquid molecules. In addition to electrostatic attraction specific adsorption of surface active ions in the Stern layer (by Van der Waals and hydrogen bonding) alters the potential at the Stern plane and may even reverse this in relation to that of the surface. The outer (Gouy) layer is diffuse and contains solvated ions which are arranged so that the ionic density decreases exponentially to that of the bulk liquid. These are "indifferent ions" since they are not specifically adsorbed. The surface and adjacent liquid phase charges are often represented (hypothetically) as a parallel plate condenser with the two opposing charged surfaces separated by a distance $1/\kappa$. This is termed the thickness of the diffuse layer. These characteristics of the double layer are represented schematically in Figure 2.4.

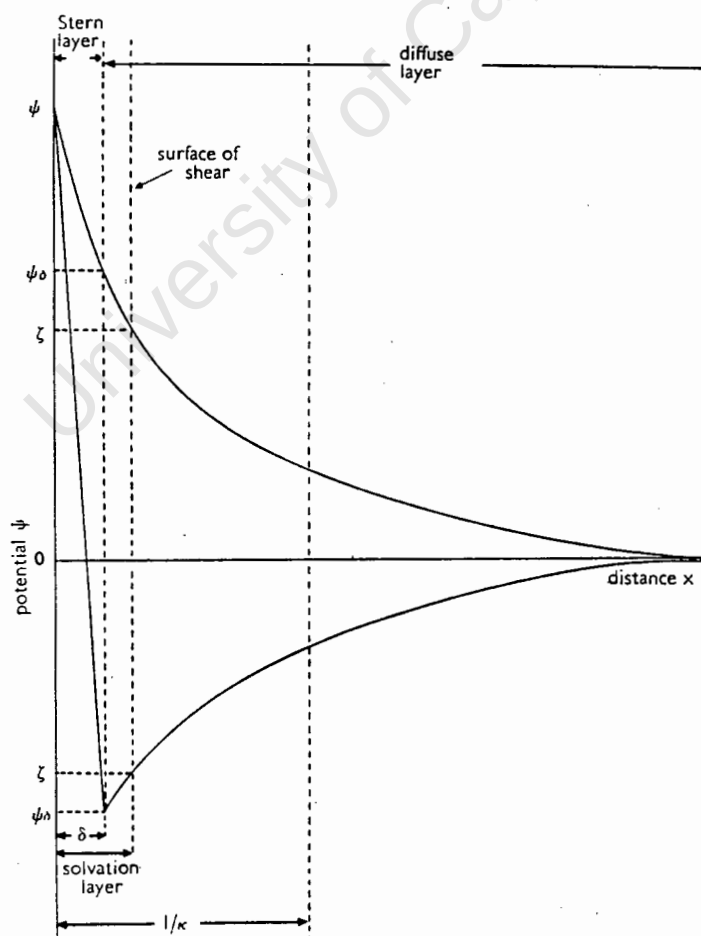


Figure 2.4 : Potential decay curves for an electrical double layer whose surface potential is ψ . The lower curve results from strong adsorption of counter ions in the Stern layer. (From Parfitt, 1967).

The potential which develops across the interface (the Galvani potential, ϕ) consists of either a distribution potential, ψ , or an interfacial potential, χ , or both depending on the polarity of the oil (elaborated below). According to classical Nernst theory, the distribution potential arises from the differences in solubility of positive and negative ions in the two liquid phases (oil and water). Unequal solubility in the two phases results in one phase adopting a negative charge in relation to the other.

Most of the potential change across the interface occurs in the phase of lower dielectric constant (the oil) (Davies and Rideal, 1961, p.60). The dielectric constant (relative permittivity) is a measure of the extent to which the medium reduces the strength of the field associated with the ions. Water which is capable of hydrating ions extensively, thereby diminishing their effective ionic fields, has a high dielectric constant (about 80), while hydrocarbon oils have a low one (about 2).

The interfacial potential, χ , is produced by either a dipole array or a charged film adsorbed or spread at the interface. The dipoles may be those of water or of adsorbed non-ionic surfactants like MIBC. The charged film would consist of ionic surfactants, either soluble (adsorbed) or insoluble (spread). The presence of charged surfactant at the interface leads to the unequal distribution of counter ions in the phase in which the head of the charged surfactant resides and this also contributes to ψ , and is usually termed ψ_0 since it is a distribution charge associated with the interface. In the testwork only a non-ionic surfactant (MIBC) was used though ionic surfactants may have been present as impurities in some of the commercial oils tested.

If the oil is highly polar, i.e. if ions will readily dissolve in it, an electrical double layer will be set up in the oil phase. The electrical double layer will compensate for the presence of the surfactant ions and dipoles at the interface by the adjustment of ion populations within the phases. The interfacial potential, χ , will then be rapidly neutralized so that the total potential drop is totally dependent on the distribution potential (Figure 2.5a).

The oils selected for this testwork are not highly polar. However, even with only slightly polar oils (like benzene) such a compensating double layer may eventually arise providing that there is sufficient oil for the required level of dissolution of the ions. The interfacial potential, χ , will then diminish with time as shown in Figure 2.5b. However, for very small droplets this may be impossible so that an interfacial potential will contribute to overall potential in these cases.

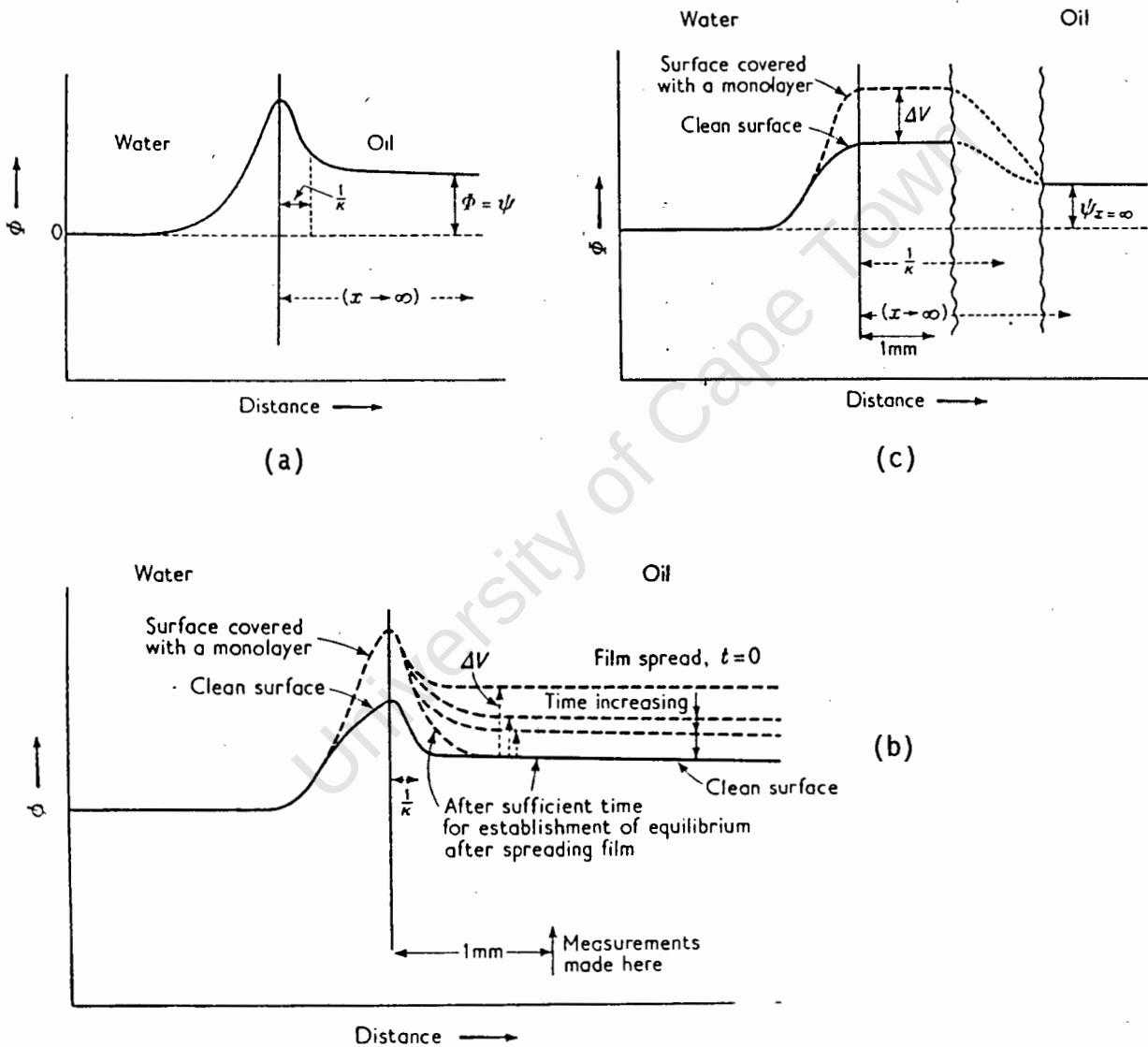


Figure 2.5 : Variation of ϕ (relative to the interior of the water phase). (a) For a polar oil. (b) For a slightly polar oil. (c) For a non-polar oil. (After Davies and Rideal, 1961).

For paraffinic oils the development of an oil phase double layer is impossible since ions are insoluble in these oils. For the

same reason the distribution potential contribution to overall potential is non-existent since all ions are insoluble. In this case the overall potential consists only of that resulting from interfacial adsorption of ionic species or dipole arrays (Figure 2.5c).

Charge or dipole accumulation or depletion at the interface is integrally related to the interfacial tensions and is quantified by the Gibbs adsorption equation, which is considered in more depth in Section 3.2.7. At this stage it must suffice to say that a net increase in the number of surface charges or dipoles will accompany a decrease in interfacial tension. Oils with low interfacial tension are expected to produce smaller droplets than those with higher interfacial tensions under the same agitation conditions.

Oil droplets (especially industrial grade oils) are known to possess a negative charge in water (Mackenzie, 1969; Ng, 1982; Mishra, 1987, p.114) which is in agreement with the theory reviewed above. Again, however, this will be dependent on other conditions. The presence of surfactant ions may enhance or alternatively diminish and even reverse the charge on the surface depending on the surfactant charge and the amount adsorbed. This action is not considered further since only a non-ionic surfactant (MIBC) was used, and this class of surfactant is typical of that used in industrial coal flotation (as frothers).

The electrophoretic data of Douglas (1943) indicates that droplets of oil containing aromatics (no surfactants) are likely to be more negatively charged/polarized than droplets of other blends. This may be ascribed to the inherent polarity of these oils. Ng (1982) reported that Wen (1977) studied high purity hydrocarbon oils and impure industrial fuel oils using an electrophoresis technique and found that the impure oils had a less negative charge than the pure oils; a result he attributed to organic impurities [evidently surface active] present in the former. Electrophoresis measurements yield the zeta potential which is similar to the Stern potential but may be quite different from the surface potential if specifically adsorbed ions or dipoles (surfactants) are present (Figure 2.4). Wen (1977) found that droplets of pure oils were all negatively charged above pH 2 while those of fuel oils only exhibited a negative charge above pH 5. The pure oils all exhibited similar zeta potentials. Douglas

(1943) found straight-chain paraffins all exhibited similar electrokinetic behaviour, being negatively charged above pH 2, indicating that their interfaces with water all have the same affinity for OH^- ions. It is therefore expected that the aliphatic oils studied in this thesis will all produce similar droplet size distributions.

Parfitt (1967) pointed out that the charged droplet with its electrical double layer(s) is as a whole electrically neutral so that no net electrostatic force exists between droplets large distances apart. Upon close approach of the two droplets the respective diffuse portions of the double layers interpenetrate giving rise to repulsive forces. However molecular forces of attraction (London-Van der Waals) increase and it is the balance between attractive and repulsive forces which determines whether droplets will coagulate or be repelled. Since attraction varies with the square of the distance between particles and repulsion decreases exponentially with distance (Parfitt, 1967, p.11), repulsive forces will dominate at intermediate distances giving rise to the energy barrier opposing coagulation (introduced in Equation 2.13 and depicted in Figure 2.6 below). A similar argument can be applied to the encounter of coal particles with oil droplets and air bubbles (see Sections 3.2.4 and 5.2.2).

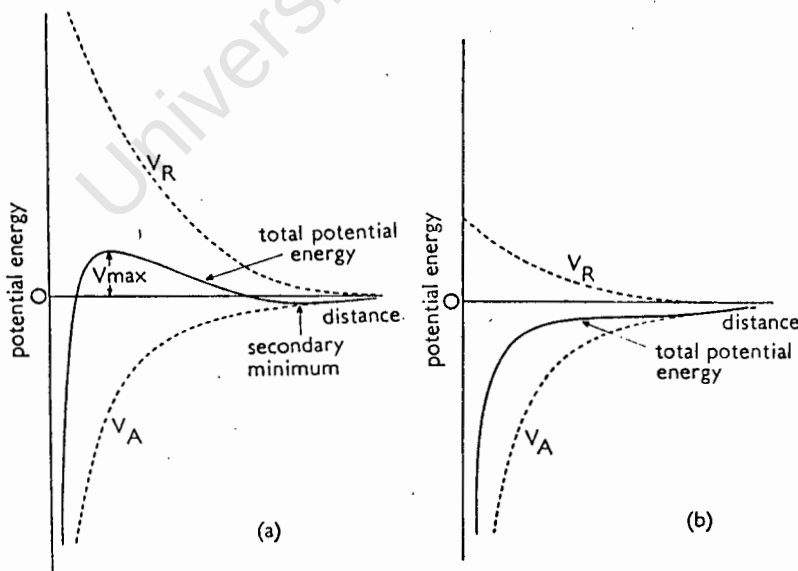


Figure 2.6 : Potential energy curves for the interaction of two charged particles, showing the balance between attractive (V_A) and repulsive (V_R) potential energies. Electrolyte strength such that (a) shows an energy barrier; and (b) attractive forces dominate at all distances. (From Parfitt, 1967).

The repulsive forces which arise as a result of the interaction of the diffuse ionic layers can be reduced by compression of the double layer, i.e. by decreasing $1/\kappa$. This may be achieved by increasing the indifferent electrolyte concentration (Parfitt, 1967, p.7; Shaw, 1985, p.153). As a result of the contraction of the diffuse layer it is possible that no potential energy barrier to coagulation may be encountered (as shown in Figure 2.6b). A similar argument would apply to air bubble-coal particle interactions and explains the success of "salt flotation" processes in which the addition of inorganic electrolytes (or the use of sea water) has been found to boost flotation performance.

Consideration of electrostatic theory shows that droplet charge is critically dependent on the types of surfactant present as well as on the type and purity of the oil phase and factors such as pH. Only a non-ionic surfactant (MIBC) was consciously added to the dispersion systems tested in this thesis. The presence of surfactant impurities in some commercial oils will however affect the surface charge, if they are ionic, which is quite likely. The contribution of such impurities to surface activity is largely unquantifiable and adds to the difficulty in interpreting experimental results. In a practical situation evaluation and maintenance of plant performance will be aggravated since commercial oil stocks are likely to differ considerably (in these terms) from oil to oil and from batch to batch.

It is evident from the above review that pH and water quality have a significant influence on oil droplet interfacial characteristics and are therefore likely to affect flotation performance considerably. pH was not adjusted in this testwork, remaining at near neutral pHs (the natural pH of the water or the coal pulp) where all the oils tested, irrespective of type or purity, are expected to possess a negative charge, though to varying degrees. Water quality (indifferent electrolyte strength) will influence the potential across the interface and the effective extent of double layer repulsion. Distilled water was used in the droplet sizing experiments. In an actual flotation situation the ions present in the pulp water would be expected to enhance oil-oil, oil-coal and air-coal coagulation.

2.2.6 Sizing of the droplet dispersions

A Coulter Counter was used for sizing droplet dispersions. The Coulter Counter principle embodied in various models has been widely used for sizing emulsions and dispersions. Nevertheless a discussion of its suitability for droplet size analyses is important since the procedure requires that the oil dispersion being investigated be transferred to an electrolytic solution and diluted considerably to enable measurement. It is therefore important to be aware of the possible consequences of these actions on the original droplet size distributions. The theory of operation of this instrument is discussed first.

2.2.6.1 Coulter Counter - theory of operation

The Coulter Counter sizes (giving the spherical equivalent) and counts particles suspended in an electrolyte. Analysis is achieved by drawing the suspension through an accurately sized aperture (in a glass aperture tube) by applying a controlled external vacuum or syphon effect. Electrodes are immersed on either side of the aperture with an appropriately selected current flowing between them through the aperture via the electrolyte.

As a particle passes through the aperture, it alters the resistance between the electrodes. (The resistivity of the particle has little effect on the response). This produces a voltage pulse with a magnitude proportional to the particle size, provided this size is between 2 and 40 % of the aperture diameter. The series of pulses generated by the passage of successive particles is electronically scaled, integrated and counted. These counts are discriminated in "size channels". The size thresholds of each channel correspond to voltage levels and are set during calibration of the instrument. Setting one channel on the Model Ta II (the instrument used) automatically sets the others. Any pulses falling below the minimum voltage threshold set are rejected, i.e. particles smaller than the minimum size threshold are ignored.

2.2.6.2 Suitability of the Coulter Counter for oil drop size analysis

Groves and Freshwater (1968) pointed out that the instrument is limited to much the same range as an optical microscope as loss of count by "shadowing" of very small particles makes accurate small particle (below $1\text{ }\mu\text{m}$) detection difficult. However the Coulter Counter has overwhelming advantages in that the number of particles which can be counted is vastly greater and analysis times are considerably shorter. Garrett (1965) emphasized that high particle counts in dispersion analyses should be considered mandatory since large droplets are few in number (and hence easily missed) but have a significant effect on total volume.

Walstra and Oortwijn (1969) found that the Coulter Counter (Models A and F) tended to broaden very narrow dispersions (so-called mono-dispersions). Coincidence effects produced broadening of similar magnitude. However these effects (elaborated below) were slight and had virtually no effect on the peak of the frequency distribution. They would not have much influence when distributions are naturally broad, as was the case with the oil dispersions investigated.

Two coincidence effects may be encountered when a Coulter Counter is used :

Primary coincidence occurs when more than one particle is in the sensing zone of the aperture tube at any instant, producing a single pulse and therefore undercounting, i.e. one of the particles is not sensed.

Secondary coincidence occurs when several droplets smaller than the counting threshold (e.g. $1.26\text{ }\mu\text{m}$ for the $70\text{ }\mu\text{m}$ tube) pass through the sensing zone together and mimic a larger particle thus boosting the count in larger size ranges.

Secondary coincidence is of course significant in instances where a large proportion of the dispersion population falls below the range of the aperture tube in use. This is one reason for employing a twin-tube technique (Section 2.3.4.2.a). As data correction is virtually impossible when coincidence is high, because of the unquantifiable nature of the coincidence effects, the Coulter Manual

suggests that concentrations be kept low and the aperture tube small (these measures largely overcome primary and secondary coincidence respectively). This was done.

Returning to the discussion on the suitability of the Coulter Counter, Sikdar and Randolph (1976) have demonstrated the accuracy of a Model T Coulter Counter used in the Population Mode. They used solid particles and 50, 100 μm and 200 μm aperture tubes. Accuracy was found over the entire operable size range of both the 50 and 100 μm tubes. Spurious counts were however detected with a 200 μm tube in the lowest three size channels (they attributed this to secondary coincidence).

Shotton and Davis (1968b) reported some researchers as having found that the dilution of emulsions with saline solution had no effect on droplet size, while others had reported the reverse. In their own investigation they diluted emulsions (1 : 250 000) using both saline solution and distilled water and found no difference in droplet size.

No change in size would occur with homogeneous (oil only) droplets as a result of changing interfacial tension *after* droplet formation since a liquid (the droplet) is virtually incompressible. Some researchers (Davis and Burbage, 1978) have reported that droplets of a multiple emulsion (water-in-oil-in-water) may change as a result of the osmotic gradient, i.e. oil droplets containing water droplets within themselves may shrink when contacted with saline solution. The dispersions investigated in this thesis are simply oil-in-water. This can be stated with confidence since very little oil was used in relation to water and multiple emulsions are in any event produced by re-emulsifying water-in-oil emulsions (Davis and Burbage, 1977).

Although individual droplet size will not change because of changes in the interfacial tension, the presence of salts could encourage droplets to aggregate. Groves (1968) pointed out that the presence of an electrolyte can be expected to reduce interfacial energy barriers and hence decrease the dispersion stability since coalescence and aggregation would be more favoured. The theory behind this is discussed in Section 2.2.5.1. When sizing oil emulsions Singleton and Brown (1965) found that the count in the smaller sizes (below 2 μm) actually increased with time. They attributed this to

aggregation of even smaller droplets caused by dilution with saline solution. Lemberger and Mourad (1965) have demonstrated that the presence of various sodium salts prevents or reduces deaggregation of aggregated hexadecane droplets, in other words aggregation is encouraged.

An opposite and disconcerting effect reported by Hallworth and Carless (1972) and Bernstein et al (1971) was the fall in droplet count when using the Coulter Counter for repeat analyses of dilute emulsions. The former worked with light petroleum and paraffin emulsions and could not explain the apparent loss of the oil satisfactorily. The latter investigated the following possible contributing effects : adsorption of the oil onto the vessel wall, volatility of the oil at high dilution, "creaming" (migrating to the surface of the continuous phase) of large drops and finally solubility of the oil in saline solution at high dilution. They concluded that the latter was the cause of count loss and reported that this could be overcome by presaturating the saline solution with the oil. Presaturation will also largely overcome any loss due to adsorption on the vessel walls. The solubility effect was however only prevalent at high dilutions.

Shotton and Davis (1968a) found that a soap (potassium laurate) concentration above the CMC (critical micelle concentration) stabilized liquid paraffin emulsions at high dilution and therefore facilitated accurate counting/ sizing. They made up a 0.11 v/v stock emulsion and diluted it 1 : 5×10^{-5} with distilled water or saline. They found dispersions with a soap concentration above the CMC to be stable even after 45 minutes while those at lower soap concentrations showed rapid count drops. Their conclusion was that emulsion droplets retained their original interfacial films upon dilution. In this regard, it appears that stabilization of emulsions requires the stabilizer (emulsifier) to be present when the emulsions are created.

Mima and Kitamori (1966) studied the stability and flocculation of oil droplets in dilute emulsions (10^{-4} % v/v). This is the same order of dilution used in testwork in this thesis. They found flocculation at such dilutions rare and that size distributions measured represented those of the primary (uncoagulated) droplets themselves. The droplet size distributions measured by the Coulter

Counter were therefore assumed to represent those found in the flotation cell (the dispersion vessel used).

2.2.7 Modelling the droplet distributions

2.2.7.1 Background

The statistical nature of mixing produces a relatively broad distribution of droplet sizes, the dispersion process being affected by both the breakup and coalescence of the drops.

In general, researchers indicate implicitly that the distributions of oil droplet sizes in dispersions or emulsions all have a single maximum, i.e. there are no secondary maxima. An exception was Sprow (1967) who reported Sullivan and Lindsey (1962) as finding (by photographic means) twin distributions in dilute emulsions. Cooper (1937) reported that volume (weight) distributions were nearly symmetrical apart from a hump (secondary maximum) in small radii produced as a result of daughter droplet formation when larger droplets were split. Nevertheless it appears that a single droplet population can be assumed, though it should be borne in mind that maxima will not manifest themselves as separate peaks unless they are 2σ apart (where σ is the standard deviation).

Mugele and Evans (1951) compared the suitability of Rosin-Rammler, Nukiyama-Tanasawa and log-normal distribution functions, in modelling droplet dispersions. The first two and especially the second were reported as being unsatisfactory. A log-normal function was found to be the most appropriate and they introduced a means of incorporating a maximum size to reduce the bias inherent in a log-normal distribution (because of its theoretically infinite maximum size). None of the three functions was suitable for modelling dispersions of droplets where the minimum size was large (200 μm).

Sprow (1967) found the Schwarz-Bezemer equation gave a good fit for the system iso-octane in salt water. This equation is :

$$\ln V \% = \ln 100 + a/d_{\max} - a/d$$

where :

- V % = cumulative volume % below diameter d;
- $d_{\max}$ = the largest drop size present;
- a = a characteristic diameter related to the distribution function maximum.

He found that $a/d_{\max}$ was independent of impeller speed and so the average droplet size was directly proportional to a and therefore to $d_{\max}$. However the other literature reviewed suggests that the Schwarz-Bezemer equation is seldom satisfactory in modelling dispersions and that it lacks a firm theoretical basis.

Herdan (1953) noted that many dispersion systems obey the arithmetical or geometrical (log) forms of the normal distribution. He indicated that materials showing a normal distribution are relatively rare and are found chiefly amongst particles produced by chemical processes, like precipitation.⁴ Brodnyan (1960) studied lattices produced during emulsion polymerization and found that radii plotted against weight (volume) produced a relationship which was normal in some cases and log-normal in others.

Normal and log-normal distributions are valuable in modelling in that they are uniquely defined by their mean and standard deviation parameters. Furthermore modelling the data by normal distribution functions is important in that in many statistical tests normality is implicit and validity of the tests therefore depends on whether a sample can be adequately represented by some form of this distribution. A log-normal distribution is also useful because it can only be positive which coincides nicely with the physical constraint of a non-negative droplet size.

Shotton and Davis (1968b) believed that all their emulsions (paraffin stabilized by potassium arabate or -laurate) obeyed a log-normal law if allowance was made for particles below the limit of the sizing apparatus (Coulter Counter). They provided a method for correcting the log-normal distribution (truncated because of an inability to measure the small sizes) to provide a more correct distribution. This was essentially done by extending the linear

⁴ For the derivation of the normal distribution, assumptions made in this derivation and the consequent applicability to particle size analysis, refer to Herdan, 1953, p.102.

portion of a log-probability plot to the truncation size to give the percentage probability undersize at this point and so allow for correction.

Groves and Freshwater (1968) reported that Troesch (1954) applied statistical theory to the breakdown of droplets under turbulent conditions and deduced that the droplet size frequency should be normal. Rajagopal (1959) derived a rigorous statistical proof of the appropriateness of the log-normal distribution. He considered randomness due to violent breakup of the liquid-liquid interface by turbulence or during cavitation, formation of daughter droplets, disruptions due to collision and to coalescence. These stages were considered as a Markoff chain. This is a discrete random process in which the probability that a system will be in a given state at the $k+1$ th trial depends only on the state of the system at the previous (k th) trial. The observed empirical applicability of a log-normal law to emulsion droplet distributions produced under turbulent and hence random conditions was hereby placed on a firm theoretical basis.

The overwhelming conclusion from a review of the literature is that a form of the normal distribution would be a likely and theoretically valid model for modelling oil-in-water dispersions.

2.2.7.2 Normal and log-normal distributions

The normal distribution function is :

$$y = \frac{1}{\sqrt{(2\pi) \cdot \sigma}} \cdot e^{(-\frac{1}{2}(x-\mu)^2/\sigma^2)} \quad [2.21]$$

where σ = the (arithmetic) standard deviation

μ = the (arithmetic) mean

The log-normal distribution function is :

$$y = \frac{1}{\sqrt{(2\pi) \cdot \ln \sigma_g}} \cdot e^{(-\frac{1}{2}(\ln x - \ln \mu_g)^2/\ln^2 \sigma_g)} \quad [2.22]$$

where σ_g = the geometric standard deviation

μ_g = the geometric mean

The normal distribution is symmetrical about its mean. Differences between the mean and the actual chance variable value are equally likely either side of the mean. The log-normal distribution is strongly positively skewed (skewed to the right) and in this case it is similar ratios of the chance variable and the mean which are equally likely either side of the mean of the distribution.

The geometric standard deviation is the deviation of the distribution of ratios around the geometric mean. Its (natural) logarithm is the standard deviation of $\ln x$.

The arithmetic mean of a log-normal distribution is related to the geometric mean as follows :

$$\mu = e^{(\ln \mu_g + \frac{1}{2} \ln^2 \sigma_g)} \quad [2.23]$$

Caution : μ and μ_g must be the same order of mean, e.g. volume means or number means.

The probability of droplets falling within a given size range (b-a) is given by the integral of the density function. For example, with a normal distribution this would be,

$$P[a \leq x \leq b] = \frac{1}{\sqrt{(2\pi) \cdot \sigma}} \cdot \int_a^b e^{(-\frac{1}{2}(x - \mu)^2/\sigma^2)} \cdot dx \quad [2.24]$$

This integral can be solved numerically or with the aid of standard normal tables.

Specially prepared probability graph paper for both normal and log-normal functions is available. Should data plotted on this paper yield a straight line it indicates that such functions might be appropriate models. A good apparent fit is however not proof that the dispersions do in fact obey the distribution function. An appropriate statistical goodness-of-fit test is required (see Section 2.5.2).

2.2.8 Summary

The mechanical agitation used to disperse oily collectors within a flotation cell leads to the formation of a large number of differently sized oil droplets. The very low oil-phase volume used in coal flotation results in the formation of an oil-in-water dispersion irrespective of the mode of conditioning, the nature of the oil or the type and concentration of surfactants present.

The pressure within any one oil droplet is greater than that in the surrounding medium since the former must balance both the external pressure and the effect of the oil-water interfacial tension. The excess pressure opposes oil droplet breakage during agitation and encourages coalescence since the overall interfacial energy is thereby reduced. Excess pressure is small for large droplets but becomes significant as their size decreases. An oil droplet $1\text{ }\mu\text{m}$ in radius will possess an excess pressure of 100 kPa (if oil-water interfacial tension is $50\text{ mN}\cdot\text{m}^{-1}$).

Oil droplets tend to coalesce as this reduces the free energy of the system. Appropriate surfactants can be used to reduce the rates of coalescence. The dynamics of surfactant migration to, and adsorption at, the newly created oil-water interface following droplet breakage implies that there is a limit to the size of droplet which can be stabilized since very small (i.e. high specific surface energy) droplets tend to coalesce too rapidly.

Surfactants reduce the rate of coalescence by lowering the oil-water interfacial tension. They stabilize the interface by promoting electrostatic repulsion and hydration effects which oppose coalescence. The surface charge on oil droplets is accompanied by the development of adjacent aqueous phase electrical double layers. The interaction of these double layers, following droplet collision, results in electrostatic repulsion. In addition, hydration of surface charges leads to water-dipole orientation and this increases the fluid viscosity in the interfacial film. This in turn restricts fluid flow from between droplets and impedes coalescence.

Oil droplet surface charge and potential control droplet coalescence and will also affect the interaction of oil droplets with a

charged coal surface. The accumulation or depletion of surface charges or dipoles is integrally related to the interfacial tension.

The surface charge on the droplet originates from adsorption of surface active ions and/or by the preferential migration of cations (such as H_3O^+) away from the interface in relation to anions (OH^-). Ionization of ionogenic species in some impure hydrocarbon oils will also contribute to surface charge. Unless an excess of cationic surfactants are specifically added, and this would be improbable in coal flotation, oil droplets will be negatively charged over the mid-pH range typically found in coal flotation.

The potential across the oil-water interface (the Galvani potential) consists of either a distribution potential or an interfacial potential or both, depending on the polarity of the oil. The Galvani potential of highly polar oils is controlled by the distribution potential since the development of an oil-phase electrical double layer rapidly counteracts the development of an interfacial potential. With strictly non-polar (paraffinic) oils the Galvani potential only consists of an interfacial potential. Both potentials may arise with slightly polar oils (such as benzene homologues), especially if the droplets of the oil are small, as their limited volume restricts the full development of an oil-phase electrical double layer.

Molecular forces of attraction (London-Van der Waals) between oil droplets dominate at close range while forces of repulsion (electrostatic) tend to exert their influence at greater ranges. The interplay of the two forces invariably leads to a potential energy barrier to oil droplet coagulation. This barrier can be reduced or even eliminated by reducing the range of electrostatic repulsion forces by compressing the aqueous-phase electrical double layer. This can be achieved by increasing the concentrations of indifferent electrolytes. These are non-potential determining ions and are not specifically adsorbed. In the context of flotation (air bubble-solid interaction) this phenomenon explains the success of salt flotation processes.

MIBC is a commonly used coal frother (surfactant). Its presence is expected to increase the size of oil droplet formed since the MIBC molecule is preferentially solvated by oil molecules rather than hydrated by water molecules. A water-in-oil dispersion is therefore

favoured though the low oil-phase volume used in coal flotation makes this physically impossible. Surfactants with a hydrophile-lipophile balance (H.L.B.) value below 7 are classed as water-in-oil emulsifiers. The H.L.B. value of MIBC is 6.05.

The use of MIBC in conjunction with an ionic surfactant may enhance oil dispersion over and above that typically induced by the ionic surfactant alone, even though MIBC alone normally induces the reverse behaviour. The ionic surfactant controls the electrostatic component of inter-droplet repulsive forces while MIBC boosts the surface hydration. The two surfactants in combination therefore retard droplet coalescence significantly.

Thorough oil dispersion is vital to the success of coal flotation but in this context it has been inadequately quantified. Oil dispersions may be readily and accurately measured by using a Coulter Counter. The instrument is incapable of measurement below a minimum size but this is very small ($1\text{ }\mu\text{m}$ or less).

The normal distribution function in its arithmetic or geometric (log) form has been used by several workers to model empirical oil dispersions and has been found to be theoretically valid in terms of the statistical nature of droplet breakage and coalescence.

2.3 EXPERIMENTAL PARTICULARS

2.3.1 Introduction

The experimental work concerned measurement of oil droplet size distributions for various oils under various agitation conditions. Temperature, pH and water quality were not altered and remained consistent for the entire set of experiments. The primary purpose of the work was to compare the oil droplet distributions of various oil types at conditions similar to those used in the flotation testwork reported in Chapter 5 (where pulp temperature, pH and water quality were not regulated).

The oils were aliphatics, aromatics or mixtures of the two types and were either pure or commercial (impure) stocks. Tests were conducted

both in the absence and in the presence of MIBC which was the frother used in the flotation testwork.

The agitation conditions investigated were long as opposed to short agitation times, and vigorous as opposed to gentle agitation. The latter conditions were controlled by altering the volume of water in the vessel (flotation cell) while maintaining a constant impeller speed, or by altering the impeller speed at a constant water volume.

2.3.2 Reagents tested

The oils used were dodecane, hexyl benzene, Shellsol K, Shellsol AB and Pegasol 3745 boiling range cuts (180-190, 210-220 and 240-250°C). Details of the properties of these oils may be found in Table 1.3 and Table 1.4 (Chapter 1). In addition blends of dodecane and hexyl benzene were made up to investigate the effect of the aliphatic/aromatic ratio on dispersion characteristics. On occasion MIBC was used in conjunction with the oils (to mimic instances where this was done in the batch flotation experiments).

All the dispersions were produced in filtered distilled water (see Section 2.3.4.1).

2.3.3 Sizing, equipment

A model Ta II Coulter Counter fitted with a Population Accessory was used for analyzing the droplet dispersions. This instrument gives the number of particles in each size range ("channel") as well as the exact volume accumulated in each channel (as a percentage of the total volume recorded). The exact volume is obtained, irrespective of particle shape, by integrating the individual electrical response for each particle to give its individual volume, and accumulating these volumes within the appropriate channel. The droplet volume distributions, given directly by the Coulter Counter, generally had a bell-shaped appearance suggesting a normal distribution.

2.3.3.1 Setup of the Coulter Counter

Two aperture tubes were used, with 70 μm and 280 μm orifice diameters respectively. Each tube has a linear measuring range from 2 to 40 percent of its actual orifice diameter. If a significant proportion of the distribution falls beyond these limits with either tube then the other tube should be used in conjunction with it.

3.07 μm standard polyvinyl toluene lattices and 19.71 μm polystyrene particles (supplied by Coulter Electronics) were used to calibrate the machine for the 70 and 280 μm tubes respectively. The "half count technique" suggested in the Coulter Manual was used for instrument calibration. The size calibration setting obtained for each tube with this technique was then adjusted so that the thresholds (particle diameters) conformed to a scale based on a 1 μm diameter and increasing by $^{3/2}$ in successive channels. (See Appendix 2.3 for calibration settings). It is important to calibrate the two tubes so that the overlap channels have the same thresholds in order to allow segments of the overall distribution obtained with each tube to be matched.

The electrolyte used was Isoton II (a proprietary saline solution from Coulter Electronics).

2.3.4 Experimental procedures

2.3.4.1 Preparation of the dispersions

A Leeds-type 3 litre batch flotation cell was used to prepare the dispersions of the oils in water (no air introduced). This was the same cell used for the batch flotation testwork (Chapter 5) so that mixing characteristics would be directly comparable.

To ensure that particle counts were restricted to those of oil droplets alone, the distilled water used in producing the reagent-in-water dispersions was filtered through 0.45 μm Millipore membrane filters. Distilled water was used since tap water blocked the membrane filters rapidly. It was also considered desirable to preclude the possible influence of any surfactants present in tap water. Batches of

distilled water were filtered each day to prevent high extraneous counts which result if the water is left for any length of time (due to micro-organism growth). (This can be prevented by u.v. radiation of the filtrate but this was not done).

Mixing of the oils in the distilled water was undertaken with volumes of water and mixing conditions identical to those used in batch flotation experiments (Chapter 5). The idea was to emulate flotation conditions in which the oils were dispersed prior to the addition of solids. Two conditions were used :

1. Oils dispersed in 1 litre of water, usually at 1200 rpm (very vigorous agitation because of the low liquid level). Dosage was 200 μ l. This corresponds to the "low level prior mixing" (11pm) conditions used in the batch flotation testwork (Section 5.3.3.4).
2. Oils dispersed in 3 litres of water, usually at 1200 rpm (mild agitation). Dosage was 400 μ l.

200 and 400 μ l dosages of oil were selected since these dosages had been used in earlier flotation testwork (Fickling, 1986). The 400 μ l dosage was not used at the lower (1 litre) mixing condition since good dispersion found at the 200 μ l dosage could reasonably be expected to apply at the 400 μ l dosage. At full cell conditions (3 litres) the higher dosage was selected when evaluating the degree of dispersion. The degree of dispersion at 200 μ l would be no better and it was felt that repeating the testwork with this dosage was unnecessary.

The oil dispersions produced were the order of 10^{-4} v/v and were diluted about 100 times with saline solution (Isoton II) for Coulter Counter analyses. Dilution was therefore of the order of 10^{-6} and hence similar to that of Shotton and Davis (1968a). These dispersions were not stabilized though Shotton and Davis suggested using a soap for this purpose. (The object of this section of the thesis was to investigate droplet sizes in a flotation cell, where such stabilizers would not be used. Stabilization by using a soap while the dispersions were created could have affected the dispersions and was therefore considered to be unfeasible).

The effects of agitation intensity and agitation time were investigated. In the former instance impeller speeds of 800, 1200 and 1600 rpm were used. In the latter instance the normal dispersion time of 2 minutes was prolonged to 5 minutes.

The collector oil was introduced to the cell using a Gilson Pipetteman and always released below the surface of the water. MIBC was added to the water with a microsyringe unless added mixed with the oily reagent. Typical dosages were $12 \mu\text{l.l}^{-1}$ of water, the dosage most often used in the flotation testwork.

2.3.4.2 Size analysis of the dispersions

Lloyd et al (1978) compared the error inherent in a Coulter Counter analysis (Model T) with that arising from sampling. Sampling errors were found to be the larger. They found that the particle counts (but not the volumes) in each size channel followed a Poisson distribution and proposed a simple test to indicate the efficiency to which the instrument is being used : The particle count standard deviation in each interval divided by the square root of the average number of particle counts for that interval should not exceed 3.⁵ Their work led them to conclude that the instrument was precise. In this thesis precision was assumed and counts were not performed more than twice on any particular sample.

A sample of the dispersion was removed with a 5 ml disposable syringe and immediately transferred to the beaker containing Isoton II electrolyte on the Coulter Counter. Depending on the particular oil used, between 1 and 4 ml of dispersion were introduced into 100 ml of Isoton II. Dilution was adjusted to ensure that coincidence levels (a function of droplet numbers - see Section 2.2.6.2) were kept below 5 % as recommended by the Coulter Counter manufacturers. Any possible change in electrolyte conductivity as a result of dilution and hence a shift in calibration was ignored.

The dispersion was stirred into the electrolyte and the mixture then analyzed. Stirring was continued during analyses with the

⁵ In a Poisson distribution the standard deviation in the counts (frequency) is equal to the square root of the average count (frequency). The ratio of the former to the latter will only exceed 3 once in every thousand experiments.

280 μm tube to prevent larger droplets "creaming". It is assumed that the droplet distributions measured were representative of the primary distributions created in the flotation cell, i.e. that no flocculation or coalescence had occurred. Mima and Kitamori (1966) found that flocculation in such dilute dispersions is rare. Nevertheless, most analyses were done immediately to minimize this possibility.

With reagents containing a significant proportion of aromatics and mixed in one litre of water, a few minutes of quiescent standing had to be allowed prior to analysis. Without this step the presence of minute air bubbles caused errors in the distribution, especially in the upper size ranges which are significant because a droplet in this region constitutes a significant proportion of the total dispersion volume. This phenomenon is illustrated in Figure 2.7 which shows the measured dispersion for a sample immediately after withdrawal from the flotation cell and the repeat analysis conducted after a few minutes of standing. The former analysis includes the air bubbles while these are absent in the latter.⁶

The standing time was sufficient to allow the air bubbles to escape but insufficient to lose larger droplets by creaming. The approximate time was determined from Stokes law assuming spherical oil droplets, i.e.

$$v = \frac{2gr^2(\rho - \rho')}{9\eta} \quad [2.25]$$

where the symbols have their conventional meaning. Air bubbles were found from trial analyses to have a diameter of 30 μm or larger (see Figure 2.7).

This standing procedure was found to be unnecessary when the reagents were dispersed in three litres of water (full cell) as air was not induced by the impeller. These "full cell" analyses provided a qualitative check on the shape of the distribution expected for dispersions created in the lesser volume (especially with regard to the existence of multiple peaks).

⁶ Air bubbles produced in the presence of aromatic oils following induction of air by the impeller, though a nuisance here, provided an inkling of why these oils have such a profound effect on coal flotation.

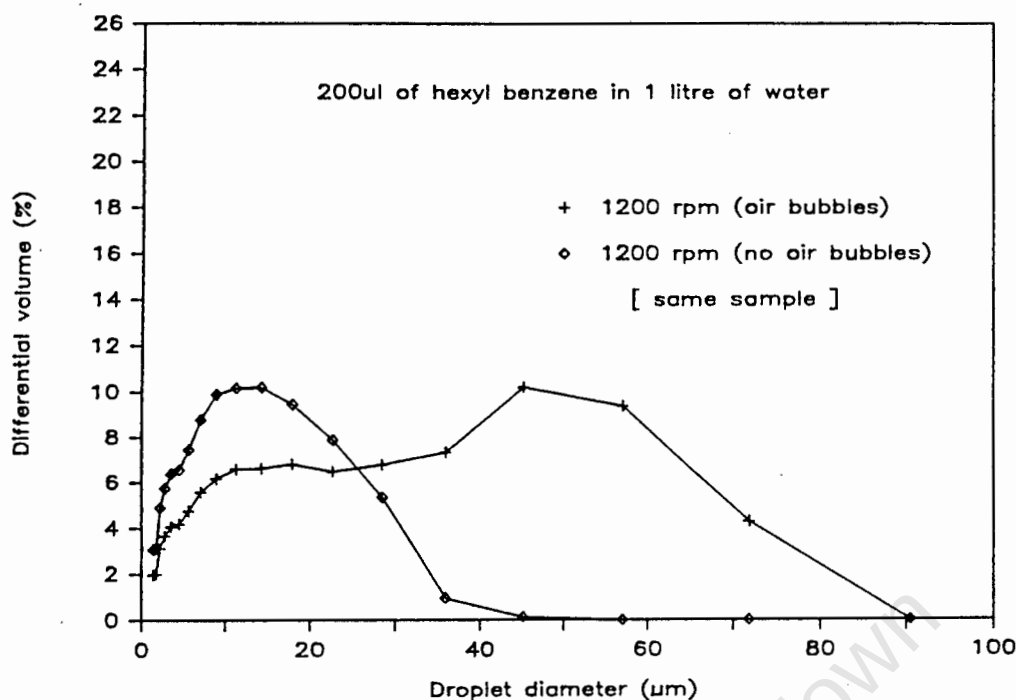


Figure 2.7 : Particle size distribution (based on volume) showing the effect of leaving the diluted hexyl benzene dispersion to stand for a few minutes prior to analysis.

The dilute dispersions were not stabilized with emulsifiers nor were saline (Isoton) solutions pre-saturated with the oil being investigated.* Some decrease in the counts, especially below three microns and above 30 μm , was noticed upon repeat analysis, particularly after the dispersions were left to stand for several minutes. The decrease in the counts in the larger sizes could be attributed to creaming and was largely overcome by continuous stirring during analysis. The decrease in the very fine sizes might be due to oil dissolution at these very low concentrations (Bernstein et al, 1971), despite the high insolubility of many of the reagents, especially the alkanes. Dissolution is enhanced if the droplets are very small as explained in Section 2.2.1.4. Fortunately particle count loss in the smaller size ranges translates to a minute loss in terms of volume. Indeed, qualitative mass balance checks (see Appendix 2.1) indicated that very little reagent (in terms of volume) was unaccounted for.

As the primary purpose of the size analyses was qualitative comparison between oils, the only precaution taken against the count

* Chiefly because of the difficulty in determining the quantity of oil to be used and of removing very small undissolved (excess) oil droplets which would affect the distributions to be measured.

loss effect was to carry out the analyses immediately after dilution with saline solution. Nevertheless, the count loss effect should be borne in mind when studying the droplet number (frequency) distributions (Section 2.6.2) as the numbers of droplets in the finer size ranges may be even greater than those indicated.

In the Coulter Counter analyses, the actual number of droplets in each size channel was recorded as well as the differential volume percent. Counts were later corrected for background (electrolyte) counts and in isolated cases for coincidental passage of droplets.

The particles (droplets) counted were assumed to remain spherical under the gentle agitation conditions used during analysis. By using the droplet numbers and the geometric mean diameter for each channel a volume very similar to that measured by the instrument could be calculated. This agreement was particularly useful when producing a complete distribution of a widely distributed dispersion, i.e. using left-hand and right-hand portions of the distribution, each obtained with a different aperture tube (twin tube technique).

a) Twin tube technique

70 μm and 280 μm aperture tubes were used. An analysis of the smaller droplet sizes (down to 1.26 μm) was done with the former and of the upper range (up to 80 μm) with the latter. It was not possible to quantitatively remove oil droplets larger than 28 μm , which is the maximum size for linear response for the 70 μm tube. However, in relation to the droplet numbers in the smaller size ranges, there were very few of these (and larger) droplets in the dispersions; and being liquid these droplets could be drawn through the aperture. In addition, allowing the diluted dispersion a short standing time prior to analysis allowed the larger droplets to cream. They were counted using the larger tube in a repeat experiment.

Sikdar and Randolph (1976), who measured particles of polydivinyl benzene latex as well as glass beads, found spurious counts in the lower 3 channels of a 200 μm tube. In the testwork reported in this chapter, the lower three channels of the 280 μm tube were not

used so the likelihood of similar errors is small, i.e. secondary coincidence (caused by very small droplets) was negligible at the $6.35\ \mu\text{m}$ threshold of the $280\ \mu\text{m}$ tube. The very small droplets far outnumbered those counted but were too small to be detected at this threshold even if several passed through the detection zone simultaneously. Nearer the $6.35\ \mu\text{m}$ threshold the number of droplets was on a par with those counted and their number to volume ratio was insufficient to produce any significant coincidence effect.

Small tube counts were made on a set volume of the dispersion-electrolyte mixture ($0.5\ \text{ml}$). By checking the analysis time ($\sim 6.5\ \text{s}$) it was possible to determine qualitatively the accuracy of the particular count run, e.g. partial blocking of the orifice by a larger particle led to longer analysis times. Size analyses with the larger tube counting was based on total droplet number rather than volume. 30 000 droplets were normally counted.

To match the two truncated distributions in order to create the overall distribution, the total number of droplets counted in the selected overlap channels (6.35 to $16\ \mu\text{m}$) by the $70\ \mu\text{m}$ tube was divided by the overlap count from the $280\ \mu\text{m}$ tube, to give a scaling factor which was then used to scale the larger tube counts,

$$\text{Scaling factor} = \frac{70\ \mu\text{m tube count in overlap channels}}{280\ \mu\text{m tube count in overlap channels}}$$

The small tube counts up to and including the $5.04\ \mu\text{m}$ threshold were used in conjunction with the scaled large tube counts from the $6.35\ \mu\text{m}$ threshold to $80.6\ \mu\text{m}$ to give a more complete population distribution. The droplet volume below the $1.26\ \mu\text{m}$ threshold was negligible (as shown by the volume distribution plots and confirmed by a mass balance on a $0.5\ \text{ml}$ sample analyzed with the $70\ \mu\text{m}$ tube - Appendix 2.1). The sub $1.26\ \mu\text{m}$ volume was thus not accounted for in the volume percentage calculations, although the Coulter Counter manual does give extrapolation techniques for determining the volume of particles below the counting threshold where such a volume is significant.

In some instances the twin tube technique was unnecessary as the volume beyond the tube thresholds was negligible or small. However if only a single tube technique was used and this volume was later found to be significant, it was estimated from the undersize obtained using the twin tube technique with a similar reagent at similar conditions.

2.4 RAW DATA EVALUATION

2.4.1 Size intervals

All the size analyses data concern size intervals rather than discrete sizes. In evaluating such data it is important to use size ranges and their respective margins with care. The following should be borne in mind when studying the results:

1. The Coulter Counter defines size ranges based on the left hand threshold, i.e. the lower size of the range in question.
2. Differential (channel) volumes and numbers were related (by choice) to the geometric mean droplet diameter of the size range (channel) in which the data was measured (though this is not strictly correct as discussed in Section 2.4.3).
3. Cumulative undersize plots must be based on the right hand threshold of the size range so that all the data acquired for the range is below this upper size.

A SIZE RANGE



Lower threshold	Geometric mean	Upper threshold
(defines size	(differential vol.	(Cumulative under
on C. Counter)	and number plots)	size plots)

2.4.2 Definition of means

$$\text{Arithmetic mean} = \sum x_i f_i / N$$

where x_i is a value of the property and f_i is the number of observations of that value. N is the total number of observations.

f_i/N tends to the probability of x_i as N tends to ∞ .

$$\text{Geometric mean} = (x_1 \cdot x_2 \cdot x_3 \dots x_N)^{1/N}$$

$$\text{or } \ln(\text{Geometric mean}) = 1/N \sum \ln x_i$$

Note : Arithmetic mean $\geq$ Geometric mean

2.4.3 Calculation of interval volumes

The volume distribution was calculated from the geometric mean diameter for each interval.

$$\begin{aligned} \text{Geometric mean diameter for interval} = \\ \sqrt{(\text{lower size threshold} \times \text{upper size threshold})} \end{aligned}$$

In retrospect it became apparent that another interval mean should have been used in some instances, e.g. for those dispersions which could be modelled by an arithmetic normal distribution function. Furthermore, Herdan (1953, p.47) reported that, when dealing with particle volume, the most appropriate mean is one of higher order, i.e. based on x^3 (x having units of length). A higher order mean more correctly represents the average volume of a large number of particles in a size interval, than does the first order mean.

Appendix 2.2 shows how the higher order mean is calculated but more importantly that the differences between the various interval means, including first and higher order means, are very small because of the comparatively narrow size intervals. As stated above, the calculations were originally based on the geometric interval mean. Because relative volumes (percentages) calculated on this basis were in good agreement with the Coulter Counter values, and in light of the very small differences between the interval means, this mean was retained as the basis of the calculations reported below.

2.5 MODELLING THE DROPLET DISPERSIONS

Fitting the experimental data to a model is useful in that model parameters provide a concise means by which to compare the various dispersions.

The distribution of droplet diameters can be based on the number (frequency), weight (or volume), surface area and so on of the droplets. The former two distributions were considered in this work. It is important to remember which type of distribution is being referred to in the discussion or when reading the literature, as the form or shape of the distribution invariably changes when going from one dimensional basis to another (as explained in Section 2.6.2.1).

2.5.1 Reduction of experimental data

For most of the oils cumulative volume undersize versus droplet diameter (right hand edge of the size interval) plotted on linear probability paper gave straight lines in the 10 % to 90 % probability region. This indicated that the data might be well fitted by a normal distribution. (Hexyl benzene was the only reagent to deviate markedly from a straight line on normal-probability paper under most of the dispersion conditions).

Beyond the 10 % and 90 % limits deviations from the straight line invariably occurred. In other words, the tails of the experimental sample distributions differed from those of a true normal distribution. However measurement errors in the left-hand tail region (very small droplets coupled with coincidence errors) and especially the right-hand tail region (where very few droplets were counted) were probably significant and these regions can be reasonably ignored when fitting a straight line to the data on normal-probability paper.

Shotton and Davis (1968b) reported that values obtained for the largest droplet sizes were subject to statistical scatter and were ignored for curve fitting purposes. Groves and Freshwater (1968) reported Drinker and Hatch as fitting curves within the 20 to 80 % probability region and ignoring points outside these marks. The scaling

of probability paper also exaggerates deviations from a straight line as 0 % or 100 % probability is approached.

The volume data periodically had to be transformed to a natural logarithm basis and this transformed data then followed a normal distribution. Straight line plots were obtained on log-probability paper.

After confirming the likelihood of fitting a normal or log-normal distribution to the data for each experiment from probability plots, the appropriate distribution function was then fitted to the data using a Nelder-Mead non-linear optimization technique. In each case the data were fitted to the function

$$Y = \frac{K_1}{\sqrt{(2\pi) \cdot K_2}} \cdot e^{(-\frac{1}{2}(X - K_3)^2 / K_2^2)}$$

where : Y is the differential volume percent

K_1 is a y-axis scaling factor

For a normal distribution :

X is the droplet mean diameter

K_2 is the standard deviation in droplet diameter

K_3 is the mean droplet diameter

For a log-normal distribution :

X is substituted by $\ln X$

K_2 is the natural logarithm of the geometric standard deviation

K_3 is the natural logarithm of the geometric mean

The sample means, $\bar{x}$ and $\bar{x}_g$, for normal and log-normal distributions respectively, were used to represent the (unknown) means μ and μ_g of the theoretical distributions. Similarly, the sample standard deviations, s and s_g were used to represent the (unknown) standard deviations σ and σ_g of the theoretical distributions.

The K - variables were optimized to give the best function fit to the data. The "best fit" criterion was based on the minimum least

squares error summation. K_1 , the y-axis scaling factor, has no influence on the mean and standard deviation of the distribution and was calculated to enable the distribution to be drawn quickly and to the correct scale in the Figures.

Care was taken when selecting the data points to reject outliers or points likely to misguide the distribution unduly. Unsatisfactory data points were usually evident on the probability plots, but the cumulative nature of these plots could be misleading in that one erroneous point might confound subsequent points.

The dispersions studied displayed a well defined maximum droplet size and so strictly speaking a truncated distribution should have been used. However the distributions in their original form gave quite adequate fits and as the primary objective of the size analyses was to make qualitative comparisons between the oils no further refinements were considered.

2.5.2 Goodness-of-fit tests

Goodness-of-fit was tested statistically in two ways :

1. Using the well-known Kolmogorov-Smirnov one sample test, which concerns agreement between an observed cumulative distribution and a theoretical continuous cumulative distribution function as shown in Figure 2.8.
2. Using a more rigorous test proposed by Stephens (1974) in which an adaption of the Kolmogorov statistic is used.

A Chi-squared distribution test was not suitable as there were insufficient values per interval. A single volume value was available for each size interval whilst the Chi-squared test requires a minimum of 5.

One aspect of Stephens's test can be used to determine goodness-of-fit between an experimental distribution and a theoretical normal distribution whose mean and standard deviation are derived from the

experimental data.⁷ This was applicable to the experiments undertaken. In applying the test the standard deviation and mean generated by the Nelder-Mead optimization technique were used.

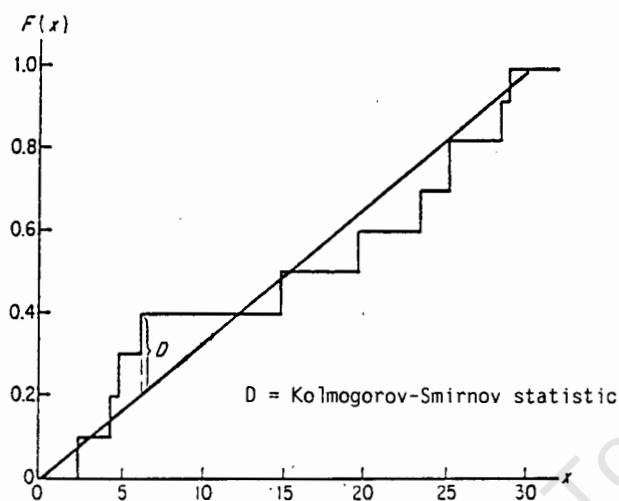


Figure 2.8 : The Kolmogorov-Smirnov test

The distributions with the most apparent (visual) deviations were tested and, with one exception, were found to be statistically acceptable fits at the 5 % significance level. The rejected distribution was that for a 20 % (v/v) mixture of hexyl benzene in dodecane which was neither normal nor log-normal. This distribution is discussed in the following section.

The tests were not applied to all the distributions. The fact that acceptable statistical fits were obtained with distributions displaying the larger visual deviations led to the implicit conclusion that the theoretical distributions were good fits in the other cases. In discussing the results, the statement that "the experimental data were well fitted by a theoretical distribution" implies statistical acceptability at the 5 % significance level.

Appendix 2.4 gives worked examples of the application of the two goodness-of-fit tests (Kolmogorov-Smirnov and Stephens) to experimental data.

⁷ Use of the experimentally determined mean and deviation is not strictly valid for the ordinary Kolmogorov-Smirnov test.

2.6 RESULTS AND DISCUSSION

2.6.1 Volume percentage distribution

Each distribution was characterized by its sample mean and sample standard deviation to give an idea of its position and spread. The log-normal curves were characterized by their geometric means and geometric standard deviations. The arithmetic means for these distributions were also calculated. The dispersion sample statistics were assumed to follow those of the true (flotation cell) population closely because aggregation and creaming were minimal and the number of droplets sampled was very large (above 30 000).

The assumption that the distributions were all normal (or could be transformed to this basis) was not always strictly true. Fortunately slight skewing had little effect on the position of the volume mean diameter; thus means and standard deviations are included for all the distributions to allow qualitative comparisons. These values are given in Table 2.1. Raw data is included in Data Appendix 2 (available on request).

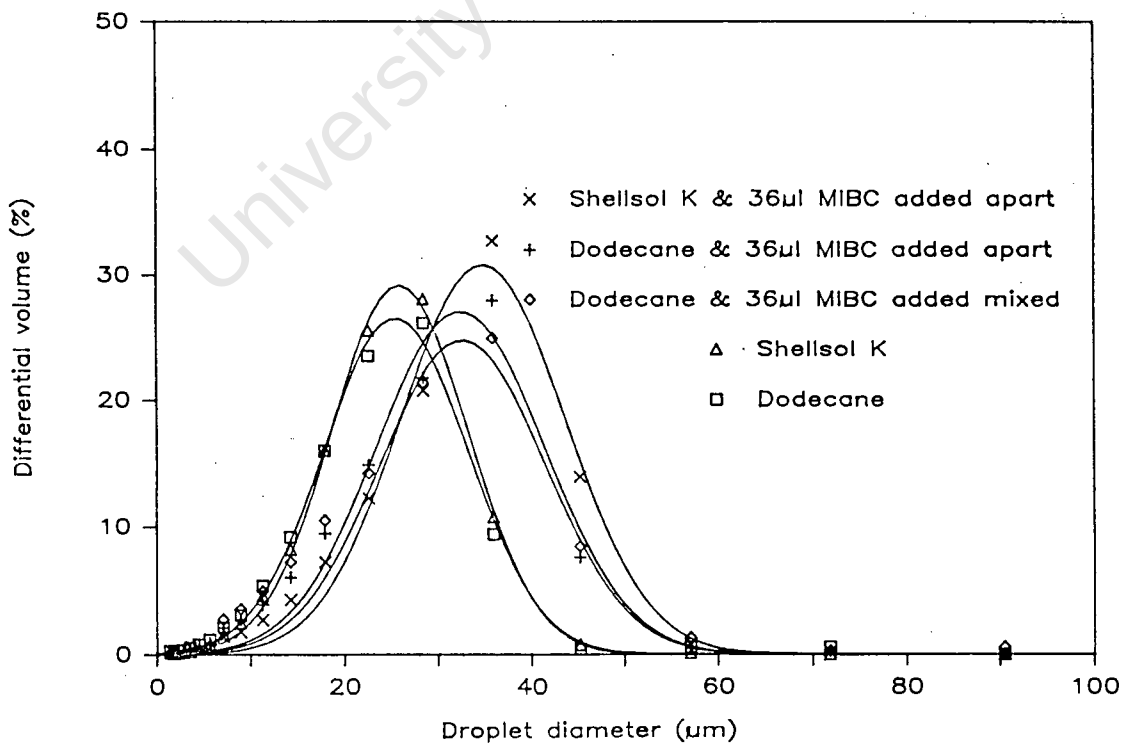


Figure 2.9 : Droplet size distribution (based on volume) for 200 µl of aliphatic oils in 1 litre of water in the presence and absence of MIBC. Impeller speed 1200 rpm. Normal distribution function fitted to empirical data points.

Table 2.1 : Characteristics of the reagent dispersions

Reagent	Agitation Time (min)	Impeller Speed (rpm)	Frother (36 μ l MIBC)	Arithmetic mean drop size (μ m)	Arithmetic std. dev. (μ m)
200 μ l of reagent : one litre of water					
Dodecane	2	800	-	42.15	12.59
Dodecane	2	1200	-	25.55	7.63
Dodecane	2	1200	yes	32.46	8.92
Dodecane	2	1200	y(mixed)	32.70	8.77
Dodecane	5	1200	-	26.64	7.18
Dodecane	2	1600	-	19.93	5.76
Shellsol K	2	1200	-	25.96	7.21
Shellsol K	2	1200	yes	34.88	8.72
Pegasol 180-190	2	1200	-	25.01	6.66
Pegasol 210-220	2	1200	-	25.86	6.71
Pegasol 210-220	2	1200	yes	32.52	8.61
Pegasol 240-250	2	1200	-	25.25	8.01
Shellsol AB	2	1200	-	22.17	8.48
Shellsol AB	2	1200	yes	18.38	9.57
10 % dod.in h.b.	2	1200	-	26.93	9.81
20 % dod.in h.b.	2	1200	-	23.42	11.32
Hexyl benzene	2	800	-	33.56	11.69

400 μ l of reagent : three litres of water

Dodecane	2	1200	-	35.45	7.53
Dodecane	2	1200	yes	34.91	8.22
Dodecane	5	1200	-	32.75	7.84
Hexyl benzene	2	1200	-	29.66	6.82
Hexyl benzene	2	1200	yes	29.94	6.81
Hexyl benzene	5	1200	-	26.59	6.38

*Log-normal distributions*200 μ l of reagent : one litre water

				Arit/Geo. mean drop size (μ m)	Geometric std.dev. (μ m)
Hexyl benzene	2	1200	-	14.79/11.25	2.10
Hexyl benzene	2	1200	yes	16.35/12.26	2.14
Hexyl benzene	5	1200	-	9.19/ 6.06	2.45
Hexyl benzene	2	1600	-	4.37/ 3.66	1.81
40 % dod.in h.b.	2	1200	-	13.92/10.14	2.22

2.6.1.1 Dispersions produced by 200 μ l of oil in one litre of water

a) Dodecane

Figure 2.9 shows that at 1200 rpm the dodecane dispersion follows a normal distribution closely. The mean dodecane droplet diameter was 25.5 μ m. The addition of MIBC, either separately or mixed with the dodecane prior to addition to the water, had the effect of increasing the mean droplet size from 25.5 μ m to 32.6 μ m. Because the volume proportion of small droplets appeared to remain reasonably constant, some negative skewing of the distribution resulted. The method of MIBC addition, i.e. independently or mixed in the oil apparently made no difference, probably because MIBC is fully soluble in either phase at the dosage levels used. Complete solubility will naturally restrict its oil-water interfacial activity.

The finding that MIBC addition increases mean droplet size was initially surprising since MIBC is widely believed to enhance oil dispersion. Experimental results obtained in this testwork show that it usually does not. This fact has been theoretically verified above by calculations based on the hydrophile-lipophile balance (H.L.B.) value of MIBC (Section 2.2.4).

The fact that MIBC is attributed with oil emulsifying behaviour probably lies in a common misconception of the action of surfactants. Surfactants induce different interfacial phenomena according to their H.L.B. values. A surfactant which is an adequate wetting agent may have little or no oil emulsifying or detergency properties if its H.L.B. value is too low. The H.L.B. value of MIBC is sufficiently low for it to be classified as a W/O emulsifier with little wetting power and certainly none of the oil emulsifying, detergency or oil solubilizing properties of the more powerful surfactants.

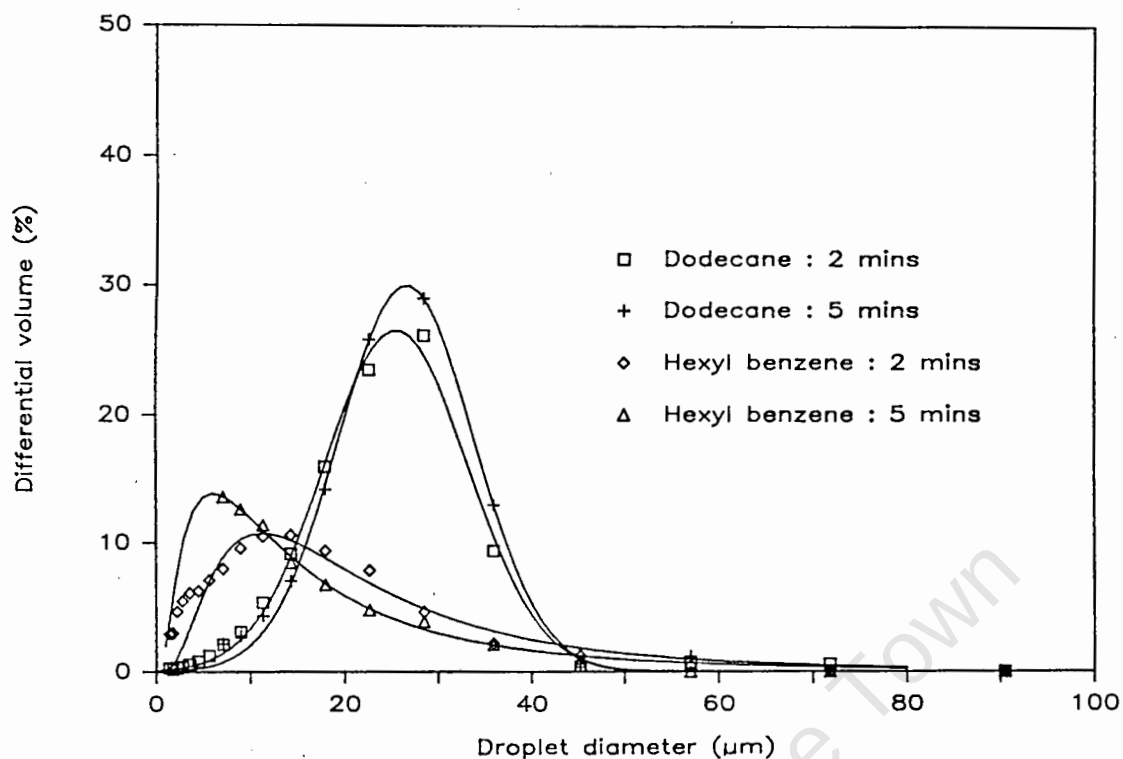


Figure 2.10 : Droplet size distribution (based on volume) for 200 μl of dodecane and hexyl benzene in 1 litre of water. The influence of agitation time. Impeller speed 1200 rpm. Normal and log-normal distribution functions fitted to empirical data points for the oils respectively.

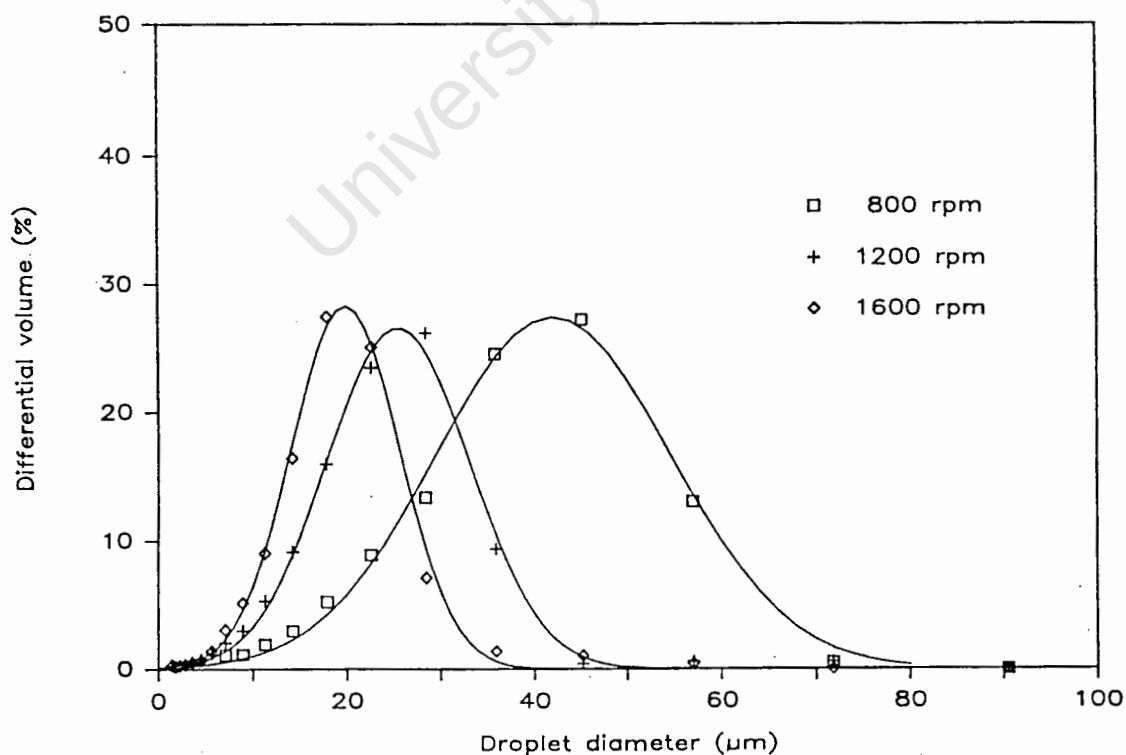


Figure 2.11 : Droplet size distribution (based on volume) for 200 μl of dodecane in 1 litre of water. Effect of increased agitation intensity on the distribution. Normal distribution function fitted to empirical data points.

Figure 2.10 indicates that increasing the agitation time from 2 to 5 minutes has no effect on the degree of dispersion of dodecane. The equilibrium droplet population has obviously been attained after 2 minutes under these agitation conditions. Figure 2.11 shows that increasing the agitation intensity, by raising the impeller speed from 800 through 1200 to 1600 rpm, decreased the mean droplet size and the spread of the dispersion considerably; as would be expected. In all cases a normal distribution fitted the experimental volume-based distribution well.

b) Shellsol K

Figure 2.9 shows that the behaviour of this industrially produced almost exclusively aliphatic oil was very similar to that of dodecane. The data fit a normal distribution well with an almost identical mean and spread to that of dodecane.

The addition of MIBC increased mean droplet size from 25.9 μm to 34.9 μm in a very similar manner to its effect with dodecane (see (a) above). There are evidently no or insufficient surfactants in Shellsol K capable of overriding the influence of MIBC. This is not surprising because powerful surfactants (oil emulsifiers) are usually ionic and hence insoluble in non-polar oils. The characteristic slight negative skewing was again in evidence.

c) Pegasol 3745 boiling range cuts

Pegasol 3745 is an industrially produced oil which is largely aliphatic (about 80 %). Figure 2.12 shows that the experimentally observed distributions of a range of boiling cuts of this oil are well modelled by normal distributions. The increasing boiling point (and viscosity) of the cuts had no effect on the mean droplet size produced under these experimental conditions though the highest boiling range cut (240-250°C) produced a slightly broader distribution.

Again the addition of MIBC produced an increase in the mean droplet size (from 25.9 μm to 35.5 μm with the 210-220°C cut) and

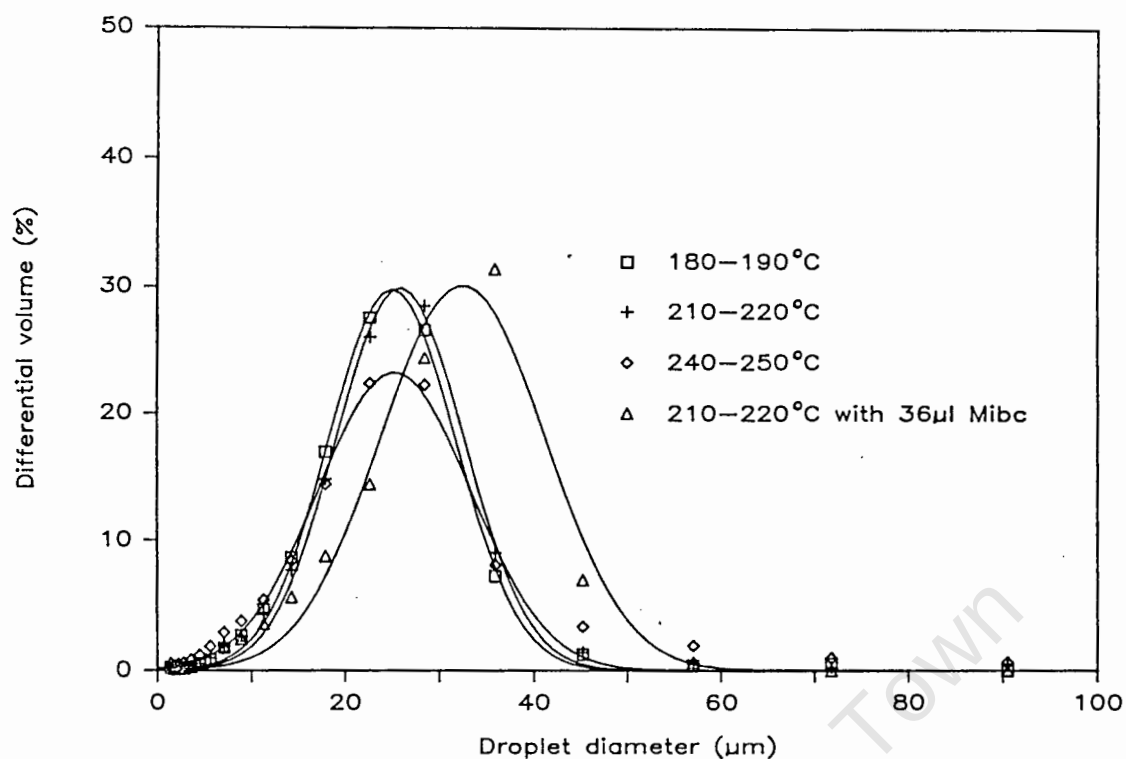


Figure 2.12 : Droplet size distribution (based on volume) for 200 μ l of Pegasol 3745 boiling point cuts in 1 litre of water. Effect of increased boiling range (and viscosity) and MIBC on the distribution. Impeller speed 1200 rpm. Normal distribution function fitted to empirical data points.

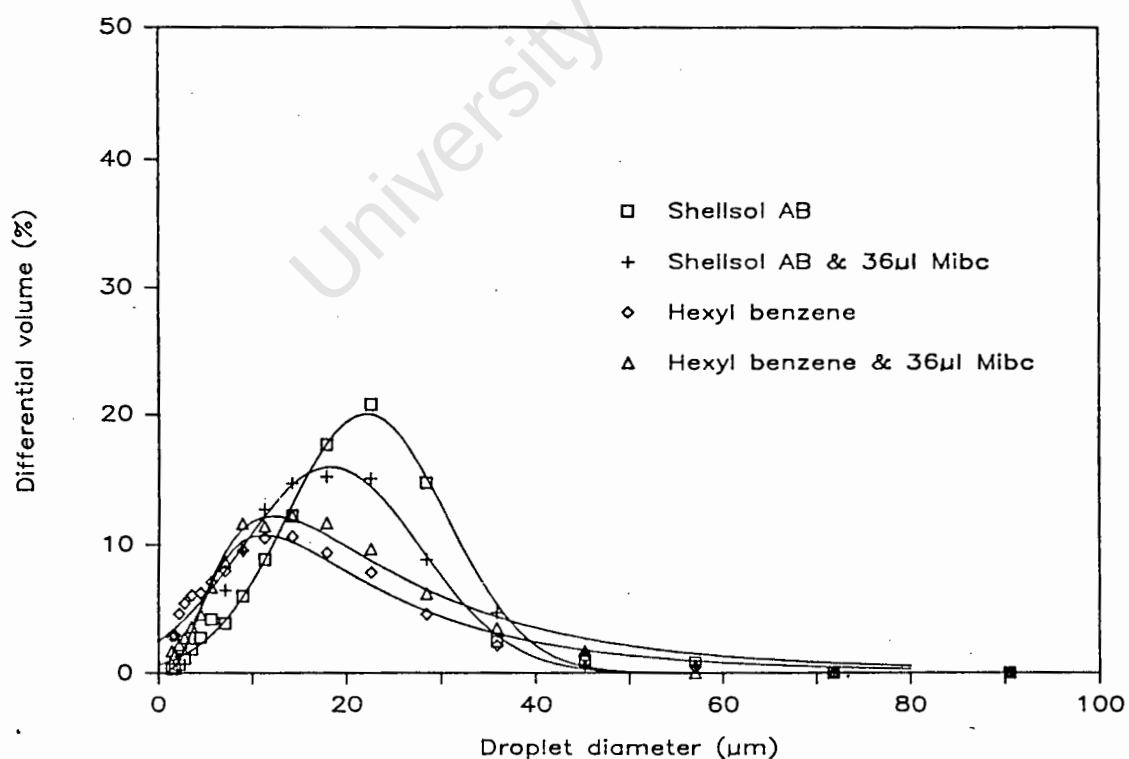


Figure 2.13 : Droplet size distribution (based on volume) for 200 μ l of aromatic oils in 1 litre of water in the presence and absence of MIBC. Impeller speed 1200 rpm. Normal and log-normal distribution functions fitted to Shellsol AB and hexyl benzene empirical data points respectively.

spread of the distribution (see Table 2.1). It is thus still the dominant surface active substance.

It is interesting to note that all the aliphatic oils used in the testwork program produced a very similar mean droplet size (based on volume), which was of the order of 25 μm in diameter. This is in accordance with the findings of Douglas (1943) that paraffins exhibit similar electrokinetic behaviour and must therefore have similar interfacial (electrical) properties.

Harkins and Beeman (1929) analysed dispersions obtained with octane and with a commercial heavy paraffin with a viscosity 150 times that of the octane. They reported that changes in oil viscosity had no significant effect on droplet size distributions (based on frequency), although a slight increase in the number of larger droplets was observed. This phenomenon was evident with the 240-250°C cut as shown in Figure 2.12.

Mullins and Becker (1956) who used peanut oil, codliver oil, glyceryl riconoleate and glyceryl trioleate also showed that the viscosity of the internal phase had no influence on size distribution. In his review, Garrett (1965) stated that providing the oil is not too polar, the nature and viscosity of the oil are of little importance to droplet dispersion or to its stability. Somewhat polar oils, like aromatics or those containing products of hydrocarbon molecule oxidation, would however be expected to have different droplet size distributions. Garrett (1965) also reported that Sherman (1964) came to a similar conclusion.

d) Hexyl benzene

Figure 2.13 shows that at 1200 rpm the droplet dispersion produced by hexyl benzene, a pure aromatic oil, is log-normal in character. The presence of a large number of fine droplets, together with the co-existence of some substantially larger ones, make this inevitable.

More small droplets were produced than with aliphatic oils since hexyl benzene is more readily dispersed, having a lower

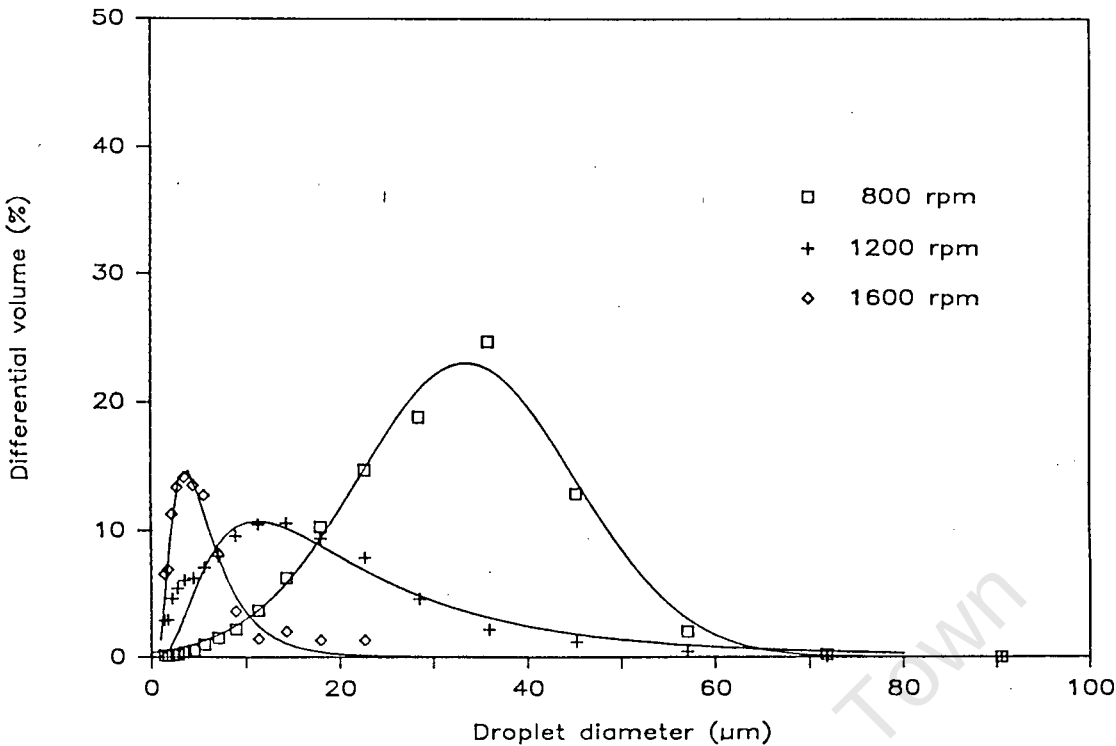


Figure 2.14 : Droplet size distribution (based on volume) for 200 μl of hexyl benzene in 1 litre of water. Effect of agitation intensity on the distribution. Normal (800 rpm) and log-normal (1200 and 1600 rpm) distribution functions fitted to empirical data points.

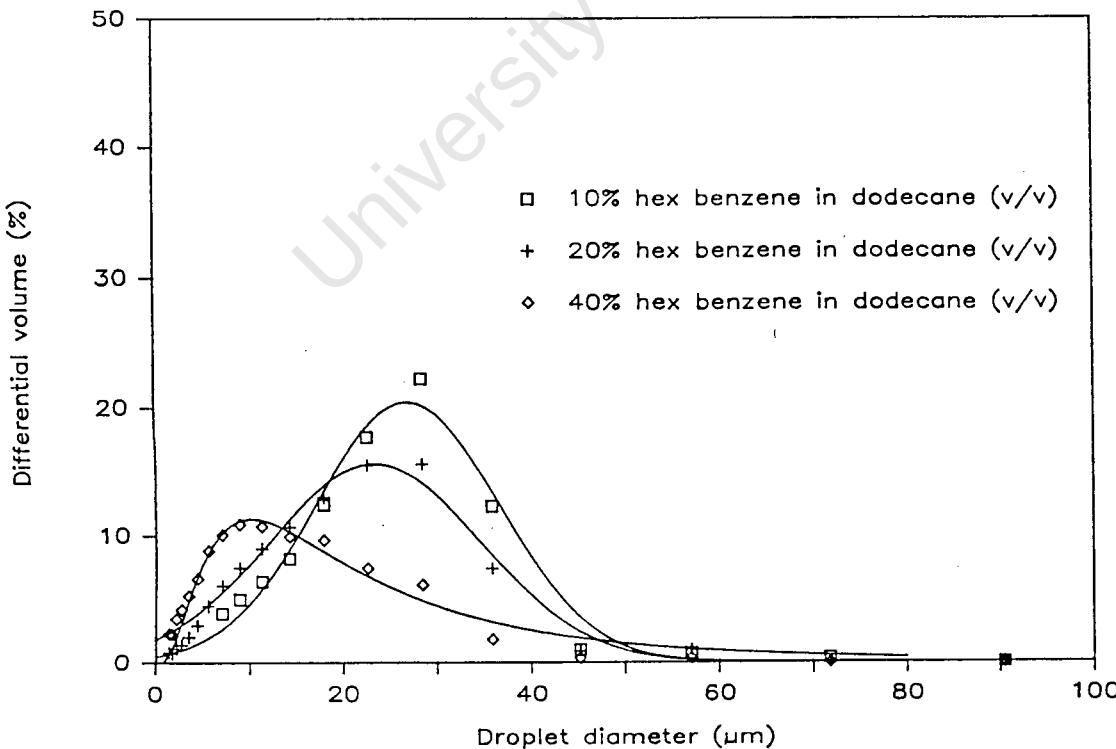


Figure 2.15 : Droplet size distribution (based on volume) for 200 μm of dodecane/hexyl benzene mixtures (in various proportions) in 1 litre of water. Effect of increasing hexyl benzene content on the form of the distribution. Impeller speed 1200 rpm.

interfacial tension (35 mN.m^{-1} compared to a typical figure of 50 mN.m^{-1} for pure aliphatics).

The existence of an appreciable number of large droplets, indicates that coalescence was also more prevalent. This is in agreement with the observations of Rehfeld (1974) who found increasing instability with an increasing spreading coefficient. Spreading coefficients can be calculated from the LHS of Inequality 2.6 using the interfacial tensions given in Table 1.4. The concurrent existence of small droplets and substantially larger ones also supports the findings of Narsimhan et al (1984) that droplet breakage is erosive rather than thorough (Section 2.2.2 above).

It is also evident from Figure 2.13 that the addition of MIBC again increased the mean size and spread of the distribution by a small amount. This is not surprising since the oil is pure and thus no other surfactants are present.

Figure 2.14, shows that decreasing the impeller speed to 800 rpm caused the distribution to become normal in character. This is because comparatively few small droplets were formed, as would be expected. At 1200 rpm deviation from normal behaviour was marked and a log-normal distribution gives an acceptable fit. At 1600 rpm the log-normal distribution provides a good approximation to the actual distribution.

Figure 2.14 also shows that hexyl benzene is very amenable to dispersion under appropriate agitation conditions; far more so than dodecane (and, by analogy, other aliphatic oils). Strong agitation at 1600 rpm produced a fine, narrowly sized dispersion with a mean size of $4.4 \mu\text{m}$ in contrast to one of $19.9 \mu\text{m}$ for dodecane. Figure 2.10 shows that increasing the agitation time from 2 to 5 minutes (at 1200 rpm) also improved the approach to the theoretical log-normal distribution and reduced the [arithmetic] mean droplet size from 14.8 to $9.2 \mu\text{m}$. Hexyl benzene clearly does not attain its equilibrium dispersion population within two minutes at 1200 rpm, though the distribution is not too far removed from the equilibrium one.

e) Shellsol AB

Figure 2.13 shows that this largely aromatic (more than 95 %) commercially produced reagent oil gave rise to droplet distributions which are normally distributed. This is in contrast to the pure aromatic, hexyl benzene, which produced dispersions which are log-normally distributed (see (d) above). This indicates that Shellsol AB was either not as readily dispersed as hexyl benzene, or was more prone to coalescence.

According to the findings of Wen (1977) (discussed in Section 2.2.5.1 above), pure hexyl benzene is expected to possess a greater surface charge since it is pure, than Shellsol AB which is impure. Hexyl benzene will therefore be more resistant to coalescence and smaller droplets will persist. Differences in droplet size distributions can apparently not be attributed to differences in the viscosities of these oils. Garrett (1965) stated, after reviewing the literature, that oil viscosity has little influence on dispersion, and that oil surface tension is of secondary importance to the influence of surface-active species (at the oil-water interface) in this regard.

It is possible that under marginally increased agitation conditions the distribution of Shellsol AB would be similar to that of hexyl benzene. The sensitivity of aromatic oils to agitation conditions is clearly shown in Figure 2.14.

Also in contrast to hexyl benzene behaviour was the fact that MIBC addition reduced the average droplet size of the Shellsol AB dispersion, though the distribution still increased in spread. These two factors together led to the data having more of a log-normal distribution in the presence of MIBC (imposed by the physical impossibility of a negative droplet size : the left hand side of the distribution fitted tended to negative values).

Shellsol AB was the only reagent for which MIBC addition reduced droplet size. According to the theory discussed above this must be a result of the presence of surface-active impurities. These are evidently present in sufficient quantities to overcome the comparatively weak surface activity of MIBC and its tendency to hinder oil dispersion. A further possibility is that the joint action of powerful surfactant impurities (which are particularly prevalent in commercial oils with a high aromatic content such as

Shellsol AB) and MIBC will further boost the dispersive action of the surfactant impurities, as explained in Section 2.2.4.1.

f) Hexyl benzene and dodecane mixtures

Increasing proportions of hexyl benzene mixed in dodecane produced progressively larger deviations from a normal distribution as shown in Figure 2.15. This shows conclusively that the nature of the dispersion formed is strongly dependent on the oil type, in addition to the influence of any intrinsic oil-sourced (or additional) surfactants. 10 % (v/v) hexyl benzene in dodecane produced a dispersion which is normal in character with much the same mean as pure dodecane but somewhat more spread (comparatively more small droplets). Deviation increased with the 20 % mixture and with 40 % hexyl benzene a log-normal distribution is evident, the mean and standard deviation being very similar to that obtained with pure hexyl benzene (see Table 2.1).

The dispersion produced with the 20 % mixture shows considerable deviation from the theoretical normal distribution. In fact the fitted distribution predicts negative droplet sizes; and was rejected by the statistical goodness-of-fit tests (see Appendix 2.4). Figure 2.15 clearly shows that the 20 % dispersion was an intermediate between normal and log-normal distributions.

2.6.1.2 Dispersions produced by 400 μ l of oil in three litres of water

Under the less turbulent conditions inherent in a full flotation cell (containing 3 litres of water) mean droplet sizes were somewhat larger than those obtained when mixing the oils in only one litre of water at similar impeller speeds; as expected. Figures 2.16 and 2.17 show that both dodecane and hexyl benzene produced dispersions which are well fitted by normal distribution functions. The behaviour of hexyl benzene is not surprising in that mild agitation conditions (800 rpm) are already known to induce dispersions which are normal in character (Figure 2.14).

After two minutes of agitation time, the mean droplet size of the hexyl benzene dispersion was not markedly smaller than that

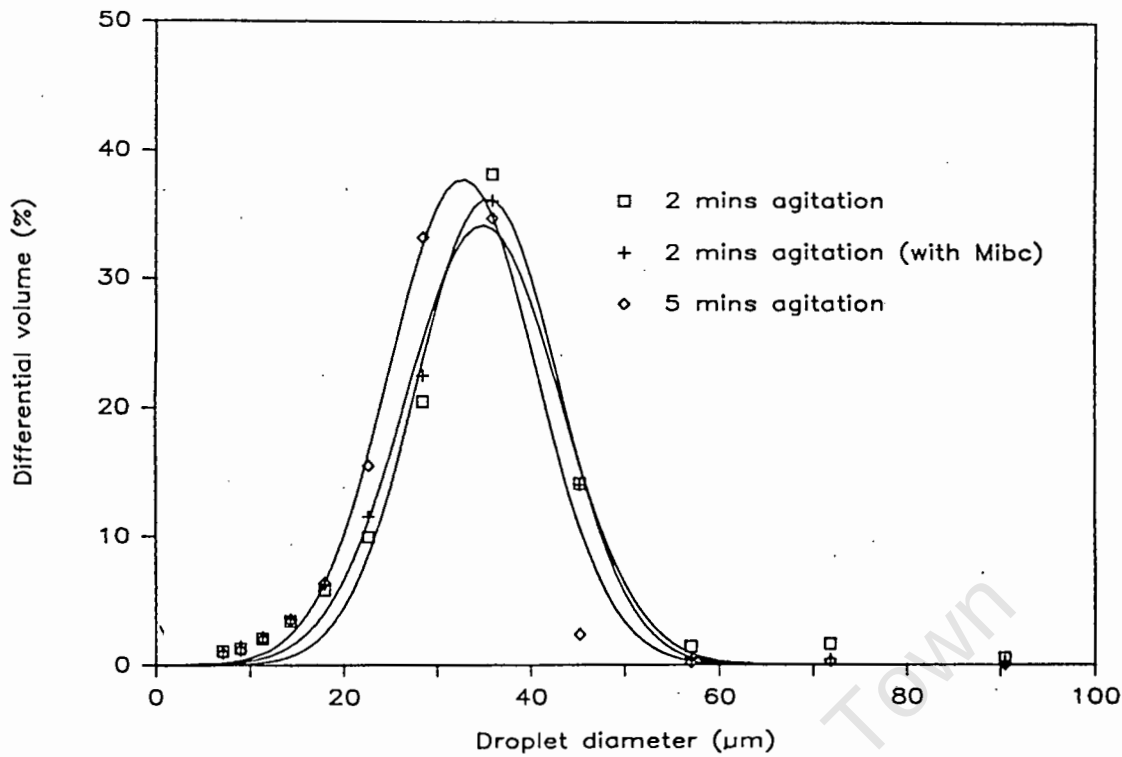


Figure 2.16 : Droplet size distribution (based on volume) for 400 μl of dodecane in 3 litres of water. Effect of agitation time and the presence of MIBC on the distribution. Impeller speed 1200 rpm. Normal distribution function fitted to empirical data points.

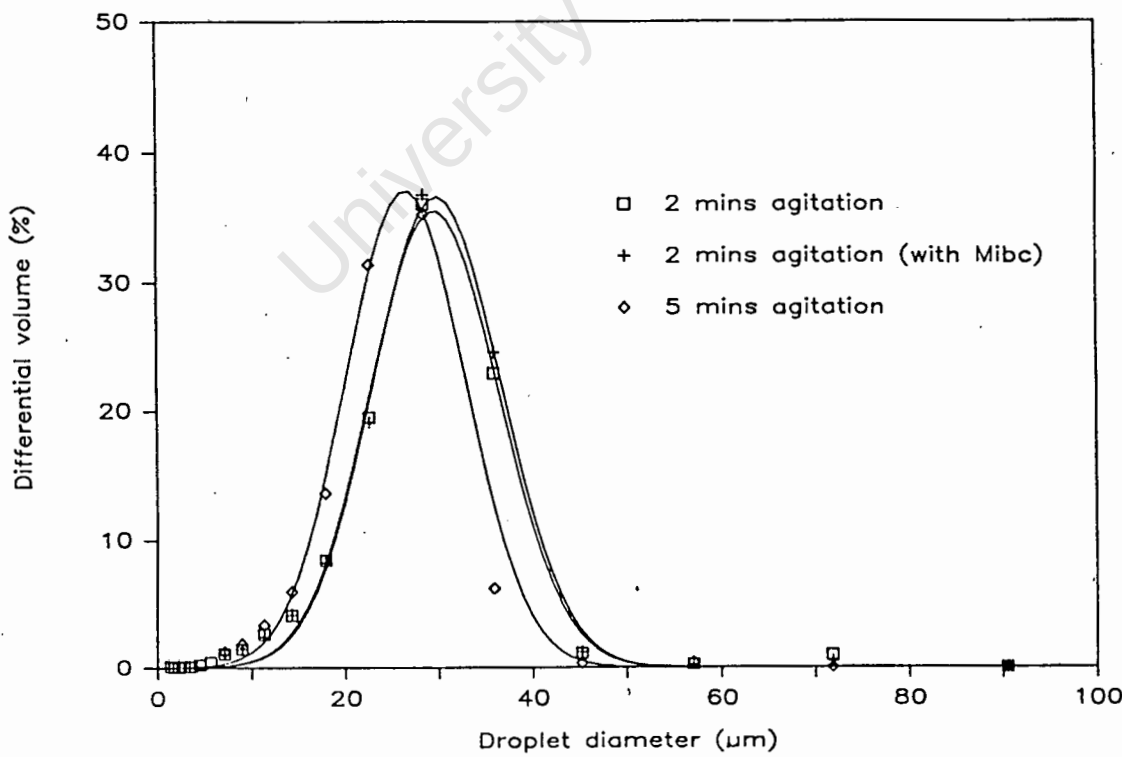


Figure 2.17 : Droplet size distribution (based on volume) for 400 μl of hexyl benzene in 3 litres of water. Effect of agitation time and the presence of MIBC on the distribution. Impeller speed 1200 rpm. Normal distribution function fitted to empirical data points.

obtained with dodecane (30 and 35 μm respectively). The difference in mean size can be ascribed to the difference in interfacial tension. Increased agitation time (from 2 to 5 minutes) lowered the mean droplet sizes somewhat but the distributions remained similar in all other respects. The small reduction in size following prolonged agitation indicates that the dispersions of both oils had approached their equilibrium distributions after two minutes of agitation.

The size deviation (spread) of the dodecane distributions is similar to those obtained in the tests in which 200 μl of oil was added to 1 litre of water (Section 2.6.1.1.a above). The hexyl benzene spread cannot be compared as the form of the distribution has changed. The presence of MIBC had no apparent effect on the dispersions and certainly did not aid in dispersing the reagent oils. Since the more gentle agitation conditions tend to disperse the oils less, an effect which MIBC generally supports, the overall result was that the influence of the MIBC in increasing droplet size was not patently manifested as it was under more vigorous agitation conditions.

2.6.2 Droplet number distributions

So far all the distributions discussed have been based on droplet volumes. It is obviously possible to represent droplet size distributions in terms of surface area, number, etc. Volume-based distributions can be misleading in that they create the impression that most droplets are of the order of the mean (volume) size, which is not true at all. Figures 2.18 to 2.25 represent the same dispersions already discussed but their distributions are now based on droplet frequency. Points of difference will be emphasized in this section.

These differential number distributions all show the very large number (millions) of reagent droplets to be found in every millilitre of pulp water at the dosage levels used. 200 μl of reagent per litre of water corresponds to a dosage of about 2850 g.tonne^{-1} of coal (5 % solids m/m); and 400 μl of reagent in three litres of water corresponds to about 1900 g.tonne^{-1} of coal (5 % solids). They also show that in terms of frequency, very small droplets dominate the dispersions.

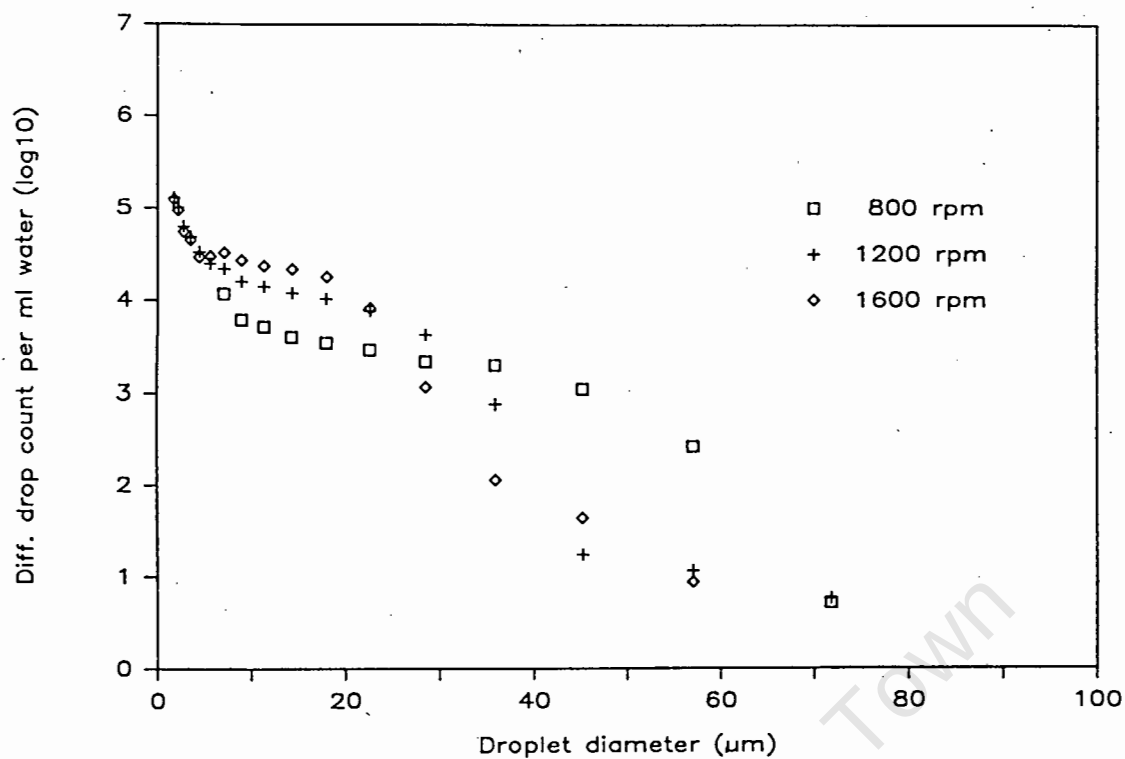


Figure 2.18 : Droplet size distribution (based on frequency) for 200 μl of dodecane in 1 litre of water. Effect of increased agitation intensity on the distribution.

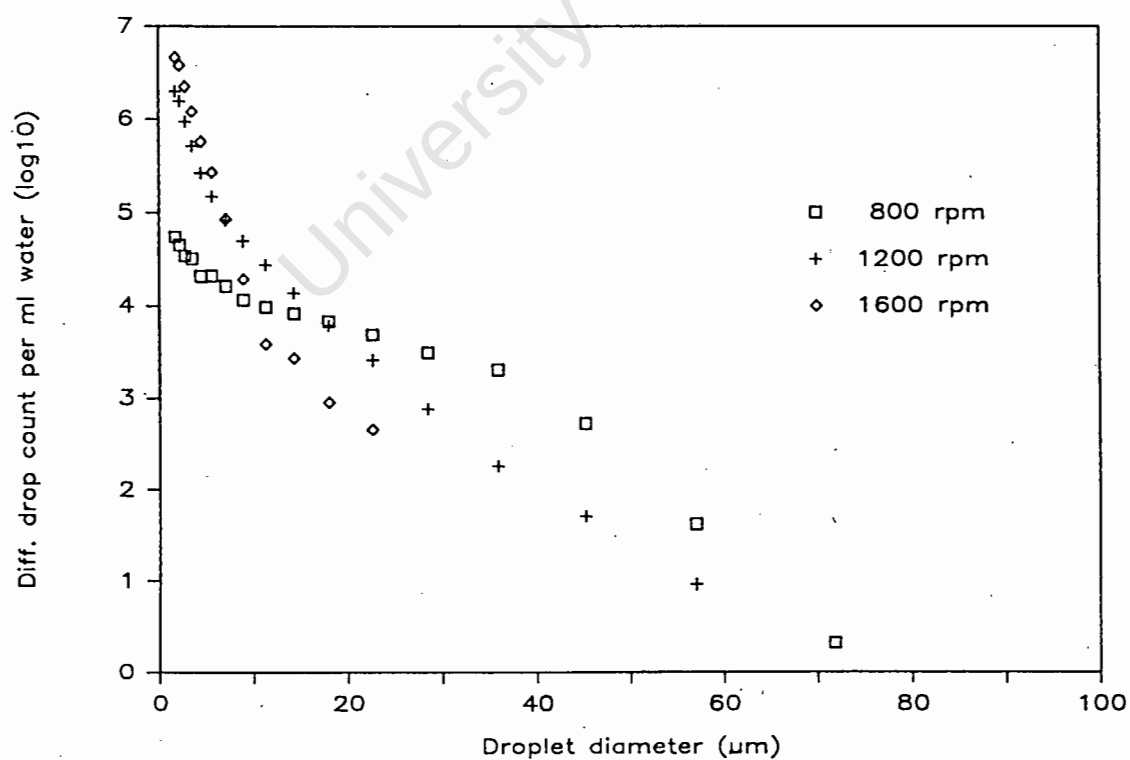


Figure 2.19 : Droplet size distribution (based on frequency) for 200 μl of hexyl benzene in 1 litre of water. Effect of agitation intensity.

The numbers of droplets below the $1.26\text{ }\mu\text{m}$ threshold were probably very large although their cumulative volume was insignificant. This was based on the extrapolation of the number distribution plots and bearing in mind a possible minimum droplet size of the order of $0.1\text{ }\mu\text{m}$ or less (Garrett, 1965, Groves and Freshwater, 1968).

All the frequency distribution figures also emphasize the importance of counting a very large number of droplets in a size analysis of an oil dispersion. Only 10 or so of the largest droplets normally exist amongst the millions of droplets found in each millilitre of pulp water. However their contribution to the volume distribution is important. Some counting techniques, such as those done by microscope, may therefore result in erroneous volume distributions if such large droplets are missed or if too many are coincidentally present in the small sample volume being analysed.

Figures 2.18 and 2.19 clearly show the increase in droplet numbers in the smaller size ranges with increased agitation intensity (impeller speed) in tests with dodecane and hexyl benzene respectively; as expected. The number of droplets increased by at least an order of magnitude as impeller speed was increased from 800 to 1600 rpm. The increase was most marked for the aromatic reagent.

A comparison of Figures 2.20 and 2.21 with Figures 2.22 and 2.23 shows the difference in droplet numbers when reagents were dispersed in three litres as opposed to one litre of water. At the latter condition where agitation was that much more intense (for the same impeller speed) the numbers of droplets were at least two orders of magnitude greater. (Dosage at high intensity conditions was 1.5 times (per litre of water) that at the low intensity conditions). On this basis the milder agitation conditions would be expected to yield poorer flotation results since the oil is more poorly distributed. Nevertheless the cumulative number of droplets per millilitre is still large so that actual in differences flotation performance may not be great.

It is evident from the form of the number distributions that the arithmetic normal distribution function cannot be used to represent them. However those oils which obeyed a log-normal volume distribution (hexyl benzene and mixtures in which its proportion was high) appear to do so in terms of droplet number. Consider Figure 2.24 for example. The number of hexyl benzene droplets rises steadily towards a maximum.

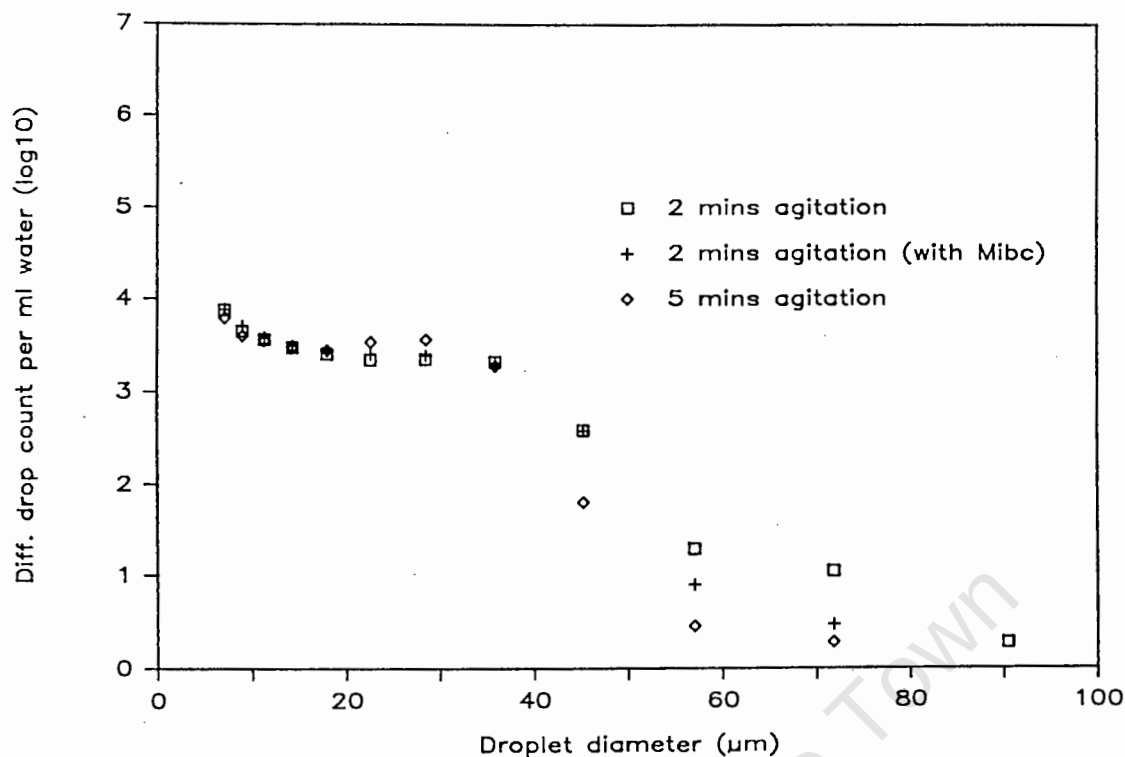


Figure 2.20 : Droplet size distribution (based on frequency) for 400 μ l of dodecane in 3 litres of water. Effect of agitation time and the presence of MIBC. Impeller speed 1200 rpm.

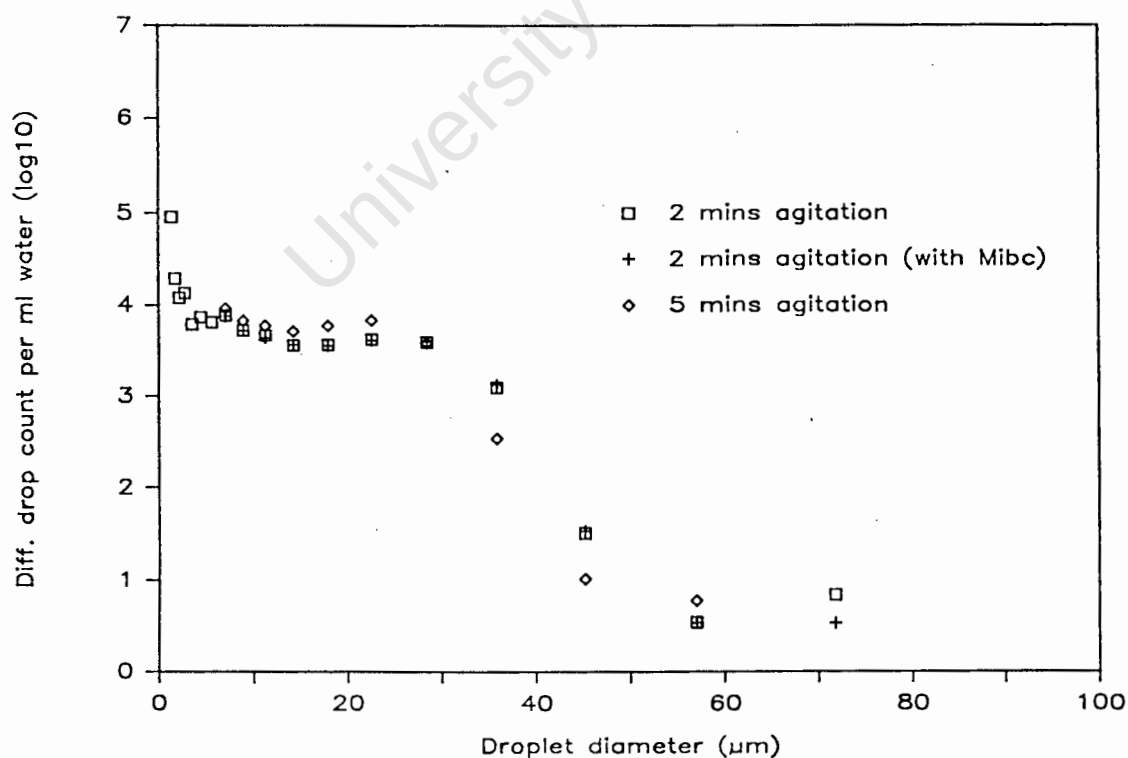


Figure 2.21 : Droplet size distribution (based on frequency) for 400 μ l of hexyl benzene in 3 litres of water. Effect of agitation time and the presence of MIBC on the distribution. Impeller speed 1200 rpm.

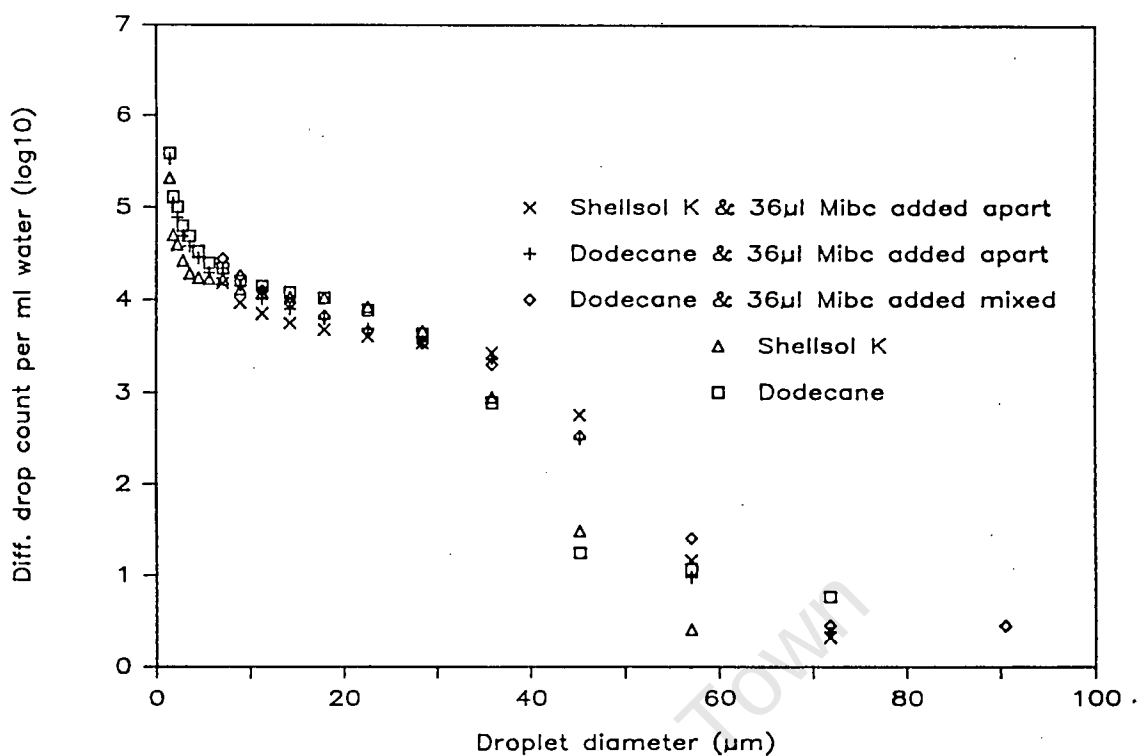


Figure 2.22 : Droplet size distribution (based on frequency) for 200 μ l of aliphatic oils in 1 litre of water in the presence and absence of MIBC. Impeller speed 1200 rpm.

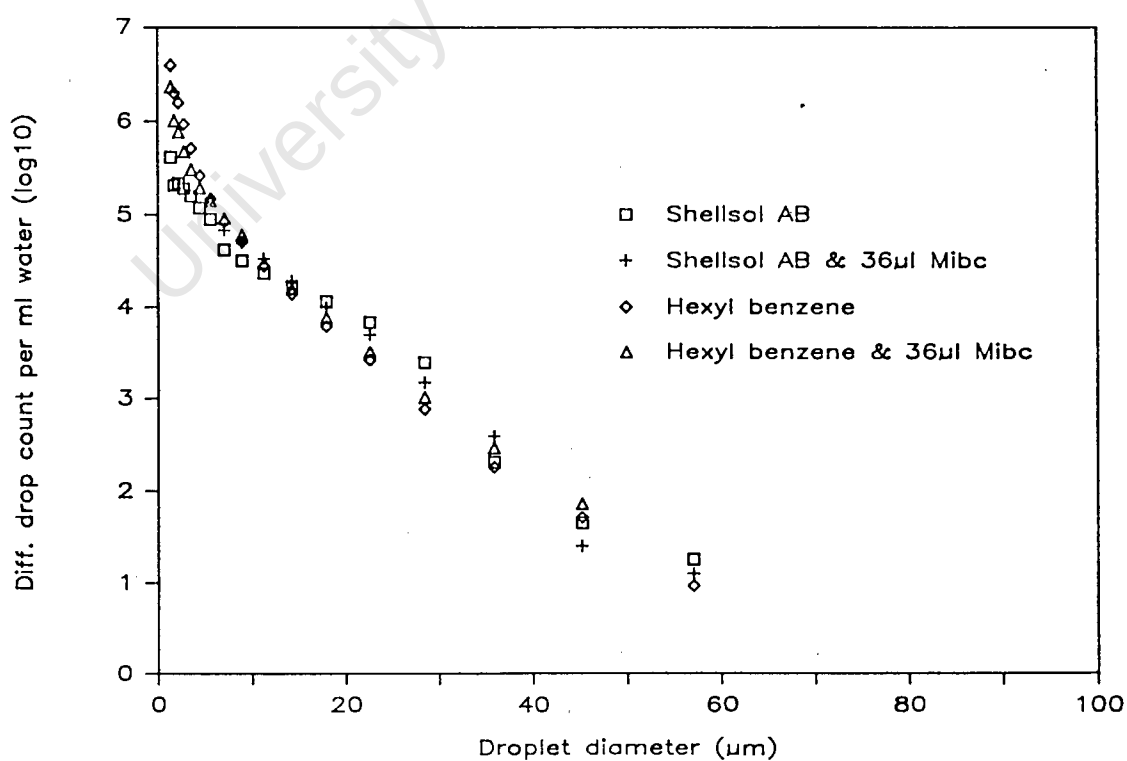


Figure 2.23 : Droplet size distribution (based on frequency) for 200 μ l of aromatic oils in 1 litre of water in the presence and absence of MIBC. Impeller speed 1200 rpm.

Although this experimentally measured maximum is very near to the vertical axis, and the true population maximum may yet be higher, the distribution must inevitably reach a maximum and then drop sharply to some minimum positive value since a negative droplet size is physically impossible. The distribution can thus be envisaged to be log-normal in character with the distribution mean at some very small droplet diameter. In contrast the dodecane frequency distribution displays a distinct S-shape. This characteristic shape was found with all the oil dispersions displaying normal (volume-based) distributions. The frequency-based distributions of the Pegasol 3745 boiling range cuts provide more examples of this shape (Figure 2.25). While an arithmetic normal frequency distribution is clearly not possible, the existence of the S-shape also precludes the possibility of the experimental frequency data conforming to a log-normal distribution.

Frequency distributions are indeed log-normal if the volume distributions are log-normal. This can be concluded, as may the fact that the normal distributions based on volume will no longer be normal if based on another dimension, from a knowledge of Kapteyn's transformation.

2.6.2.1 Kapteyn's transformation

In the derivation of the normal distribution function it is assumed that the small causes (that affect dispersion in this case) are independent of the object (the oil drop) on which they may or may not act. However a cause which acts by chance alone with regard to, say, volume will no longer be completely independent of the object (oil droplet) if the dimension is changed, i.e. if the distribution is weighted differently.

Kapteyn introduced a form⁸ of the normal law which would be unaffected by changes in the powers of the variable by using a transformation of the variable, x , i.e. $z = (x + k)^q$. The log-normal distribution is a special case of this transformation. Therefore if a distribution obeys a log-normal law in one dimension it will do so in all other dimensions (powers of the variable) and furthermore will retain the same geometric (log) standard deviation.

⁸ The complete distribution is given in Herdan, 1953, p.120.

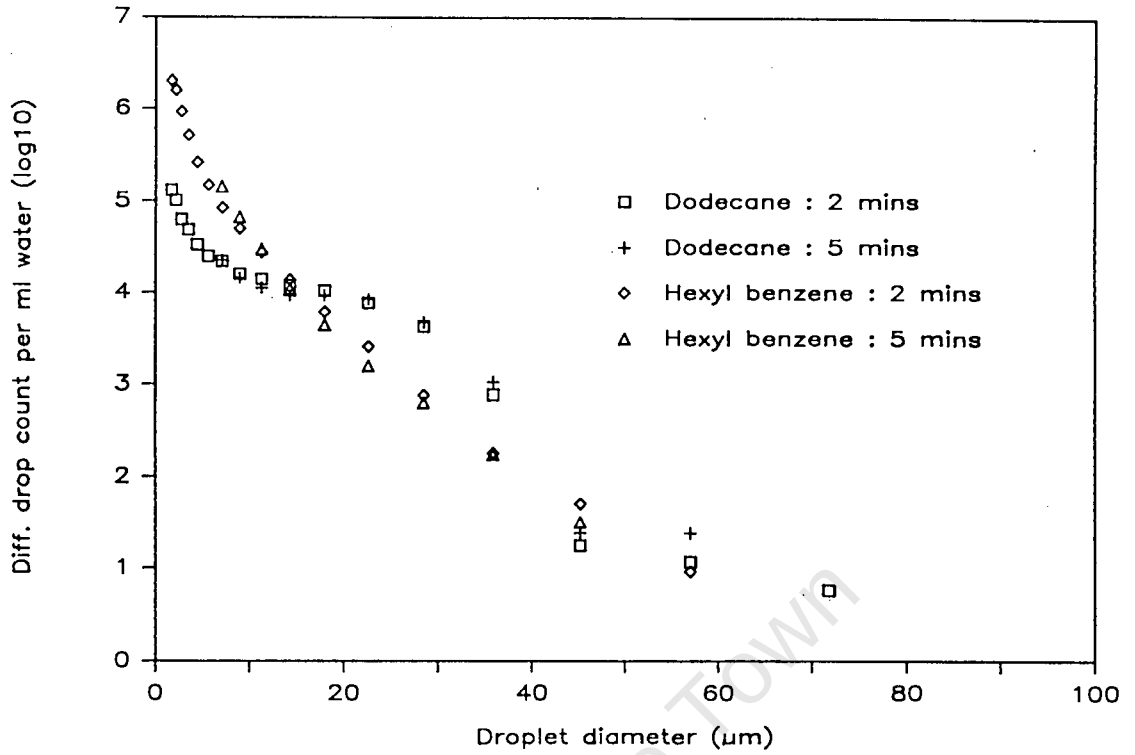


Figure 2.24 : Droplet size distribution (based on frequency) for 200 µl of dodecane and hexyl benzene in 1 litre of water. The influence of agitation time. Impeller speed 1200 rpm.

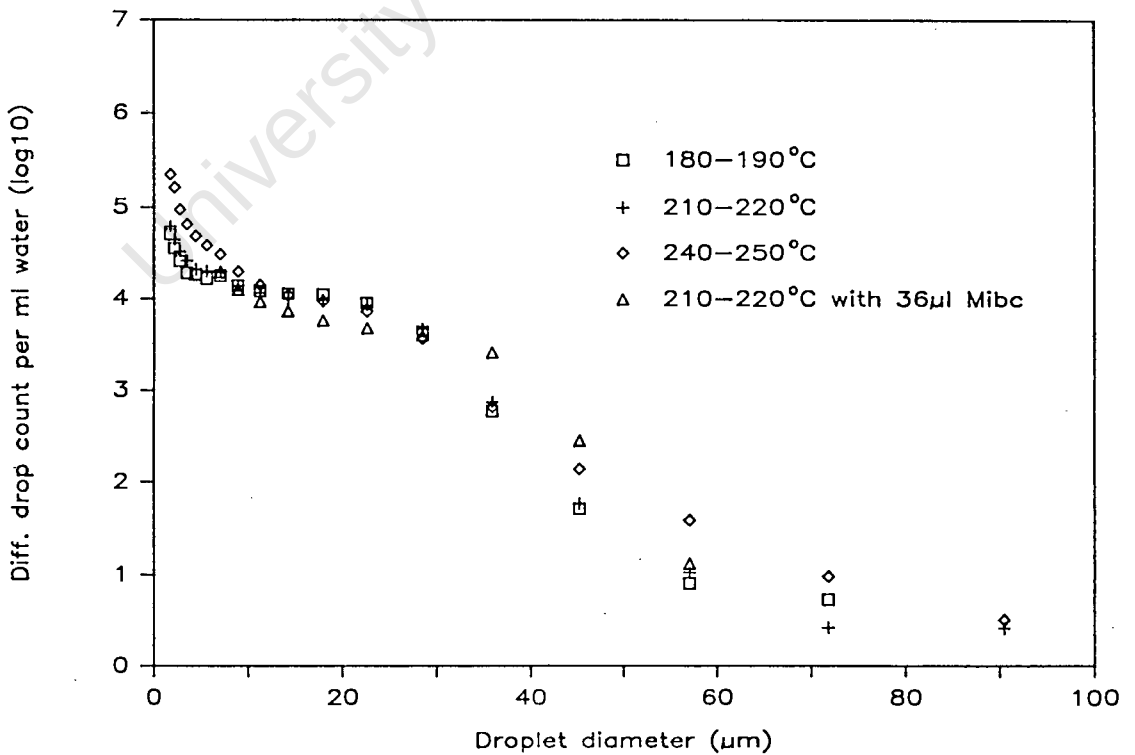


Figure 2.25 : Droplet size distribution (based on frequency) for 200 µl of Pegasol 3745 boiling point cuts in 1 litre of water. Effect of increased boiling range (and viscosity) and MIBC on the distribution. Impeller speed 1200 rpm.

2.7 CHAPTER SUMMARY

Thorough dispersion of the oily collectors is essential for successful coal flotation. Because the dispersion of typical coal collector oils has been inadequately studied, an investigation of the degree of dispersion of the types of oil used in this thesis was undertaken.

Surface charge and interfacial tension are integrally related. Interfacial phenomena (charge, electrical double layer thickness, interfacial film viscosity, etc.) control the coalescence tendencies of an oil and hence the characteristics of a dispersion formed under given agitation conditions. The oil droplet interfacial phenomena will also influence the interaction of the droplets with coal surfaces and their associated interfaces.

A review of previous work indicated that oil droplets are likely to possess a negative charge at near neutral pHs commonly found in coal flotation. In addition to the effects of pH, oil droplet surface charge is also strongly dependent on the type of oil, and the type and concentration of surfactants present.

The potential across the interface consists entirely of a distribution potential if the oil is highly polar (i.e. if it has the ability to form an internal electrical double layer) and entirely of an interfacial potential if the oil is strictly non-polar (paraffinic). Droplets of slightly polar oils (like benzene homologues) may have both potential components, though this will depend on droplet size.

The charge and/or potential and hence behaviour of the droplet in terms of coalescence, and adsorption on coal, will vary considerably with the choice of frother (surfactant) added. Only a non-ionic surfactant (MIBC) was consciously added in the tests and its effect on interfacial potential would only be via formation of an interfacial dipole array.

Droplet charge/potential will also be influenced by the presence of powerful (often ionic) surfactant impurities found in some commercial oils, especially those of high aromatic content - since ionic

surfactants are soluble in these oils. The contribution of such impurities to surface activity is largely unquantifiable and adds to the difficulty in interpreting experimental results. In a practical situation evaluation and maintenance of plant performance will be aggravated since commercial oil stocks are likely to differ considerably (in these terms) from oil to oil and from batch to batch.

The dispersions were produced in a three litre batch flotation cell under mixing conditions later used for the batch flotation testwork. No attempt was made to alter or regulate the pH or quality of the water (distilled water was used). Oil dispersions were readily and accurately measured by using a Coulter Counter (Model Ta II), though a minimum size threshold is inherent in the technique. Fortunately this size is very small and the oil volume below this threshold size is normally minimal. Dilution of the primary droplet dispersion with saline solution, which is necessary for the analysis technique, can reasonably be assumed to have no significant effect on the dispersion if measurement is done immediately and the dispersion is agitated gently.

The empirical oil dispersions could be modelled well with the normal distribution function in either its arithmetic or geometric (log) form. Various workers have shown the validity of using such functions. The fit of empirical data to the theoretical functions was statistically verified. The volume-based normal distributions were no longer normal when distributions were based on droplet number. Log-normal distributions retained their form since a log-normal distribution is independent of the order of the variable (Kapteyn's transformation).

Hexyl benzene and mixtures in which this oil constitutes a significant amount (40 %) were the only oils which followed the log-normal form and this was only under reasonably intense and/or prolonged agitation conditions. Log-normal behaviour is induced by the physical requirement of a non-negative droplet size and occurs when the distribution has a mean at small sizes as well as a significant proportion of substantially larger droplets. Dispersions of the aliphatic oils all conformed to normal distributions at all conditions tested.

At the experimental conditions, the aliphatic reagents, including the spectrum of Pegasol 3745 boiling range cuts, all produced mean

droplet sizes (based on volume) which were similar. This indicates that in these systems the interfacial properties of the oils were all similar (similar interfacial tensions and surface charges). The mean diameter (based on volume) was about $25\text{ }\mu\text{m}$ for reagents mixed at 1200 rpm in one litre of water. Similar behaviour reported in the literature infers that size similarity (between aliphatic oils) would be manifested at other agitation conditions.

Hexyl benzene was amenable to fine dispersion under appropriate agitation conditions (intensity and time). When mixed in one litre of water at 1600 rpm the mean dodecane droplet size was $19.9\text{ }\mu\text{m}$ while that of hexyl benzene was $4.4\text{ }\mu\text{m}$. The reduced size and increased number of hexyl benzene droplets suggests that flotation performance would improve with this oil. However, despite relatively poorer degrees of dispersion, all the other oils were still dispersed to the point where tens of thousands (or more) droplets existed per millilitre of water. This may be a sufficient number to permit effective flotation.

Where agitation conditions were comparatively mild (a full flotation cell for instance) the dispersions produced by the aliphatic oil (dodecane) and the aromatic (hexyl benzene) were similar in nature (both conformed to normal (arithmetic) functions). The means of the hexyl benzene distributions were somewhat smaller than those of the dodecane distributions, reflecting the differences in interfacial tensions of the two oils. The means were greater (by about 15 and $10\text{ }\mu\text{m}$ respectively) than those measured when the same oils were mixed in the cell at the same impeller speed with less water.

When droplet size (diameter) was evaluated on a number (droplet frequency) basis the same dispersions revealed that tens of thousands (or more) droplets were present in each millilitre of the primary dispersions (in the flotation cell). Oil dosages used were 133 and $200\text{ }\mu\text{l}$ of oil per litre of water in which the oil was dispersed. At conditions of high mixing intensity the numbers of droplets were about two magnitudes greater than at low mixing intensity. (The mixing intensity was altered by changing water volumes from one to three litres while maintaining the same impeller speed). Increasing impeller speed from 800 to 1600 rpm also increased droplet numbers by at least an order of magnitude. Low intensity mixing, which produces comparatively fewer droplets, could possibly induce poorer flotation performance.

MIBC (the frother) generally played no role in aiding dispersion of the reagents. The method of MIBC addition, i.e. independently or mixed in the oil apparently also made no difference, probably because MIBC is fully soluble in either phase at the dosage levels used. Complete solubility will naturally restrict its oil-water interfacial activity.

Under turbulent conditions, and in the presence of MIBC, the mean oil droplet size increased and droplet distributions broadened. An exception was the commercial oil, Shellsol AB, where mean droplet size decreased. This was attributed to the joint action of the MIBC and powerful (ionic) surfactants present in this (and similar) oils. Such behaviour is not possible with commercial "pure aliphatic" oils since powerful ionic surfactants will not dissolve in these oils. The single species (pure) reagents, which have no surfactant impurities, are entirely susceptible to the surface activity of MIBC and their mean droplet size will increase in its presence.

The reason for the increase in spread and mean of the oil droplet distribution in the presence of MIBC is that MIBC encourages oil droplet coalescence rates in relation to water coalescence rates. The MIBC molecule favours solvation by oil molecules as opposed to hydration by water molecules. It is preferentially soluble in oil as opposed to water. In other words MIBC is a water in oil (W/O) emulsifier, as shown/predicted by its low H.L.B. value (6.05). However the very low oil phase fraction used in flotation necessarily results in the formation of an oil-in-water dispersion.

Under milder mixing conditions MIBC had no apparent effect on the dispersion of oils. The more gentle agitation conditions tend to disperse the oils less. Large droplets coalesce at a slower rate than the smaller ones, the overall result being that the influence of MIBC in retarding the rate of coalescence is not patently manifested, as it is under more vigorous agitation conditions.

2.8 CONCLUSIONS

1. Thorough dispersion of oily collectors is essential for the effective flotation of coal particles possessing inadequate native hydrophobicity.
2. Aromatic oils produce smaller droplets than aliphatic oils under identical mixing conditions. This is a reflection of their lower interfacial tensions. The difference in droplet sizes will be more marked as mixing conditions become more intensive.
3. Because aromatic oils produce smaller droplets they will be better distributed in the pulp, and can therefore be expected to be better collectors than aliphatic oils at equivalent dosages. The dispersion of aliphatic oils at the dosages and under mixing conditions similar to those used in flotation will nevertheless be reasonably thorough, in terms of droplet numbers. These numbers could be sufficient to render the coal particles floatable.
4. Predominantly aliphatic and "pure" aliphatic oils should produce similar droplet size distributions under identical mixing conditions. In this respect, their effect on flotation performance is expected to be similar.
5. In the absence of other surfactants, MIBC will not promote and will usually hinder oil dispersion, i.e. induce relatively larger droplets. This last is likely to be especially apparent at vigorous agitation conditions.
6. Droplet dispersions can be statistically well represented by either the normal or the log-normal distribution function.

CHAPTER 3

ADSORPTION OF OILY COLLECTORS BY COAL

3.1 INTRODUCTION

The second sub-process investigated in this study of the effect of hydrocarbon collectors on coal flotation was the adsorption of these oils by coal. Because of the turbulent conditions in a flotation cell, a strong, stable adsorption of the collector is a prerequisite for effective flotation. This assumes that the bubble-particle aggregate is not sufficiently stable to permit flotation without a collector, i.e. that the particle surface is not sufficiently hydrophobic. South African coals are generally insufficiently hydrophobic and collectors are needed, particularly for relatively coarse material (500 μm), to effect flotation.

Obviously strong adsorption will not necessarily imply a good mass recovery if the chemical has no collecting ability (ability to promote bubble-particle adhesion). Additionally, strong adsorption does not necessarily imply beneficiation which is, after all, the objective of flotation. The collector must also be selective.

The process of adsorption of oil droplets onto the surface of coal particles is controlled by their respective interfacial characteristics. For this reason it is vital to develop an understanding of interfacial behaviour. A fairly extensive review of the literature in this regard is the subject of Section 3.2. The review covers coal particle electrokinetics, the influence of surfactants, the behaviour of the aqueous film which separates the approaching oil droplet and coal particle, oil-water-coal contact angles and the spreading of oil on wet coal. Oil droplet interfacial properties are reviewed in Chapter 2, Section 2.2 and will be referred to here. Some of the literature reviewed in Section 3.2 will be referred to in Chapters 4 and 5.

Collector adsorption (adhesion) and selectivity are traditionally evaluated by contact angle measurements. Contact angles are widely used for predicting the potential of oily reagents as flotation collectors

and in categorizing their selectivity; a small contact angle (measured in the aqueous phase) implying poor surface adhesion. Relating contact angle to the process of adsorption has a number of associated difficulties. These are discussed in detail in Section 3.2.6. At this stage it must suffice to say that a contact angle is a consequence of successful attachment, and is therefore dependent on the success of the steps occurring prior to contact. Knowledge of contact angles cannot quantify collector adsorption kinetics.

Because of the limits inherent in contact angle measurements and interpretation, a technique was developed to study the kinetics and degrees of oil adsorption onto coal and gangue surfaces directly, and so circumvent these difficulties. No technique suitable for studying the dynamics of *insoluble* collector adsorption appears to have been documented. The technique developed allowed the adsorption process to be studied under dynamic conditions, with both a more representative particle surface (only $\sim 100\ \mu\text{m}$ particles had to be excluded) and the full collector droplet size range.

The chapter commences with a review of the theory and literature of the pertinent interfacial phenomena, including the means (e.g. contact angles) used to assess those that cannot be measured directly. Then follows a description of the development of the adsorption technique and the results of the investigations in which this technique was applied. Some other interesting observations with respect to oil adsorption behaviour are also recorded. Finally, attempts at modelling the adsorption reaction are described.

3.2 THEORY AND LITERATURE REVIEW

3.2.1 Introduction

Studies of contact angle, wetting and thin film stability have been the subject of many review papers and are comprehensively reviewed in several texts. Some of the basic and widely accepted theory is summarized below but a comprehensive review of refinements to the basic theory is not included since it has no direct bearing on the results or interpretation of the adsorption studies. These were carried out using a

technique which measured the actual sub-process behaviour without recourse to indirect measurements, such as contact angle, which would have made an indepth study of the theory more important.

Contact angles are nevertheless discussed in some detail because they are a commonly used measure of solid hydrophobicity/wettability, and provide the means by which to evaluate so-called solid interfacial tensions, which cannot be directly measured. Contact angles are essential to an understanding of certain interfacial phenomena. However variability in measurement, constraints imposed by the necessity of a quiescent environment and specially prepared solid surfaces, in conjunction with the simplifying assumptions made in deriving the relations in which contact angles are used, imply that understanding is qualitative. The current level of understanding of interfacial phenomena is inadequate for predictive purposes in flotation and empirical work is essential, though the theory can be used to explain the observed results and to predict the consequences of changes made to the flotation system.

Although the theory discussed below and the literature reviewed is with particular reference to the adsorption of oil droplets onto solid particles, much of the discussion is also directly applicable to air bubble-solid attachment in most flotation situations; namely those where soluble reagents are used. However the presence of an additional liquid phase (oil) in coal flotation introduces additional complications which are seldom considered in the literature. The current literature covering alterations to the theory in such systems is discussed in more detail in Chapter 5, Section 5.2.

3.2.2 The influence of coal surface chemistry on oil adsorption

This thesis is concerned primarily with a study of the behaviour of oily flotation reagents and not with an evaluation of the potential of various coal types for flotation. The literature reviewed is therefore largely that which is directly related to the study of the behaviour of the oils in the sub-processes.

Other variables which would be introduced by changing the coal substrate are not considered in much detail, though it is acknowledged that the surface chemistry of the coal influences behaviour strongly and

that, for any one coal, interaction with oils of varying composition will differ. Pooley (1967) emphasized that the coal-collector reaction is dependent on coal type as well as on the size distribution of the coal in the pulp (a point also made by Al Taweel et al, 1986) particularly if the collector is insoluble.

Coal particles are normally more hydrophobic than the associated clay gangue minerals but the degree of hydrophobicity and consequently the extent and selectivity of the oil adsorption is influenced by many additional factors, including surface oxidation, surface porosity, water chemistry (pH, etc.) and the adsorption of colloidal slimes.

Celik and Somasundaran (1980) re-iterated that attempts to improve the understanding of coal-related interfacial mechanisms, like reagent adsorption, are hindered by the complex mineralogy and heterogeneity of the coal and its tendency to alter its surface chemistry significantly upon exposure to various environments; chiefly by oxidation. Some aspects of the physico-chemical structure of coal and its electrokinetic behaviour are briefly examined below.

3.2.2.1 The physico-chemical nature of coal surfaces

Coal is a complex mixture of organic constituents (known as macerals) and inorganic minerals. An excellent review of the constitution of the coal bulk is given by Ward and Burdon (1987). The surface properties of coal will be dictated in part by its bulk properties, but the surface will have its own unique properties owing to exposure to the atmosphere and the fact that it constitutes a phase boundary.

The chemical composition of the coal surface is widely variable and very complex. Vlasova (1973) indicated that the surface of natural coal is occupied by organic groups, inorganic minerals, free electrons, unsatisfied bonds, free radicals, oxygen containing groups and amorphous carbon.

Laskowski and Miller (1984) listed the three most important factors affecting coal surface properties as :

1. Hydrocarbon skeleton (which is related to rank);
2. Oxygen-containing functional groups; and,
3. Inorganic impurities.

Rank gives an idea of how the coal composition, and by association its surface, varies. For example, Petukhov (1979) found a high content of surface phenolic and carbonyl groups on low rank coals and an almost complete absence of these groups in high rank coals. He also found that specific surface area of coal decreased with increasing rank as the pore size and/or number decreased; and (using electron microscopy) that vitrinite of all ranks had a cellular structure, with cell size varying sharply with rank.

Fuerstenau et al (1983) believed that the functional groups, chiefly phenolic (-OH) and carboxylic (-COOH), control coal wettability by controlling the balance of hydrophilic and hydrophobic surface sites. The ratio of these sites can be determined by the adsorption of water (or methanol) and n-heptane vapours respectively onto coal (Al Taweel, 1986); or by immersion time tests of the type described by Fuerstenau et al (1985). An additional means of evaluating coal wettability (and, by association, surface characteristics) is given by Hornsby and Leja (1984). This technique and its application are reviewed in more detail in Section 5.2.3.3. Specific investigations of the surface chemistry, in terms of surface functional groups, of some South African coals were reported by Du Plessis et al (1985). Their findings were similar to those of Fuerstenau et al (1983).

Fuerstenau et al (1985) studied a series of coals ranging from sub-bituminous to anthracitic and found that the susceptibility to oxidation increased with decreasing rank, i.e. as the carbon to hydrogen ratio decreased.

Surface oxidation at ambient temperatures results in the increasing formation of oxygen-containing functional groups. This is a widely accepted phenomenon although Du Plessis et al (1985) found minimal changes in the proportion of carboxyl and hydroxyl functional groups under ambient oxidation conditions for South African coals. Further weathering can lead to the formation of water-insoluble humic acids which dissociate at normal coal pulp pHs (about pH 8) thus

enhancing surface hydrophilicity. Extreme oxidation conditions (high temperatures) can produce water-soluble acids but such conditions are unlikely to be encountered in practice.

The presence of non-liberated mineral matter will affect surface electro-chemistry and induce increased hydrophilicity (with the exception of hydrophobic minerals like pyrite). The floatability/hydrophobicity of coal is also modified by inorganic electrolytes, especially multivalent metal ions (Wen and Sun, 1977) which may even originate from the dissolution of gangue minerals from within the coal itself.

3.2.2.2 Coal particle electrokinetics

The electrical double layer between the solid surface and the bulk fluid governs coal electrokinetic behaviour. Electrokinetic studies involve the measurement of the "zeta potential", which is the potential induced by the movement of a charged particle (oil, solid or air bubble) through the bulk medium. It is the potential at the shear plane which develops in the medium between the fixed layer of fluid immediately adjacent to the particle and that further away. Zeta potential is not a measure of the actual potential at the surface but it is widely used to represent this, on the assumption that there is no specific surface adsorption other than by potential determining ions (PDIs) and that the ionic strength remains constant. Specific adsorption of surfactant ions will alter and may even reverse the zeta potential in relation to the surface potential as explained in Section 2.2.5.1.

Many studies have attempted to relate the electrokinetic behaviour of coal to its hydrophobicity and ultimately with its potential for flotation (e.g. Campbell and Sun, 1970a&b; Jessop and Stretton, 1967; Celik and Somasundaran, 1980).

Generally zeta potential becomes increasingly negative with decreasing coal rank or with an increasing degree of surface oxidation, i.e. as the number of negatively charged oxygen-containing functional groups on the surface increases. Campbell and Sun (1970b) found bituminous coals to exhibit electrokinetic behaviour very

similar to that of oxide minerals. OH^- and H_3O^+ ions can therefore be expected to be potential determining since both ions are part of the dissociation equilibria which develop between oxides and aqueous media. At low pHs the surface charge will tend to more positive values, and to negative values at high pH. At near neutral pHs coal is generally acknowledged to be negatively charged.

Maximum hydrophobicity of coal is often believed to be achieved at its point of zero charge (PZC). This is the pH where equal adsorption of OH^- and H_3O^+ ions occurs (assuming these are PDIs). Jessop and Stretton (1967) disputed this. They found the zeta potential of coal to be independent of pH in the near neutral region (mid pH range) which is the region most likely to be encountered in coal flotation if the pH is not regulated. Apparently this can be attributed to the presence of gangue minerals since Fuerstenau et al (1983) found good agreement between the electrokinetics of demineralized coal (which will be termed carbonaceous material in further discussions), pH and flotation response.

Mishra (1987) reported that the zeta potential of clays (illite, kaolinite and montmorillinite), which are the major gangue minerals in South African coals, are negative over the pH range that was measured (from 3 to 11); though the presence of multivalent metal ions can affect this, particularly with kaolinite. A negative zeta potential is to be expected since many clays exhibit a negative surface charge because of substitution in the solid lattice of one cation by another of similar physical size but of lower charge, e.g. replacement of Si^{4+} by Al^{3+} (Fuerstenau, 1982, p.18). This characteristic supports the findings of Campbell and Sun (1970b) who reported that gangue potential is independent of pH, i.e. that hydroxyl and hydronium ions are not potential determining for gangue. Wen and Sun (1977) believed this to be true of extensively oxidized coal as well.

In addition, Fuerstenau et al (1983) pointed out that the PZC relates to the solid surface specifically, but that the electrical interactions which in part influence oil adhesion are affected by electrical contributions from the solid-oil (gas) and water-oil (gas)

interfaces especially in the presence of surfactants.¹ These factors and the presence of gangue minerals of fixed charge explain why the attainment of the PZC of the coal is not necessarily a criterion for maximum flotation performance.

3.2.3 Oil-coal molecular bonding mechanisms

In the absence of surfactants the adsorption of hydrocarbon oils onto coal surfaces is a physi-sorption. Physi-sorption has electrostatic (dipole or charge) and/or dispersion (induced dipole) components, the former being specific and the latter disperse in character. Electrostatic adsorption would include the attraction of dipolar molecules to charged coal surface groups. These surface groups are also capable of inducing dipole moments (and hence dispersion forces) in non-polar molecules, particularly long chain (high molecular weight) molecules and those possessing a high degree of asymmetry. The inducement of dipole moments is relatively strong in unsaturated and aromatic hydrocarbons.

Tyurnikova and Naumov (1981, p.139) reported that Kiselev looked at the electron density distribution of typical hydrocarbon molecules in order to describe the bonding between oil and coal. Normal saturated hydrocarbons possess only σ -bonds with no local electron density concentrations. Their bonding mechanism is therefore exclusively through London-Van der Waals forces of attraction (i.e. induced dipole-induced dipole or dipole-induced dipole interactions). Unsaturated as well as aromatic hydrocarbons possess π -bonds in addition to σ -bonds. π -bonds impart local concentrations of electrons which can associate with local positive charges on the coal surface; the higher the polarization the stronger the interaction. Al Taweel et al (1986) stated that π -electrons interact with oxygen containing coal surface groups - the electronegative oxygen atom imparting positive polarity to covalently bonded hydrogen atoms. With non-pure, i.e. commercially produced oils, the additional possibility of hydrogen bonding between the various coal surface groups, both disassociated and non-acidic (Du Plessis et al, 1985), and similar groups within the oil exists. In the oil, such molecules are often products of oil oxidation. The hydrogen bonding

¹ Oil droplet electrokinetics are discussed in detail in Section 2.2.5.

mechanism presumably contributes to the success of oxidized hydrocarbons (alcohols, phenols, etc.) as coal collectors (Laskowski and Miller, 1984; Petukhov, 1979; Sorokin et al, 1979).

Klassen et al (1958) reported that at normal dosages the simplest oils (presumably saturated non-cyclic hydrocarbons) cannot float coal with a high ash content or a high degree of oxidation, while cyclic and polar compounds can. This is quite obviously related to the respective coal-oil bonding mechanisms discussed above. Non-polar oils, which are completely dependent on London forces of attraction, are evidently unable to displace water from such coal surfaces, as Baranov and Gubaidulin (1972) have shown that highly oxidized coal would float well with these oils, provided it was contacted with oil prior to pulping with water.

Van der Waals and hydrogen bonds are low energy (weak) bonds but for sufficiently long chain molecules or for a sufficient number of molecules interacting with the coal surface, their cumulative bonding energy will be large, i.e. the overall bond will be strong.

Steric (structural) factors also play a part in oil adsorption. Tyurnikova and Naumov (1981, p.140) quote Dacy and Thomas as finding n-paraffins and flat aromatics to be adsorbed faster than iso-paraffins and other off-flat molecules. n-Paraffins will be able to approach the surface closely and therefore bond strongly along their molecular axis. Side branching would inhibit this. The benzene ring, which has π -electron clouds (local polarization) on either side of it, is flat which allows approach parallel to the surface thus permitting the best interaction of its local negative charge with electro-positive coal surface groups (such as covalently bonded hydrogen atoms in oxygen-containing groups).

Typically, oils used as collectors in coal flotation are kerosene and diesel distillation cuts from petroleum refining or oily bottoms from other distillation processes. These oils are highly impure in the sense that they contain a vast number of hydrocarbon molecular species. In addition poorly refined oils will contain a number of oxidation products and organic ion impurities. Their flotation behaviour is therefore impossible to quantify on the basis of molecular composition as this cannot be accurately determined.

In this testwork typical petroleum distillation cuts were used as were some pure oils of similar boiling point. Pure oils were used to determine whether the adsorption results obtained with the commercial oils could be attributed to the nature of the oil (aromatic or aliphatic), and hence to its bonding mechanism with coal, or had to be ascribed to surfactant impurities.

3.2.4 Oil droplet-coal particle collision/adhesion

The pH of a coal pulp affects the encounter of an oil droplet with a coal particle since OH^- is a PDI for oil interfaces with water (Burkin and Bramley, 1961; Ng, 1982) and is evidently a PDI for carbonaceous material (but not for clay minerals) as discussed in Section 3.2.2.2. The presence of other potential determining electrolytes (for gangue minerals) will also affect the encounter. However these effects are not considered in any detail here since no effort was made to alter them experimentally and they are likely to have had similar influences on all the oil adsorption experiments done with a particular coal.

Oil droplets are likely to possess a negative charge in a natural pH coal pulp (see Section 2.2.5). Since coal particles also possess a negative surface charge at typical flotation pHs (around pH 8) sufficient energy must be conferred by agitation to ensure that the electrostatic repulsive forces are overcome during collision between an oil droplet and a coal particle and that the two approach one another sufficiently closely for the molecular forces of attraction to dominate the encounter.

Ng (1982) studied surface phenomena influencing the attachment/transfer of coal particles from an aqueous to a hydrocarbon phase. High speed cinematography, interfacial tension, electrokinetic and contact angle measurements were used. Ng confirmed experimentally that the maximum collection efficiency between coal and oil occurred when these particles were oppositely charged. This would be expected as the resulting electrostatic attraction would enhance the thinning of the aqueous film between them. Ng's results indicate that coal maintained a negative surface charge while the oil surface charge could be reversed (made positive) at low pHs. These results support the suggestion that mineralized coal electrokinetics are not controlled by pH though it will

have some influence via the interaction of OH^- and H_3O^+ ions with oxide minerals and oxidized carbonaceous material. Ng found that the pH at which the oil droplet charge reversal occurs with pure oils is low (pH 2). Even for impure oils this only occurs below pH 5 (see discussion in Section 2.2.5.1). Collection efficiency was found to decrease progressively as pH increased and both oil droplet and coal particle developed more intense negative surface charges.

During the approach of an oil droplet and a coal particle, the electrostatic interaction of the respective electrical double layers, and (for similarly charged droplet and solid particle) its conflict with the molecular forces of attraction, may be examined on the basis of the so called DLVO (Derjaguin, Landau, Verwey and Overbeek) theory for particle-particle interactions. This theory quantifies the behaviour of the attractive and repulsive forces between particles. These forces were discussed qualitatively in Section 2.2.5.1 and are depicted schematically in Figure 2.6.

The act of oil adhesion to coal can be broken down into three stages (as can flotation, if air bubbles are read for oil droplets). These stages are :

1. Approach of the oil droplet and solid particle (which is governed by the pulp hydrodynamic forces).
2. Thinning of the water film between the two to a point where it ruptures.
3. Retreat of the water, oil adsorption and expansion of the contact area with the accompanying establishment of a contact angle, or possibly complete wetting of the coal.

It is apparent from the above sequence of events that the formation of a three phase contact angle, which is a widely used measure for evaluating wettability, is a consequence of the successful accomplishment of the preceding steps. The existence of a contact angle also indicates that spontaneous wetting of coal does not occur.

Coal particles and collector droplets collide only when inertial or gravitational forces are such that the fluid streamlines surrounding each are crossed and other resistances, like electrostatic repulsion,

are overcome. Obviously the larger and denser the particles the less the tendency to follow streamlines.

Ng (1982) reviewed the idea of a collection efficiency factor which is commonly used in evaluating particle-bubble collision and capture (e.g. Anfruns and Kitchener, 1976; Ahmed and Jameson, 1985). It is the product of 1. a collision efficiency factor and 2. an attachment efficiency factor. Collision efficiency depends on the viscous, inertial and gravitational forces acting on the coal and oil particles and on the flow pattern around each one. Attachment efficiency is influenced by the physical, chemical and electrical characteristics of the oil and coal surfaces.

Ng (1982) provided a review of the hydrodynamic theory relating to particle-oil droplet collisions. Schulze (1984) reviewed hydrodynamic bubble-particle collision theory in considerable detail and much of this theory is directly applicable to oil droplet-solid particle encounters.

Since the oils have no influence on long range (hydrodynamic) interactions, hydrodynamic theory is not considered further.² Flotation cell hydrodynamics can reasonably be assumed to be successful in inducing particle-oil droplet collisions as cells of conventional design are known to produce good results in many mineral flotation systems. However, having assumed that hydrodynamic forces can induce the collision of oil droplet and particle it is necessary that the aqueous film separating the two be destroyed before actual adsorption can occur. The behaviour and destruction of these thin films is discussed below. This is followed by a discussion of contact angles and the spreading of oil on wet coal.

3.2.5 Thin films

The approach of the droplet and solid particle is influenced by hydrodynamic forces and bulk fluid properties (such as viscosity) to a thickness of about 1000 nm (Finch and Smith, 1979). If the aqueous film continues to thin, forces of molecular origin within the film between the particles come into ascendance and dominate at about 30 nm (Finch and Smith, 1979). For contact to occur the initially relatively thick

² However, the effect of impeller speed on oil adsorption was investigated.

film must be reduced to a point where the film is sufficiently thin to be influenced by molecular forces of attraction which ultimately lead to its rupture. A thin film is therefore one whose thickness falls within the range of molecular forces.

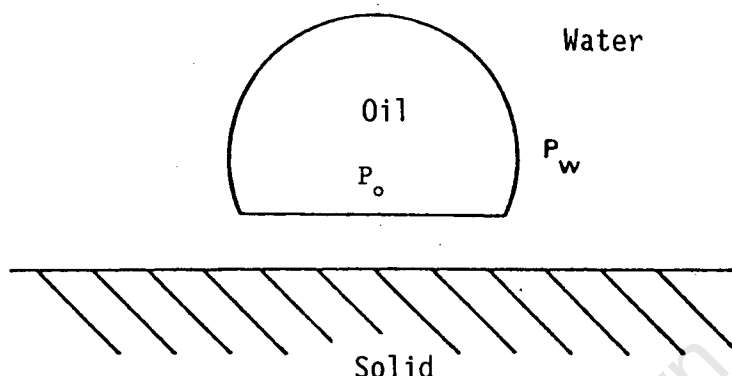


Figure 3.1 : Schematic representation of the thin film between the oil droplet and the solid surface.

A simplified view of the thin film between a deformed oil droplet and a flat, rigid solid surface is shown in Figure 3.1. The aqueous film behaves as if there were an excess pressure, π_d , acting normal to the solid surface and opposing thinning. This pressure arises as a result of the difference in interfacial free energies and is commonly termed a disjoining pressure :

$$\pi_d = P_o - P_w \quad [3.1]$$

where P_o is the pressure in the droplet and P_w the pulp (water) pressure. $P_o - P_w$ is of course equal to $2\gamma/r$, the droplet capillary (excess) pressure (Equation 2.8). Three forces are believed to comprise π_d :

1. The interaction of the solid and droplet electrical double layers, i.e. Coulombic forces.

Double layer behaviour of coal solids and strictly non-polar oils (and very small droplets of slightly polar oils) is likely to be similar in the sense that a double layer will only form within the aqueous phase surrounding each since the solubility of ions in the oil and the permeability of a solid surface are both negligible. Electrostatic interfacial phenomena are discussed in detail in Section 2.2.5. These double layers will interact on the approach

of an oil droplet and a coal particle, with consequent forces of attraction or repulsion.

2. London-Van der Waals dispersion forces of attraction between atoms.

The London-Van der Waals forces represent the induced or fixed dipole forces of attraction of atoms/molecules of water, solid and oil for each other and for themselves; including attractions through the other mediums present.

3. Interfacial structural effects which include hydration (solvation) effects such as hydrogen bonding and the formation of dipole arrays.

Should the disjoining pressure be relatively large then the film may be indefinitely stable as in the case of hydrophilic solids. On the other hand hydrophobic solids induce only a small positive disjoining pressure; or even a negative one which encourages film thinning, i.e. the destruction of the water interfaces. Oppositely charged particles induce a similar effect. With wettable solids the liquid layer separating oil droplets (or air bubbles) eventually breaks because rupture decreases the free energy of the system.

The disjoining pressure is a function of the film thickness and turns from positive to negative if the film thins below a critical level, i.e.

$$G^s(h) = \gamma_{sw} + \gamma_{wo} + \int_h^{\infty} \pi_d dh \quad [3.2]$$

where : G^s is the specific Gibbs surface free energy

h is the film thickness

γ_{sw} and γ_{wo} are interfacial tensions

The relative influences of the components of the disjoining pressure vary individually with film thinning so that the transition is non-smooth. Thin film behaviour is illustrated schematically in Figure 3.2 below. Below a certain critical thickness the film is unstable and susceptible to rupture upon thermal or mechanical shock

particularly over solid surface asperities. Ng (1982) pointed out that sharp asperities also reduce any electrostatic repulsion forces.

To rupture, the film need not be uniformly thin : one thin region is sufficient. Film thinning is complicated by elastic repulsion, i.e. "bouncing" during collision. In addition the necessary fluctuations in thickness ("rippling") within the film are generally discouraged because the consequent increase in film surface area is energetically unfavourable. However forces of attraction prevalent in wettable systems are often sufficient to overcome this stabilizing tendency. Lucassen-Reynders and Lucassen (1984) reported that film destabilization is enhanced by mass transfer across the film surface [e.g. by the transfer of surfactants between the oil-water and coal-water interfaces].

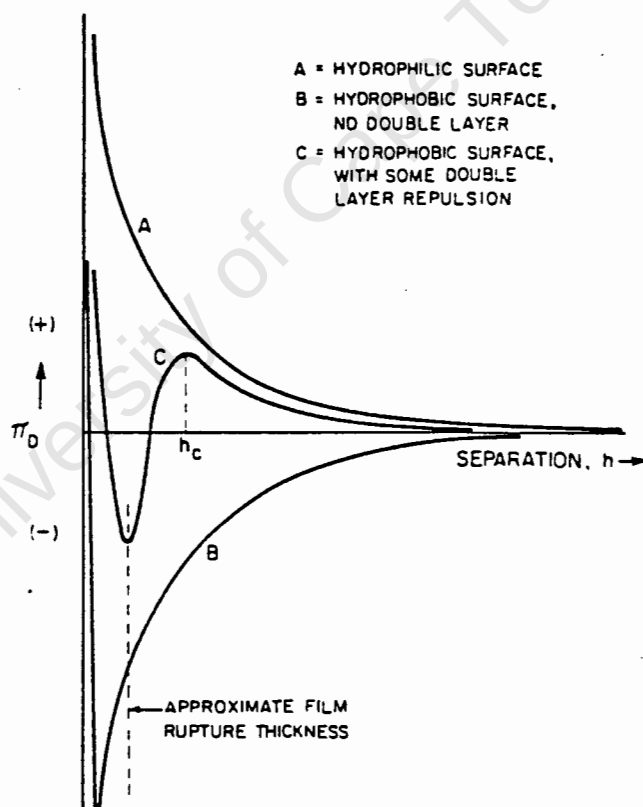


Figure 3.2 : Disjoining pressure vs. film thickness. (From Fuerstenau et al, 1983).

Though an independent phase ceases to exist following film rupture it is evident that a virgin solid surface is not exposed. The solid surface will still possess strongly adsorbed water molecules (on hydrophilic sites provided by coal oxygen functional groups and mineral matter) even if it is on balance hydrophobic, as demonstrated by Mahajan

and Walker (1971) and Chibowski et al (1985); as well as various ions and surfactant molecules.

The lifetime of the film from the onset of droplet deformation to actual droplet adsorption (film rupture) is termed the "induction time" (originally by Sven-Nilsson) and is widely quoted as being of the order of a few milliseconds. Obviously if the induction time exceeds the contact time then adsorption is impossible. Ng (1982) quotes Scheludko as pointing out that the main portion of contact time needed is not for rupturing the film but rather for the expansion of contact area needed for stable attachment.

Ralston (1983) reported that the induction times measured under static conditions have often been found to exceed the time of contact under dynamic conditions, implying that flotation should not occur. Since it does, he concluded that there must be some difference in the encounter mechanisms under dynamic and static conditions. Part of the explanation for the discrepancies in induction times is evident in the work of Smith and Duckmanton (1957) who found that induction times on freshly cleaved surfaces were almost instantaneous while those on polished surfaces (which are normally used in contact angle measurements) were of the order of seconds.

Collision/contact time between particles in a flotation system is known to be very rapid. Drainage of fluid (by gravity or capillary action) from between two essentially immobile interfaces (solid and oil) is too slow to allow for sufficient drainage within this contact period. In their review Lucassen-Reynders and Lucassen (1984) concluded that a probable mechanism which allows this drainage to be sufficiently accelerated is if the oil- (or air)-water surface is mobile and moves with the draining liquid. Surface tension gradients, caused because this movement alters surfactant coverage, also enhances drainage (Marangoni effect). Kirchberg and Töpfer (1964) and Ng (1982) reported that particles have been observed to slide over one another following most collisions and it is during this stage, as the interface moves, that attachment appears to occur. Nevertheless, Ralston (1983) indicated that a full interpretation of transport and fluid flow phenomena in relation to thin films is still lacking.

3.2.6 Contact angles

One condition for the successful attachment of oil or air to the solid is that the former two phases should more readily wet the solid than the aqueous phase does. A classical measure of solid wettability is the contact angle, i.e. the angle at which the fluid-fluid interface meets the solid. This is conventionally measured in the aqueous phase, though many researchers are careless in stating in which phase the angle was measured thereby complicating understanding of their arguments.

The measurement of contact angles is of necessity made under static conditions and does not take into account the turbulent conditions in a flotation cell. Eveson et al (1956) pointed out that the contact angle obtained under quiescent conditions will not prevail under flotation conditions because of centrifugal and other forces. The measurements also give only a limited idea of the strength of the solid-collector adsorption bond. Špetl and Dedek (1966) pointed out that contact angle measurements (advancing, receding or stationary) merely represent the final phase of the adhesion process. Previous essential processes such as collision and water film rupture must be tacitly assumed; the contact angle gives no indication of the dynamics of these processes. In their review, Finch and Smith (1979) concurred with this opinion (as did Fuerstenau et al, 1983), pointing out that contact angle is a consequence of successful attachment, and is therefore dependent on the success of the steps occurring prior to contact.

The steps preceding oil adsorption thus cannot be quantified by simply measuring contact angles. In addition, contact angle measurements are subjective and vary from operator to operator. Fuerstenau et al (1983) believed this to be one reason for conflicting results in the literature. Bailey and Gray (1958) confirmed that hysteresis is also always a problem in contact angle measurements. This problem is further compounded by the heterogeneous nature of coal surfaces, as contact angle measurements are limited to a single droplet which obviously only occupies a small part of the surface; a different angle may be manifested elsewhere on the surface.

According to Bailey and Gray (1958) it is difficult to relate contact angle measurements to flotation (floatability) since in

flotation the coal (solid) would not be free of contaminants and the particles would not be smoothly polished.

3.2.6.1 Equilibrium contact angle

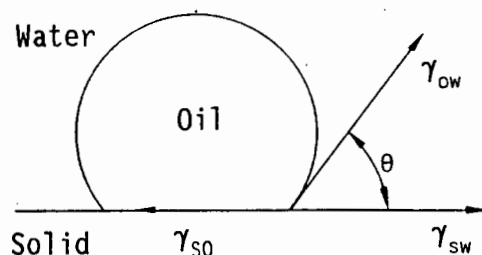


Figure 3.3 : Three phase (oil, solid, water) line of contact on a smooth undeformable solid surface

Figure 3.3 depicts the classical three phase line of contact between oil, solid and water phases on a smooth, flat undeformable solid surface. The complication of a real highly irregular solid surface is difficult to quantify and is normally overlooked. Remembering the convention that the contact angle is measured in the water phase, a contact angle of 180° implies that the surface is completely wet (by oil or air) while one of 0° implies no wetting whatsoever. For practical purposes, if the contact angle is below 90° (above 90° when measured within the droplet or bubble) the fluid is considered not to wet the solid surface, i.e. it will readily run off the surface.

γ_{1a} for which the liquid just completely wets the solid, i.e. for which $\theta_e = 180^\circ$, is often termed the critical surface tension of wetting of the solid, γ_c , a concept introduced by Zisman (1964) for the wetting of a low energy solid by a series of homologous organic oils in air. If γ_{1a} is larger than γ_c the solid is completely wet; if smaller, a contact angle forms. By analogy, the value of γ_{ow} at which the oil makes a contact angle of 180° with the solid could be termed γ_c . The usefulness of Zisman's concept is discussed further in Section 5.2.3.3.

If equilibrium is assumed, i.e. if all phases are mutually saturated with each other, the three interfacial tensions can be

resolved horizontally to yield Young's equation (sometimes called the Young-Dupre equation) :

$$\gamma_{wo} \cdot \cos \theta_e = \gamma_{so} - \gamma_{sw} \quad [3.3]$$

In their review Lucassen-Reynders and Lucassen (1984) reported that this equation has also been derived from thermodynamic principles (the derivation is given in Adamson, 1960). They also emphasized that the γ -quantities are interfacial tensions and not interfacial free energies, which are only numerically equivalent for single components (see Section 2.2.1.1).

Finch and Smith (1979) pointed out that experimental proof of the equation is hampered by the inability to measure the surface tensions where solids are involved. This is in fact the very reason for which the relation is used! Lucassen-Reynders and Lucassen (1984) concurred, but reported that the relation has been found to hold on mercury and solids just above their melting points.

The derivation of Young's equation assumes implicitly that the curvature of the 3-phase contact perimeter is sufficiently gentle. Should the wetted perimeter be small, high curvature with its associated line tension (the 3-phase "interfacial tension") will influence the force balance. Essentially line tension is the force required to increase the length of the contact line (perimeter) and may be positive or negative unlike surface tension which is always positive. If positive it opposes the formation of three phase contact. Lucassen-Reynders and Lucassen (1984) recorded that little is known about line tension at this stage. For very small droplets line tension may be important but it is generally ignored as the Young equation is invariably adequate. If it is accounted for then the equilibrium balance becomes :

$$\gamma_{wo} \cdot \cos \theta_e = \gamma_{so} - \gamma_{sw} - \gamma_{swo}/r \quad [3.4]$$

where γ_{swo} is the line tension and r is the radius of droplet contact.

From Equation 3.3 it is evident that a three phase line of contact is established if

$$\gamma_{wo} > \gamma_{so} - \gamma_{sw} \quad [3.5]$$

No contact is established if this inequality does not hold. For oils a possibility of the oil engulfing the solid exists if

$$\gamma_{wo} < -(\gamma_{so} - \gamma_{sw})$$

i.e. if $\gamma_{sw} > \gamma_{so} + \gamma_{wo}$ [3.6]

Inequality 3.5 indicates that adsorption is favoured if γ_{so} is relatively low and γ_{wo} and γ_{sw} are relatively high. A low γ_{so} is favoured if the specific solid surface energy, G^s , is low which it is in the case of hydrophobic solids like coal, and γ_o (G_o^s) is low, which it is for non-polar oils.

Interfaces involving non-polar substances such as oil or "pure" coal (which is not excessively oxidized) will induce low interfacial tensions as polar interactions are largely absent and London-Van der Waals dispersion forces dominate. Adamson (1967) and Lucassen-Reynders and Lucassen (1984) reported that the semi-empirical theory of Fowkes is well able to predict contact angles in these systems. Fowkes' theory allows estimation of the interfacial tensions on the basis of the dispersion interactions (London and Van der Waals forces) between two phases in contact. This is very useful for strictly non-polar solids. As soon as polar interactions occur at the interface the prediction of the interfacial tensions becomes increasingly unreliable. It is therefore not possible to predict behaviour from Inequalities 3.5 or 3.6.

On the other hand the water-oil interfacial tension can be readily measured. Thus, in theory, Equation 3.3 could be used to circumvent the need to measure or predict solid interfacial tensions. However the problems associated with contact angle measurement (discussed earlier) make this equation of qualitative use only. Experimental verification of adsorption behaviour is still required.

Some additional problems associated with contact angle measurements are now considered.

Equation 3.3 implies that there is a unique contact angle for any three phases at equilibrium, yet contact angle hysteresis is invariably manifested and more than one stable contact angle can exist. Bailey and Gray (1958) noted that the term equilibrium contact angle is misleading. Advancing and receding angles (achieved by moving the three phase line of contact and then taking the static contact angle measurement) are "equilibrium" values in that they maintain their values for some time. The actual equilibrium position of the air-water interface can be anywhere between the advancing and the receding values depending on the conditions. Because of this hysteresis the term "equilibrium" is insufficient to define the actual position of the interface.

One explanation for this hysteresis is that the system is not actually at equilibrium, but Finch and Smith (1979) reported that even systems in thermodynamic equilibrium can exhibit variations in contact angle. Given that fluids exhibit a single unique contact angle at equilibrium, the existence of contact angle hysteresis is attributed to properties of the solid. Surface roughness and surface heterogeneity are generally acknowledged as the two probable sources.

Surface roughness (surface geometry) on both a macroscopic and microscopic scale will cause the advancing or receding fluid phases to stick and jump when surface defects are encountered. Their movement over the surface will not be smooth and the contact line may even be halted by such defects. Ng (1982) found surface texture had an important effect on the spreading of droplets and Steenberg (1982) pointed out that contact angle measurements can be misleading because of the surface topography. Only on a truly planar surface will the macroscopic and microscopic contact angles coincide. Steenberg believed this is one reason for the inconsistencies which are often encountered between contact angle measurements and actual flotation performance.

Surface heterogeneity, i.e. surface energy differences, can also induce changes in contact angle. Heterogeneity is a result of the presence of :

1. various constituents of the solid itself (e.g. coal macerals; as well as the various gangue constituents), and,
2. the presence of surfactants (e.g. frothers) which are adsorbed non-uniformly upon the solid surface.

Hysteresis leads to contact angles (measured in the water phase) which are larger when the aqueous phase advances over the solid than when it recedes in the face of advancing oil (air). In flotation (contact with air bubbles) and in oil droplet adsorption the receding angle, produced as the aqueous phase retreats, would appear the most relevant though Lucassen-Reynders and Lucassen (1984) reported that the advancing angle (which is measured by the commonly used captive droplet/bubble technique) has been found to be the more reproducible measure. According to Smith and Duckmanton (1957), the advancing contact angle is useful since it determines the strength of contact. The larger the advancing angle, i.e. the smaller the receding angle within the oil, the smaller the chance of oil droplet detachment.

To account for the observed hysteresis, various correction factors have been suggested for inclusion in the basic Young equation, chiefly for altering the calculated equilibrium contact angle to yield the apparent (visually evident) contact angle. Finch and Smith (1979) provide an excellent review of these corrections.

Lucassen-Reynders and Lucassen (1984) pointed out that the importance of "equilibrium" contact angles should not be overemphasised as time for contact and adsorption is so short in a real flotation system that interfacial tensions and contact angles cannot attain their equilibrium levels. Bailey and Gray (1958) held the same opinion, stating that the equilibrium contact angle may have little application in processes where there is an advancing or receding oil (air)-water interface such as in flotation. Nevertheless equilibrium contact angles remain a very useful means for evaluating solid interfacial tensions.

3.2.6.2 Dynamic contact angles

This term is applied to reproducible but non-equilibrium contact angles in which time is a factor, i.e. the angle manifested is

dependent on the elapsed time of phase contact. Newly created interfaces (bubbles or droplets) have often been found to induce different contact angles to those of a greater age. Horsley and Smith (1951) found that although an attached air bubble initially spread rapidly over a coal surface, the final contact angle was not achieved until after about 5 minutes.

Non-equilibrium behaviour has been attributed to non-equilibrium surfactant adsorption (and hence non-equilibrium surface tensions) and/or the movement of the three phase contact line across the solid surface. Both are likely to occur simultaneously in flotation systems. The retreat of the aqueous film would induce the re-arrangement of surfactants at the solid-water and solid-oil interfaces and consequently non-equilibrium interfacial tensions.

Movement of the three phase line of contact upon impaction (which includes "bouncing" of the two particles) and during any subsequent movement across the surface of the solid may give rise to a velocity-dependent contact angle. High speed cinematographic techniques have facilitated the study of this phenomenon. According to Lucassen-Reynders and Lucassen (1984) contact line movement is significantly greater on heterogeneous surfaces [such as r.o.m. coal] where contact angles can change from 0 to 180° with increasing contact line velocity.

The relevance of this contact angle reversal to oil droplet adsorption is that contact may be lost if the newly created contact area cannot expand sufficiently rapidly to induce adequately high contact angles to overcome pulp shear forces.

Rapid expansion of the contact area is particularly important with large particles which are subject to relatively large inertial forces, as shown by the work of Baranov and Gubaidulin (1971). They found, when using hexadecane, decalin and various commercial oils, that when an oil droplet was allowed to contact coal for a very short time (0.008 s) before being withdrawn, -100 μm coal particles adhered far more successfully than coarser particles. Rapid expansion of the contact area could be hindered by flow of liquid from the "wedge" between the oil and the solid. The mechanisms of flow at this point are extremely complex and are poorly understood at present.

3.2.7 Effect of surfactant adsorption

Surfactants (surface-active agents) owe their properties to their dual nature which is induced by a small solubilizing group (which need not necessarily be ionic - weakly solubilizing groups like the hydroxyl group or ether linkages are also effective) and a long hydrophobic portion. The hydrophilic group exerts a [water] solubilizing effect which is opposed by the hydrophobic group. If a proper balance is obtained between the two portions, then the surfactant neither quite dissolves nor remains undissolved but congregates at the liquid-liquid, vapour-liquid, or solid-liquid interfaces.

Surfactants reduce interfacial tension (as explained in Section 2.2.1.3). The polar ends which project from an oil droplet into the aqueous phase encourage the formation of stable hydrate clouds (orientated water molecules) which discourage droplet adsorption on coal particles. Steenberg (1982) pointed out that work is required to strip off part of this hydration sheath before adsorption onto the surface is possible. The presence of surfactants at the oil-water interface also prevents internal oil circulation in the droplet, by immobilizing the interface, so that from a hydrodynamic point of view it behaves like a solid particle.

Aston et al (1981) emphasized that the behaviour of surfactants, in particular non-ionic surfactants like MIBC, in water-solid-oil systems is not yet thoroughly understood. Nevertheless an adequate basic theory on the action of surfactants does exist. The theory, which is discussed below, is dependent on the assumption of *equilibrium* conditions.

At thermodynamic equilibrium conditions, $\gamma = G^s$ (Equation 2.3). Hence for adsorption at equilibrium conditions, and constant temperature and pressure, Equation 2.1 gives :

$$\left(\frac{dG}{dA}\right)_{T,P} = \gamma + \sum \mu_i \left(\frac{dn_i}{dA}\right) \quad (i = 1, 2, \dots, j, \dots, r) \quad [3.7]$$

Partial differentiation of Equation 3.7 with respect to μ_j yields :

$$\frac{\partial \gamma}{\partial \mu_j} = - \frac{\partial n_j}{\partial A} = - \Gamma_j \quad [3.8]$$

where Γ_j is the adsorption density of surfactant j at a given interface. Similar equations can be derived for each of the r species present at the interface. However, the (pure) bulk phases, water and oil (phases 1 and 2), in contact are defined as having no excess at the interface.³ Hence for all adsorbed species,

$$(d\gamma)_{T,P} = - \sum_1^r \Gamma_i d\mu_i \quad [3.9]$$

Equation 3.9 is the Gibbs adsorption law and it describes how adsorption of surfactants (e.g. frothers and commercial oil impurities) alters the surface and consequently interfacial tensions.

Equation 3.9 shows that positive surfactant adsorption causes a decrease in surface tension, a phenomenon discussed earlier in Section 2.2.1.3. For ideal solutions $d\mu = RT d \ln c$ where c is the surfactant concentration in one of the phases. Very dilute surfactant solutions, as used in flotation, may be assumed to be ideal.

The species present in excess at the interface will be charged or polarized. Interfacial tension can therefore be related to interfacial charge and potential. In the absence of charged surfactants (organic ions adsorbed in the Stern layer), which is reasonably typical of coal flotation, Equation 3.9 can be rewritten as,

$$d\gamma_i = - \sigma_s d\phi \quad [3.10]$$

where σ_s is the surface charge and ϕ is the Galvani potential (potential across the interface). These concepts are discussed in more detail in Chapter 2, Section 2.2.5.1.

³ For a detailed derivation of Equation 3.8 refer to Kruyt, 1952 pp.117-118.

The Young equation (Equation 3.3) can be differentiated with respect to γ_{wo} and the Gibbs adsorption equation substituted in the RHS to give :

$$\frac{d(\gamma_{wo} \cdot \cos \theta_e)}{d\gamma_{wo}} = \frac{\Gamma_{so} - \Gamma_{sw}}{\Gamma_{wo}} \quad [3.11]$$

The product $\gamma_{wo} \cos \theta_e$ is called the "adhesion tension".

Knowledge of the adhesion tension versus γ_{wo} relation allows direct assessment of the interface adsorption (from equation 3.11) without knowledge of the solution ideality. Smith and Finch (1979) report that for low surface-energy (hydrophobic) solids a plot of the adhesion tension versus the water-oil interfacial tension (γ_{wo}) has a negative slope which implies that surfactant adsorption at the solid-oil interface Γ_{so} is always less than that at the solid-water interface Γ_{sw} . This would be expected since the former interface is between non-polar phases, i.e. there is no polar phase involved. Bhargava et al (1978) conducted interfacial studies on solid-hydrocarbon oil (kerosene and n-dodecane)-water systems and reached a similar conclusion.

From Equation 3.3 it is evident that the adsorption of surfactant can only alter the contact angle if it alters the ratio of $(\gamma_{so} - \gamma_{sw})$ to γ_{wo} . The difference $(\gamma_{so} - \gamma_{sw})$ cannot be determined directly since interfacial tensions at interfaces involving solids cannot be measured and is normally substituted by the adhesion tension which is equivalent. Again the practical limitations of contact angle measurements must be remembered.

The effect of surfactant adsorption on the contact angle is clearly evident from Equation 3.11 upon integration and rearrangement, i.e.,

$$\cos \theta = \frac{\Gamma_{sl} - \Gamma_{sw}}{\Gamma_{wl}} + \frac{K}{\gamma_{wl}} \quad [3.12]$$

The subscript 1 represents a non-polar fluid (air or oil).

Equation 3.12 shows that the adhesion tension ($\gamma_{wl} \cos \theta$) is a linear function of γ_{wl} over the entire range of surfactant concentrations up to the limiting concentration. Lucassen-Reynders and

Lucassen (1984) and Finch and Smith (1979) reported that the experimentally measured effect of surfactant adsorption on contact angle is determined largely by the polarity of the solid surface. Non-polar solid surfaces have been studied extensively. In such systems the slope (Equation 3.12) is about -1, i.e. Γ_{so} is negligible while Γ_{sw} and Γ_{wo} are about equal. This is shown in Figure 3.4 below. In effect surfactant adsorption is non-specific being about the same at the solid-water and water-oil (or water-air) interfaces and virtually non-existent at the solid-oil interface.

$$\text{i.e., } \gamma_{wl} \cos \theta = -\gamma_{wl} + K \quad [3.13a]$$

$$\text{or, } \cos \theta = -1 + K/\gamma_{wl} \quad [3.13b]$$

Lucassen-Reynders and Lucassen (1984) plotted the results of several workers and found that Equation 3.13 holds for both air and oil phases (Figure 3.4). Experimental results for different surfactants used in the same 3-phase system will all coincide with this single line (Equation 3.13) even though the γ_{wl} vs c and θ_e vs c curves are very different (where c is the surfactant concentration). This behaviour is shown as line A in Figure 3.4 below.

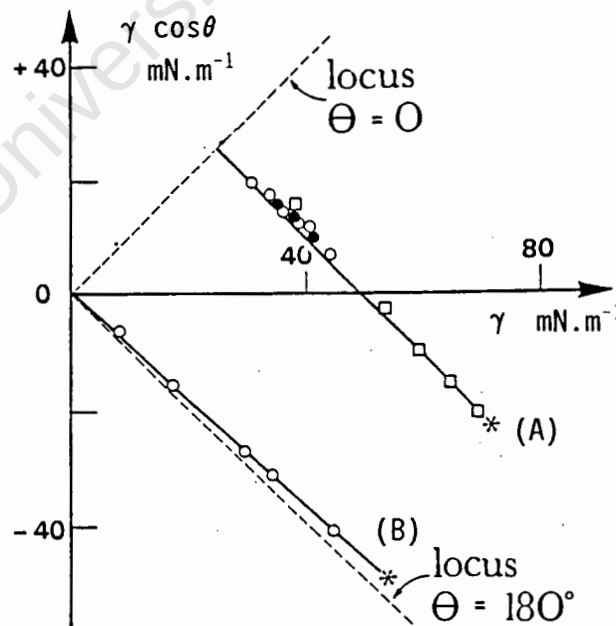


Figure 3.4 : Adhesion tension vs. interfacial tension for a strictly non-polar solid surface. Line A, solid paraffin/ water/oil. o with Aerosol OT, • with Tergitol, □ with butyric acid. Line B, PTFE/water/oil. * represents the state of the surfactant-free system. (Modified from Lucassen-Reynders and Lucassen, 1984).

K is the extrapolated value (hypothetical) of the adhesion tension when $\gamma_{wl} = 0$. The value of K (the intercept) is important as it indicates the effect that surfactant addition will have on the contact angle between water, a non-polar fluid and a non-polar solid. If K is positive the contact angle decreases with increasing surfactant concentration, i.e. decreasing surface tension γ_{wl} (Equation 3.13b). With less hydrophobic solids the decrease will depend on the surfactant adsorption levels at the various interfaces (Equation 3.12).

For interfacial interactions governed solely by dispersion forces K can be estimated from Fowkes' theory (Lucassen-Reynders and Lucassen, 1984).

$$K = (\sqrt{\gamma_1} - \sqrt{\gamma_w^d})(\sqrt{\gamma_1} - \sqrt{\gamma_s^d}) \quad [3.14]$$

where d superscripts indicate the London-Van der Waals dispersion force contributions.

If the non-polar fluid in Equation 3.14 is air then γ_1 becomes zero because of the absence of dispersion interactions within air (gaseous phase), and K has an appreciable value (30 to 50 mNm⁻¹, Lucassen-Reynders and Lucassen, 1984). Increasing surfactant concentrations hence reduce the contact angle appreciably.

If on the otherhand the non-polar fluid is oil as opposed to air the three dispersion force terms in Equation 3.14 are approximately equal in value (about 20 mNm⁻¹, Lucassen-Reynders and Lucassen, 1984). K is close to zero (Figure 3.4) and contact angles remain nearly constant, i.e. surfactants have little influence on the contact angle. Typically, then, surfactants produce a large decrease in contact angle on non-polar solids for the air/water interface but hardly affect the contact angle of the oil/water interface.

In apparent contrast Horsley and Smith (1951) and Jowett (1958) found that contact angles of air bubbles on coal did not increase with the addition of some reagents despite the fact that these reagents were adsorbed. Jowett explained this by pointing out that contact angles tend to be a characteristic of the chemical groups at the solid surface as well as of those of the reagent. A coal possessing a high native contact

angle could therefore mask the angle produced as a result of the presence of a reagent. By analogy, this author proposes that the existence of a collector oil which induces a high contact angle could mask the additional effect contributed by the frother.

Another explanation for the fact that air bubble contact angles may be less sensitive to surfactant adsorption than expected is that coal is not strictly non-polar. Γ_{sl} will therefore not be negligible. Since K will not be negligible with air it implies (Equation 3.12) that $(\Gamma_{sl} - \Gamma_{sw})/\Gamma_{wl}$ must decrease by approximately the same amount that K/γ_{wl} increases with increasing surfactant addition if θ is to remain approximately constant. Γ_{wl} will obviously increase since γ_{wl} decreases (Equation 3.9). Γ_{sw} will however now be more limited since the solid is now assuming some hydrophilic character. Γ_{sl} will no longer be negligible for the same reason. Should their difference decrease as Γ_{wl} increases, then the possibility of a reasonably consistent contact angle exists.

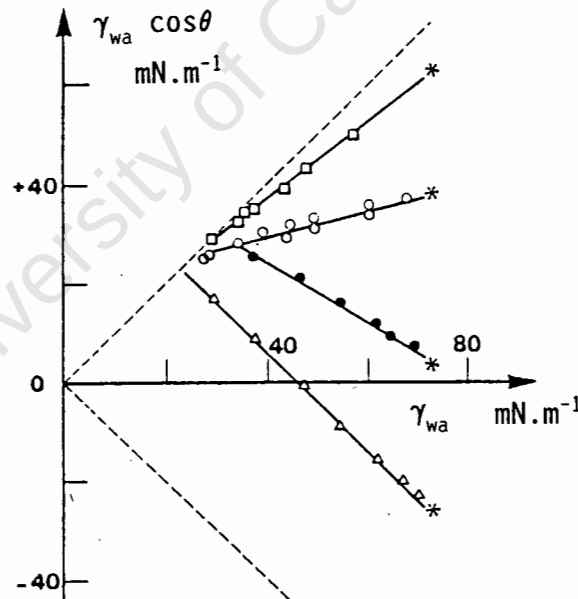


Figure 3.5 : Adhesion tension vs. interfacial tension, γ_{wa} , for solids of increasing polarity. $\square$ solid paraffin, $\bullet$ talc, Δ cellulose and o nylon. (After Lucassen-Reynders and Lucassen, 1984)

As the solid surface becomes increasingly polar, γ_{sl} increases, so the adhesion tension of the surfactant-free system increases (Equation 3.3). Surfactant addition produces non-zero Γ_{sl} , increasing the slope of the adhesion tension plot (Equation 3.11). The slope may

even become positive. Lucassen-Reynders and Lucassen (1984) plotted the results of several workers, who used talc, nylon and cellulose as the solids. The results are shown in Figure 3.5. This author presumes that unwashed coal would fall into the same category. Provided that the surfactant-free solid is not too hydrophilic, i.e. θ_0 is not zero or too close to it, the slope remains constant and K positive. Increasing surfactant concentration will still tend to decrease contact angles.

The linear relationship breaks down entirely with hydrophilic solids, i.e. where θ_0 is no longer positive in the surfactant-free system (no contact occurs).

It must be re-emphasized that the theory discussed above assumes equilibrium conditions have been attained. Lucassen-Reynders and Lucassen (1984) found that there is very little information on the effects induced by surfactant adsorption kinetics and hence their actual effects in flotation systems where equilibrium conditions may never be reached.

3.2.7.1 Adsorption promoters

Certain surface-active reagents are known to improve the rate and tenacity of the coal-oil adsorption process. Such reagents may be ionic surfactants such as long chain amines or polar non-ionic surfactants such as olefin oxides (Tyurnikova and Naumov, 1981 pp.150-164; Laskowski and Miller, 1984). These reagents are used in comparatively small quantities in relation to the non-polar oily collectors and are often termed "promoters" or "kickers". They may improve oil dispersion (Laskowski, 1986) but their performance is believed to be chiefly a result of their presence at the oil-water and/or solid-water interfaces which encourages and stabilizes the formation of the oil-solid interface. For instance, cationic promoters such as the amines have been found to be particularly useful for increasing the hydrophobicity of oxidized and low rank coal, which both exhibit a comparatively high proportion of negatively charged surface oxygen-containing groups.

Because of the low concentrations typically used the promoters (and frothers) will be present as diffuse molecular layers at the

coal-water and oil-water interfaces. It is proposed, by this author, that following contact of oil droplet and coal particle the respective diffuse layers of surfactants inter-penetrate, in an analagous manner to the mechanism postulated by Leja and Schulman (1954) for frother-collector joint action in bubble-solid adhesion.⁴ This penetration gives rise to a single layer of associated species which greatly enhance the local hydrophobic character of the surface and the stability of the droplet-coal attachment. The process is represented schematically in Figure 3.6 below.

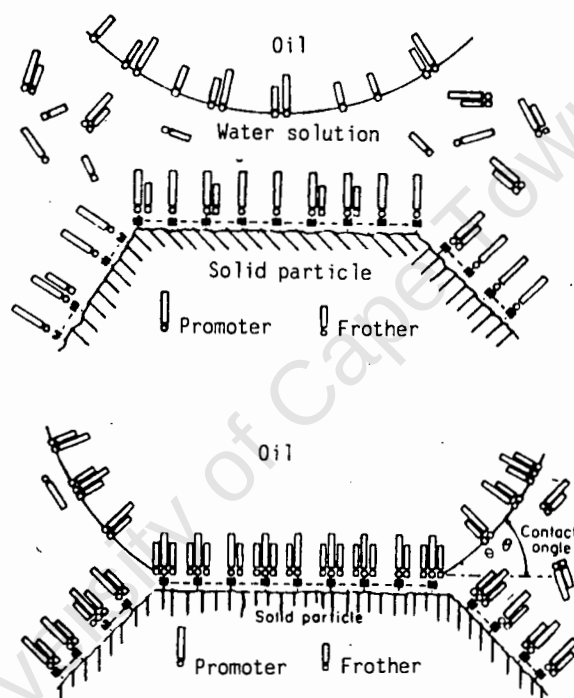


Figure 3.6 : Proposed mechanism of oil droplet attachment to a solid surface. Both surfaces showing adsorption of "promoter" surfactants as diffuse layers. Ionic and polarized species shown. (Modified after Leja and Schulman, 1954).

However, excessive dosage of promoters can lead to poorer results if multiple layers of surfactants build up at the solid-water interface and so re-induce hydrophilicity by reversing their orientation. This problem could presumably also occur when promoters are used with strongly hydrophobic surfaces.

Ng (1982) believed the strength of the oil-coal bond to be influenced by surfactants present at the oil-coal interface. He also

⁴ The collector in this case was a charged surfactant, e.g. a xanthate molecule.

observed that surfactants containing aliphatic groups increased the adhesion more than those containing aromatic groups; a phenomenon observed earlier by Burkin and Bramley (1963).

3.2.8 The spreading of oil on wet coal

Brown et al (1958) reported that the spreading of oil on wet coal is dependent on :

1. The water-oil-coal contact angle, and,
2. The oil-water interfacial tension

Two criteria of spreading were considered : the "spreading coefficient" for flat surfaces and the "spreading force" incorporating the "adhesion tension" for capillaries, cracks and so on. The spreading coefficient is defined as,

$$F_s = \gamma_{cw} - \gamma_{co} - \gamma_{wo} \quad [3.15]$$

with the subscript c representing coal. The derivation of the spreading coefficient from the work of adhesion and cohesion is given in Section 2.2.1.2. The spreading coefficient can also be expressed in terms of Young's Equation (Equation 3.3).

$$F_s = -\gamma_{wo} (\cos\theta_e + 1) \quad [3.16]$$

The spreading force, S_f , in a circular capillary is :

$$S_f = -2 \gamma_{wo} \cos\theta_e / r, \quad [3.17]$$

r being the radius of the capillary.

The spreading coefficient is probably more important than the spreading force in coal flotation pulps as :

1. The solid particles are reasonably separated so that penetration of oil between closely associated particles is unimportant, since aggregates are comparatively rare, and,
2. spreading into surface capillaries and cracks has been found to be of little significance with most oils (Brown et al, 1958).

Spontaneous spreading implies a positive F_s or S_f . The coal surface is then completely wettable and would be engulfed by the oil (Inequality 3.6). The more positive F_s (Equation 3.15), the greater is the tendency to spread. The oil will spread even if the solid-water surface tension is lowered by the presence of surfactants.

However if F_s is negative the oil droplets adopt a stable position and display a definite contact angle. It is clear from Equation 3.16 that spreading is never spontaneous if a contact angle is evident, as F_s is never positive. The surface is then only partially wettable. In order for collector (oil) droplets to spread work must be done on the system. The spreading coefficient is therefore a measure of the amount of energy needed to distribute the oil over the coal surface.

Spreading into a constricted space (e.g. the space between particles or into cracks and pores) differs from spreading on an open surface in that a spreading force exists as a result of the curvature of the meniscus. Brown et al (1958) stated that the condition for replacement of water by oil in a crack or pore is that the advancing contact angle (in the oil) is acute (the angle in the aqueous phase is therefore obtuse). Adhesion tension ($\gamma_{wo} \cos \theta_e$) must thus be negative for spontaneous replacement of water by oil. The spreading force, S_f , will then be positive. An acute aqueous phase contact angle will make it negative (Equation 3.17).

For both criteria spreading is enhanced if the contact angle, θ_e (in the water phase), is increased. A decrease in the interfacial tension between the oil and the water, γ_{ow} , favours spreading on flat surfaces and spreading into capillaries where this is not spontaneous i.e. where the adhesion tension is positive. The tendency for spreading can also be considered in terms of the affinity of the phases for one another and for themselves, i.e. in terms of adhesion and cohesion respectively. If molecules of one phase adhere more avidly to those of another, than to themselves, then spreading will occur spontaneously and vice versa.

In their testwork on the spreading of oils on wet coal Brown et al (1958) used pure component oils and impure ones containing varying amounts of surfactant to find conditions most conducive to spreading. The oils studied were paraffin, fuel oil, n-decane, n-hexadecane,

p-xylene and heavy paraffin (Nujol). Various oil additives were also used. These were m-cresol, Lubrol MOA and Tween 81, the last two of which are oil soluble surfactants (like MIBC). Various Australian coal samples were used.

It was found that spreading of oil was not spontaneous under any conditions tested, but was assisted by the presence of surfactants. γ_{wo} was clearly reduced more than γ_{sw} (Equation 3.15). This finding implies that certain frothers are likely to influence the spreading of oil on coal. Brown et al (1958) also found that the oils spread more readily on polished as opposed to rough coal surfaces, more easily on high rank than on low rank coals, and that surfactants influenced the contact angle. This latter observation supports an earlier opinion that coal should be regarded as a somewhat polar solid though sufficiently non-polar for Equation 3.12 to hold.

Tyurnikova and Naumov (1981) believed surfactants to be permanently and stably adsorbed from the aqueous phase, forming a hydrophobic adsorption layer on the coal, and facilitating the wetting by and spreading of the oil droplet. This mechanism was suggested earlier by Leja and Schulman (1954). Frother can be adsorbed onto a mineral independently of the collector and thereby decrease the total hydration of the mineral, as confirmed by Dmitrieva et al (1970). However, the adsorption and orientation of the surfactants will depend on the coal surface polarity and hence on its gangue mineral content, rank and oxidation level.

Brown et al (1958) pointed out that because oil spreading is not spontaneous coal conditioning does not end with the attachment of oil droplets, since they must be distributed or spread further by agitation and contact with other particles within the pulp. Glembotskii et al (1970) reported that spreading of oil on a hydrophobic surface is slow and that the degree to which this occurs is likely to be small in actual flotation systems. This again emphasises the importance of pulp conditioning.

3.2.9 Summary of oil-coal contact and adsorption

The adsorption of oil onto coal affects coal particle hydrophobicity and consequently coal flotation performance. It was therefore believed that it would be important to investigate oil adsorption dynamics and the factors which affect it. In this work "adsorption" is taken to mean the contact and attachment of an oil droplet to a solid particle.

The oil-coal bond is in all cases a physi-sorption, predominantly by London-Van der Waals forces, i.e. dispersion and polar electrostatic interactions, or both. Saturated aliphatic oils are largely restricted to dispersion (induced dipole) interactions while aromatic oils with their double bonds and local negative charges are also capable of electrostatic (dipole) interactions. In addition the presence of oxidized hydrocarbons in commercial oils allows for hydrogen bonding between the oil and oxygen-containing surface functional groups on the coal. Van der Waals and hydrogen bonds are individually weak but the cumulative effect over the area of droplet-solid contact produces a strong bond. The absence of polar interactions with saturated aliphatic oils limits their adsorption on comparatively high energy, i.e. high ash or oxidized coal, surfaces. This is a result of a limited ability to displace water from such surfaces since the oils will wet a dry coal surface. In effect water adheres more strongly to the coal surface than oil would, i.e. the system achieves a lower energetic state (interfacial tension) with water than with oil.

Both oil droplets and coal particles are likely to possess negative charges in unregulated pulps where the pH is about 8. This implies that sufficient kinetic energy must be available during mutual collisions to overcome electrostatic repulsion and allow for the particles to approach sufficiently closely for molecular forces of attraction to come into play.

Assuming that the hydrodynamics ensure effective collisions, the thermodynamic possibility of oil droplets adhering to the coal exists if the aggregate possesses a lower free energy than the individual constituents. This is generally the case as higher energy water-coal and water-oil interfaces are replaced by a comparatively low energy oil-coal

interface. However prior to actual adsorption, the thin aqueous film separating the two particles must be thinned to such an extent that it ruptures and retreats, thereby permitting the adsorption of the oil droplet. The higher the surface energy of the coal (which corresponds to an increase in gangue mineral content and/or the level of oxidation) the more stable the disjoining aqueous film and the less readily oil is adsorbed.

Following aqueous film retreat, a contact angle will be established. Since none of the oils studied will completely wet coal, i.e. spread spontaneously on a coal surface, the coal-water interfacial tension must be less than the sum of the coal-oil and water-oil interfacial tensions. Also very few oils will spread spontaneously into surface cracks and pores. Mechanical work is required to enhance spreading. This highlights the importance of coal pulp conditioning.

Oil droplet adhesion is adequately modelled by Young's equation. It is however important to bear in mind that the contact angle established usually displays hysteresis since the advancing angle is numerically greater than the receding angle. This hysteresis is generally attributed to surface roughness and surface chemical heterogeneity. The term "equilibrium contact angle" is misleading since either contact angle (receding or advancing) may retain its value for some time. Dynamic contact angles also exist in the sense that the contact angle is time dependent. It varies as surfactant adsorption densities (and hence interfacial tensions) change progressively from their initial values towards their equilibrium values. Inter-particle collisions induce the 3-phase line of contact to move across the solid surface, thereby altering the established surfactant adsorption levels and producing a similar effect. Dynamic contact angles will be prevalent in a flotation pulp and are likely to be quite different to their static counterparts, which can be measured.

Surfactants change surface tensions by adsorbing at various interfaces and they may hence affect the contact angle and the spreading of oil on coal. The degree of adsorption at the various interfaces will determine this and qualitative predictions of their effect in dynamic situations may be made using Young's equation in combination with the Gibb's adsorption equation. With hydrocarbon oil, changes in contact angle as a result of surfactant adsorption are small if the coal is very

hydrophobic since only dispersion interactions occur at the oil-water and coal-water interfaces. However, the effect on contact angle increases with increasing coal hydrophilicity, i.e. gangue content or oxidation. Most coals have some hydrophilic character and oil adsorption will therefore be affected by the presence of surfactants. With such coals the strength of the oil-coal bond may be increased, particularly with aliphatic surfactants.

The oil-coal-water interfacial behaviour is not fully understood and is further complicated by the impossibility of categorizing the coal surface which has widely varying properties within any one coal. Physicochemical surface heterogeneity also varies considerably from one coal to another. The three most important factors influencing the coal surface properties are the carbonaceous (hydrocarbon) skeleton, the quantity and type of inorganic impurities and the existence of oxygen containing surface functional groups. These factors together determine the electrostatic properties of the coal (which in turn influence its interfacial tensions).

3.2.10 Techniques for measuring/infering adsorption

Contact angle measurements are the traditional means of evaluating oil adhesion. They essentially quantify the wettability of the solid. Various other methods have been developed to study solid wettability and by association oil adsorption. Fuerstenau et al (1985) outlined a technique to assess the wettability of coal surfaces using a modified immersion time test. Solids are placed on the surface of liquids of varying surface tension and the proportion of material imbibed (wetted) and unimbibed are determined. Hornsby and Leja (1984) and Laskowski (1986) have used water and methanol solutions to evaluate coal "surface tension" and hence its floatability. This technique is considered in more detail in Section 5.2.3.3. All these tests evaluate solid surface properties from which, like contact angle measurement, reagent (e.g. oil) adsorption behaviour must be inferred. They do not provide a direct means of assessing oil adsorption dynamics in flotation pulps.

A better appreciation of the adsorption dynamics of oil onto coal is believed to be important, by this author, for a better understanding of coal flotation. Eveson et al (1956) who studied the adsorption of

phenol from solution by low rank coals acknowledged that in the context of flotation, the first few minutes of adsorption are of particular importance. However they were unable to measure this adsorption with any accuracy.

There is apparently no documented technique for studying the adsorption dynamics of oils onto coal within a coal pulp. Recently, Smitham and Firth (1982) studied the equilibrium (final) adsorption extents of an oil onto coal size fractions. They used a radiotracer (n -[1- ^{14}C]-hexadecane) dissolved in kerosene to quantify the adsorption levels of this oil onto various size fractions of $-500\text{ }\mu\text{m}$ deslimed coal (no $-38\text{ }\mu\text{m}$ material). The coal was a sample of Young Wallsend (Newcastle- Australia) coal washed at an S.G. of 1.35. Oil and coal were conditioned for 90 s in a 1 litre Denver cell. Thereafter the coal slurry was screened into its original size fractions. The oil was extracted by refluxing a sample of coal with toluene and then using a Scintillator Spectrometer to determine scintillation counts in the toluene extract. By back-calculation the adsorbed oil concentration was determined. Like the technique of Eveson et al (1956) however, this technique did not evaluate the oil adsorption kinetics. The final extent of adsorption was tacitly assumed to occur after 90 s.

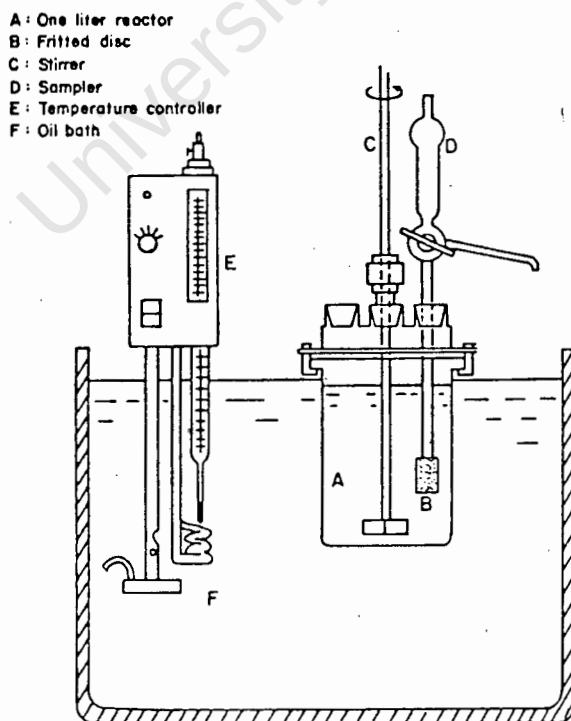


Figure 3.7 : Experimental apparatus used to study xanthate adsorption kinetics. (After Haung and Miller, 1978).

Unfortunately documented techniques for measuring reagent adsorption kinetics/dynamics are restricted to soluble collectors. For example, Haung and Miller (1978) developed a procedure to study the kinetics of the xanthate-pyrite reaction using a small (1 litre) stirred batch reactor containing the ore pulp and a xanthate collector. A fritted glass sparger was used to sample the pulp (sampling was discrete). After further filtration, which was carried out immediately to remove remaining fine solids and so quench the reaction, the xanthate concentration was determined by UV spectrophotometry. Figure 3.7 is a diagram of the apparatus.

It was originally anticipated that a similar apparatus and procedure could be used to study the kinetics of the oil-coal adsorption reaction. However for a number of reasons this proved to be impossible, and a new technique had to be developed. These reasons, together with details of the new technique that was developed, are set out below in Section 3.3.

3.3 DEVELOPMENT OF THE TECHNIQUE FOR MONITORING ADSORPTION OF OILS

3.3.1 Introduction

To investigate the second sub-process in the study of the effect of hydrocarbon oils on coal flotation, a suitable method was sought to study the kinetics of oil droplet adsorption onto coal (or other solid) particles. Initially a method similar to that developed by Haung and Miller (1978) was considered. This method is described in Section 3.2.9 above and applies to water soluble collectors. It was thought that a similar procedure would permit the study of the adsorption reaction of coal and water-immiscible hydrocarbon collectors, in terms of both kinetics and the ultimate adsorption levels attained; but several difficulties were encountered. These are enumerated below and the steps taken to solve them are described. The method that was finally developed is then set out in detail, its limitations discussed, and its repeatability demonstrated. The phenomenon of oil mass loss is also described.

3.3.1.1 Difficulties encountered in developing a method

In attempting to apply a procedure similar to that of Haung and Miller to the coal-hydrocarbon collector system, it became apparent that the chemical constitution of the oily collectors and their immiscibility with water would present several problems. These were :

1. the difficulty in removing representative samples of the water-oil dispersion while simultaneously separating them from the pulp solids; and doing this rapidly enough to quench the reaction and so enable the adsorption to be studied as a function of time;
2. the absence of functional groups in the collectors selected, which limited chemical analytical techniques;
3. the presence of two liquid phases (as an unstable oil-in-water dispersion) in the samples and the need to prepare these samples for chemical analysis;
4. the low concentrations of collector, which necessitated a very sensitive chemical analytical technique. For instance an initial collector dosage of 2500 grams per ton of coal in a 5 % (m/m) solids pulp corresponds to about 130 ppm of collector in water (mass basis). The concentration dropped rapidly from this level during the experiments as adsorption ensued.

3.3.1.2 Overcoming problems

To take a sample of the pulp liquid only (i.e. to preclude solids and therefore further adsorption), solid particles had to be significantly larger than oil droplets so that separation of the two on a size basis was possible. The minimum solid particle size was determined on the basis of the results of the oil dispersion studies made previously using the Coulter Counter (Chapter 2). As shown in Chapter 2, every millilitre of pulp liquid contains millions of small collector droplets. The droplet numbers decrease rapidly with increasing size, but most of the collector volume (mass) is concentrated in the upper size ranges so these droplets must not be

excluded. Consequently, the minimum solid particle size was chosen to be somewhat larger than the maximum oil droplet size.

Initially attempts were made to take liquid samples from the pulp using sintered glass and stainless steel filters. However, in addition to any sorption effects, severe errors were introduced on account of the pores in these filters being inconsistent in size. Many large droplets (and therefore much of the oil mass) were trapped in the constrictions within the smaller pores, making these filters unsuitable for use.

Eventually, suitable filters were made by building up clusters of hypodermic needles of selected bores, as shown in Figure 3.8. Multiple needles overcame blocking problems and were found to give very rapid and excellent separations.

Because n-paraffins contain no double bonds, functional groups, etc. it was not possible to use U.V. spectroscopy to analyse the samples. Gas-liquid chromatography (GLC) using a packed column (OV-101 on Chromosorb W) and a flame ionization detector (FID) was chosen for determining the oily collector concentration in the pulp samples. The GLC instrument was sensitive enough to measure the small oil concentrations accurately.

GLC requires micro-litre quantities of liquid for analysis. Because a sample withdrawn from the pulp is a dispersion, it is difficult to take a representative sample of this for analysis in such small quantities, especially if any phase separation has occurred (which will undoubtedly be the case).

A liquid extraction technique using CCl_4 was thus used to render the dispersion sample amenable to GC analysis.⁵ Liquid extraction was especially useful in that the collector concentration could be increased. Fortunately, high boiling point hydrocarbon oils are insoluble in water so that partitioning between the water and CCl_4 was not a problem. Extractions using CCl_4 were rapid and complete, i.e. there was insufficient collector (if any) left in the water to permit detection by the very sensitive detector.

⁵ Homogenizing the samples with a solvent (e.g. ethanol) mutually compatible with both the collector and water, was found to be unsatisfactory because of excessive dilution and incompatibility of the solvent with the GLC column packing selected.

Analysis was quantitative, and was based on the measurement of peak heights or areas. The advantage of using peak heights, particularly with commercially produced (impure) oils, is discussed more fully in Appendix 3.1. Often both bases were used for cross checking the results.

To enable peak measurements to be related to actual concentrations an exactly known amount of an "internal standard" was added via the CCl_4 used for collector extraction. An internal standard is used to normalize peak counts, rather than having to rely on absolute counts which vary with sample volume and instrument conditions. The internal standards used were all pure hydrocarbon oils, e.g. decane. The standard used with any particular collector oil was chosen so that its peak appeared separate from the peak or peaks of the collector oil in the chromatogram.

3.3.2 The Method

The adsorption experiments were carried out in a baffled, cylindrical stainless steel vessel (9,5 cm diameter, 12 cm height). All four baffles were full length and 1 cm in width. The oils were dispersed in 500 ml of distilled water using a turbine impeller. The impeller consisted of a stainless steel disc 60 % of the vessel diameter, with eight blades, 1 cm x 0,5 cm, mounted so that 0,3 cm of blade extended beyond the disc periphery. A photograph of the apparatus appears in Figure 3.9.

Sample bottles and disposable syringes with their needle filters were weighed accurately (to 0.1 mg) prior to each experiment. 85 μl of the oil (with or without a frother) was then added to 500 ml of distilled water at 25°C (some other controlled temperature could be used). The collector oils were always added on a volume basis, i.e. 85 μl to 500 ml of distilled water.⁶

⁶ The results of the dispersion study (Chapter 2) showed that some oils will produce smaller droplets and therefore a larger oil-water interfacial area than others. They would do so during flotation. As the primary objective of the adsorption experiments was to identify the behaviour of various oils which lead to a specific flotation response, dosage based on volume was retained. No attempt was made to alter dosages so as to produce roughly equivalent oil-water surface areas. This would be unrepresentative of the industrial flotation situation and would be practically impossible to implement experimentally.

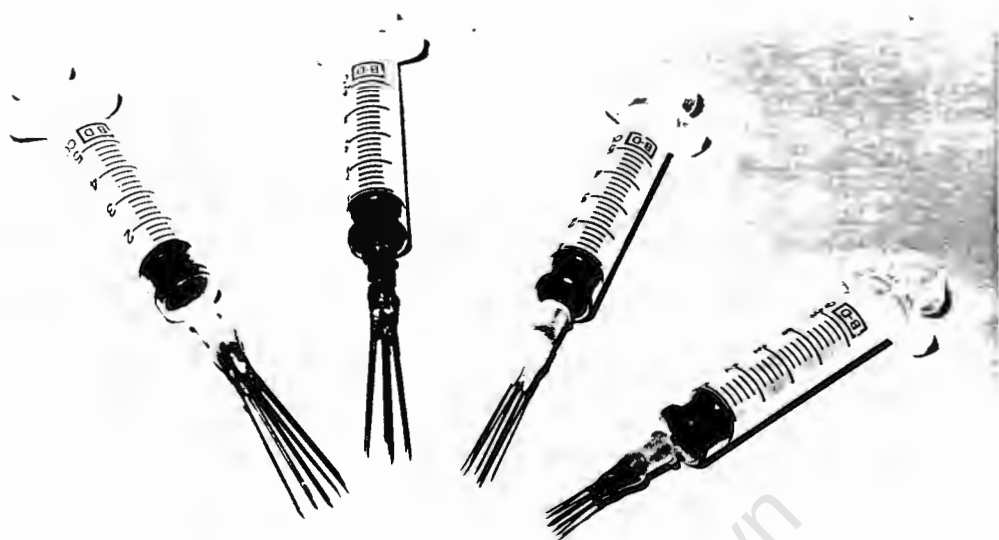


Figure 3.8 : Needle filters on disposable hypodermic syringes. The smaller the bore of the needle the smaller the minimum size which can be filtered.



Figure 3.9 : Experimental apparatus. Stainless steel vessel and turbine impeller; waterbath; needle-filters and syringes; device for adding a wetted slug of solids; and microsyringe for adding reagents.

After one minute of agitation a sample of the dispersion would be withdrawn, just before the addition of solid particles. This sample was used to normalize the rest of the results, as a time dependent loss of collector from the water was discovered. In other words the collector concentration at the time solids were added was not the same as the initial concentration. This phenomenon is discussed in more detail below (Section 3.3.5).

Immediately after this initial sample was taken solid particles were added as a pre-wetted slug. The vacuum filter-syringe device used to constitute and then to add the coal is shown in Figure 3.9⁷. This device enabled all the coal to be added at zero time and as no wash water was required to transfer the coal to the vessel, pulp density remained consistent from run to run. The mass of solids added (coal, quartz and various coal density fractions) was adjusted according to the solid specific gravity (S.G.) to ensure similar surface areas. The benchmark was **25 g** at an S.G. of 1.3. Porosity was assumed to have a negligible effect on the surface area available for adsorption. Few oils will spread spontaneously into pores (Section 3.2.8) though very small droplets may be able to enter some pores.

Sampling of the pulp was on a discrete basis. The adsorption was monitored over a 5 minute period with samples usually taken at 10, 20, 30, 45, 60, 90, 150, 240 and 300 seconds after addition of the solid particles. The pulp was sampled directly using the filters devised and 5 ml disposable syringes. Small volumes (roughly two ml) were withdrawn to prevent any significant changes of pulp density within the reactor.

At the completion of the experiment, syringes containing the dispersion samples were reweighed. Roughly 1 ml of CCl_4 containing the internal standard was then drawn into them. The filters were removed and all the syringes capped tightly. The extractions were performed by shaking the syringes on a Heidolph testtube-shaker using an adapter to prevent syringes making direct contact with the shaker. Syringes were shaken for one minute after their contents first appeared "milky". Extractions had to be carried out within the sampling syringes because any transfer of the dispersion sample from the syringes to the sample

⁷ The way in which this device works is shown photographically in Appendix 3.5.

bottles before extraction caused serious error. This is largely a result of the oily collector adsorbing onto the syringe wall.

The syringe contents were transferred to preweighed sample bottles which were capped and reweighed. Any CCl_4 lost by evaporation or absorption by the syringes was then accounted for.⁸ The mass of water was already known and therefore that of the CCl_4 could be determined. The masses of collector and standard were insignificant and were ignored in these calculations.

For analysis, 3.5 μl of the CCl_4 layer were withdrawn using a micro-syringe and injected into the GLC instrument. Detector response was linear with respect to both sample concentration and volume at the levels used in the technique (see Appendix 3.2). Knowing the ratio of collector to standard peaks (from the GLC analysis) and the masses of water and CCl_4 in each sample it is simple to calculate the collector concentration in the pulp at the time the sample was taken.

In the extract :

$$\frac{\text{Concentration}_{\text{col}}}{\text{Concentration}_{\text{IS}}} = \frac{\text{response factor}_{\text{col}}}{\text{response factor}_{\text{IS}}} \times \frac{\text{peak size}_{\text{col}}}{\text{peak size}_{\text{IS}}} \quad [3.18]$$

Where col = collector and IS = internal standard. The amount of collector adsorbed is found by difference. Standards containing known concentrations of both the collector and the internal standard in CCl_4 were also analysed to determine detector response factors if actual concentrations were required. In most instances the concentrations were normalized with that of the sample withdrawn immediately prior to solids addition. It was therefore not essential to know the detector response factors.

The adsorption technique was initially developed for use with pure oils. However it was readily extended to encompass the commercial oils used as flotation reagents in the batch flotation testwork (Chapter 5). The technique remained unchanged with the exception of the approach to interpreting the GLC results. A single dominant peak in the chromatogram was chosen to represent the oil as a whole and analysis was based

⁸ CCl_4 is denser than water and so lies beneath the water layer which provides an effective barrier to further evaporation.

exclusively on peak height. The rationale behind these choices, and its validity, is discussed fully in Appendix 3.1.

3.3.3 Method repeatability

The results obtained using the new adsorption technique are depicted in the Figures throughout the rest of this chapter as the disappearance of collector from the pulp after solids addition. This records the actual situation within the pulp. By subtraction a good approximation of the extent of adsorption can be obtained, though the persistent mass loss discussed in Section 3.3.5 should also be taken into account. For this reason and in the interests of accuracy the actual concentration within the pulp was retained as the basis for depicting results. However, adsorption is referred to directly, leaving it to the reader to do the necessary mental subtraction.

Adsorption behaviour was found to vary to a small extent between each prepared batch of any one coal sample. This was probably due to small differences in the conditions under which each batch of coal was wet-sieved and then oven dried (80°C). Some variable degree of *in situ* oxidation probably occurred. Each comparative set of experiments was done with a single batch of coal but *quantitative* comparisons with other sets of experiments should be made with caution. Generally initial adsorption rates were slightly different while final adsorption levels were much the same. In a few experiments with the washed coal, the coal from which the respective size fractions were prepared varied, as two samples were obtained from the Greenside Colliery at different times. The coal characteristics, while nominally the same, were not *identical*. (Adsorption runs in which coal from the original sample was used are asterisked in the data summary in Appendix 3.4).⁹

Good repeatability was obtained in duplicate experimental runs with the same batch of coal. Any difference is the total error accumulating within the technique as a whole, i.e. solids preparation, sampling of the pulp, dispersion, preparation and GLC analysis. Examples of the repeatability of the technique are shown in Figure 3.10.

⁹ Flotation testwork was all carried out with the more recently acquired sample.

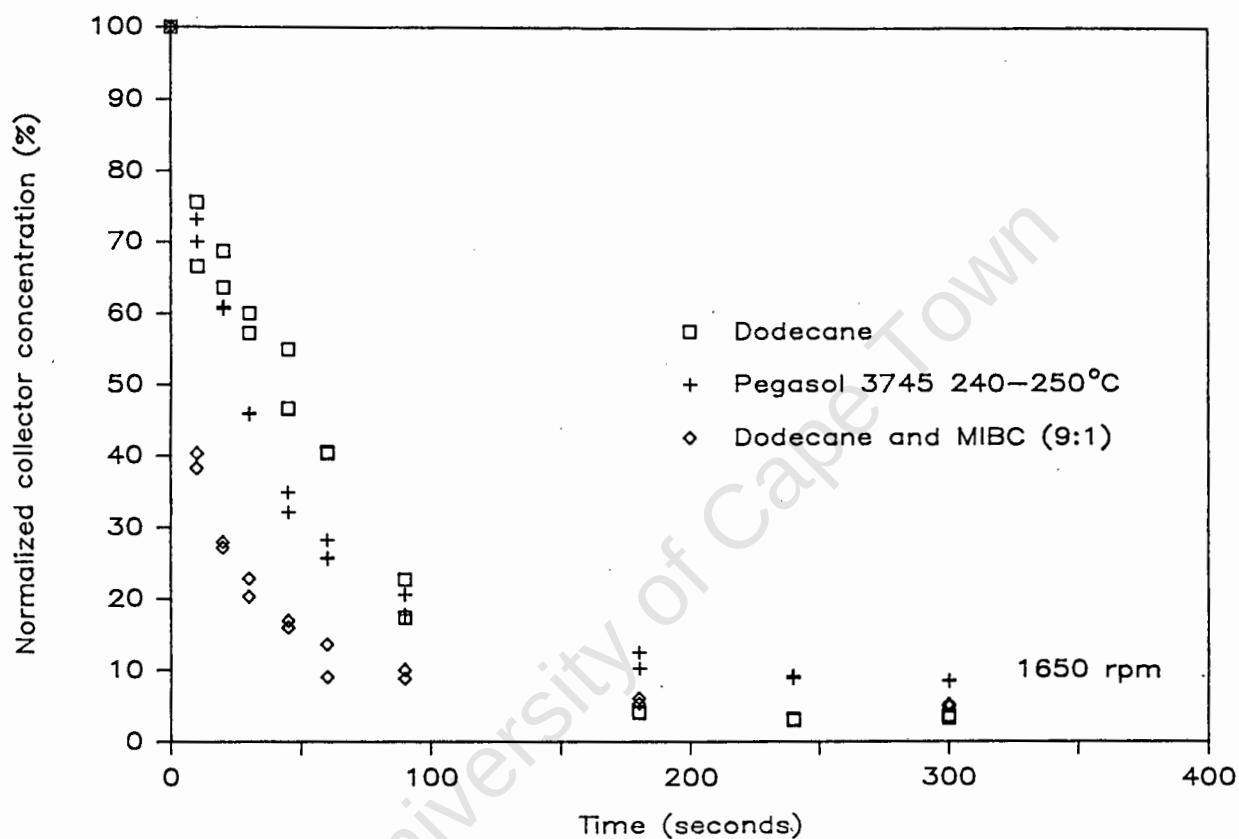


Figure 3.10 : Adsorption technique repeatability. Duplicate runs showing the rate of disappearance of dodecane, dodecane and MIBC, and the Pegasol 3745 240-250°C cut from the pulp water. Milled Greenside No. 2 seam washed coal (500-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

Figure 3.10 shows duplicate runs for experiments on Greenside washed coal with dodecane, dodecane and MIBC mixed in a 9:1 ratio and a Pegasol 3745 240-250°C cut. As may be seen the repeatability in each case is good.

3.3.4 Limitations of the technique

Oil droplet size and needle bores restricted the minimum solid particle size to which the technique could be applied to about 100 μm . Thus in applying the adsorption technique and interpreting the results it was implicitly assumed that the physico-chemical surface characteristics of a relatively coarse coal size fraction would be representative of the surface of coal of other sizes. A similar assumption has to be made with contact angle measurements and in some coal flotation washability tests in which fines carryover is a problem (Laskowski, 1986).

Since the results produced by the technique are qualitative in the sense that the entire feed coal particle size range cannot be used, a narrow size fraction of comparatively large particles (500-600 μm) was used for convenience. Though much smaller sizes or a combination of sizes can be accommodated, adsorption may at times be too rapid for measurement. The effect of particle size on the rate of oil adsorption is discussed in Section 3.4.7

Solids were screened into narrow size ranges because researchers like Pooley (1967) and Smitham and Firth (1982) have shown that the macrokinetics displayed after collector addition are dependent on the size distribution of solids in the pulp. It was thought that quantification and comparison of the micro-kinetics would be difficult with a broad size distribution, even if this were accurately known and reproducible. Even though the size range chosen has a smaller specific area than the equivalent mass of the feed coal, comparison between the behaviour of the various oils with the same coal sample remained valid.

3.3.5 Collector oil mass loss

A phenomenon which was noted from the start of this testwork was a fall-off in the concentration of collector oil within the reactor with

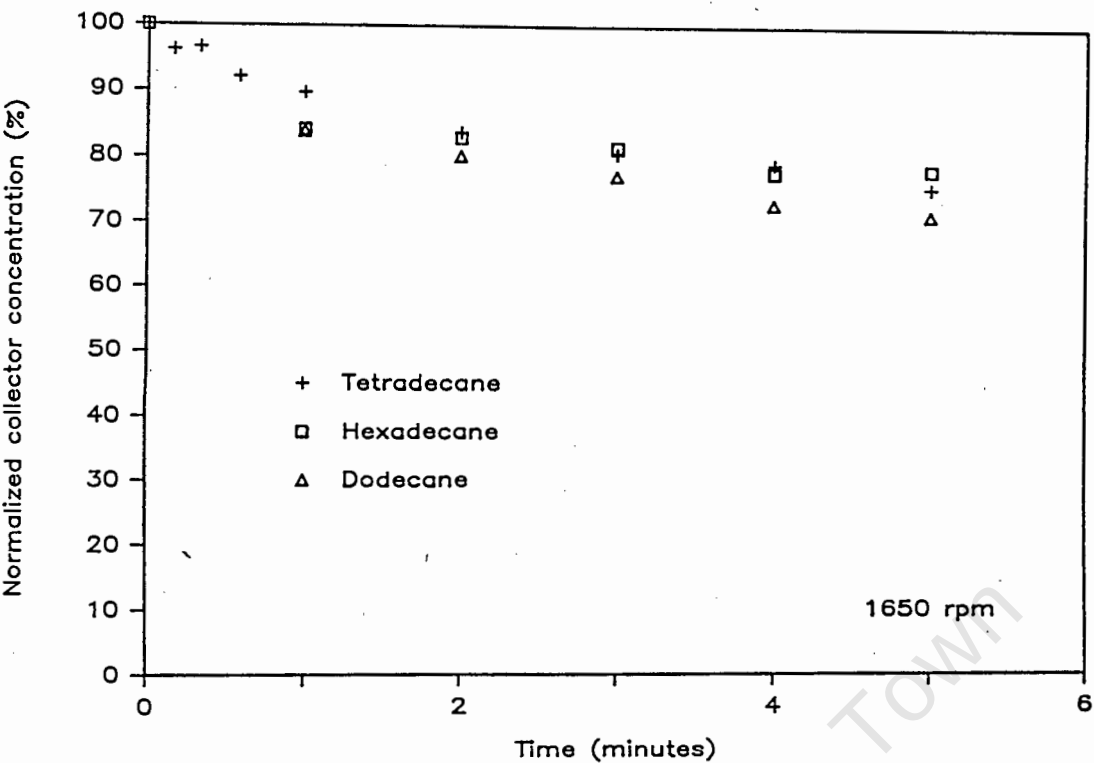


Figure 3.11 : Rate of mass loss of collector oils from the adsorption vessel in the absence of solids. 85 μ l of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

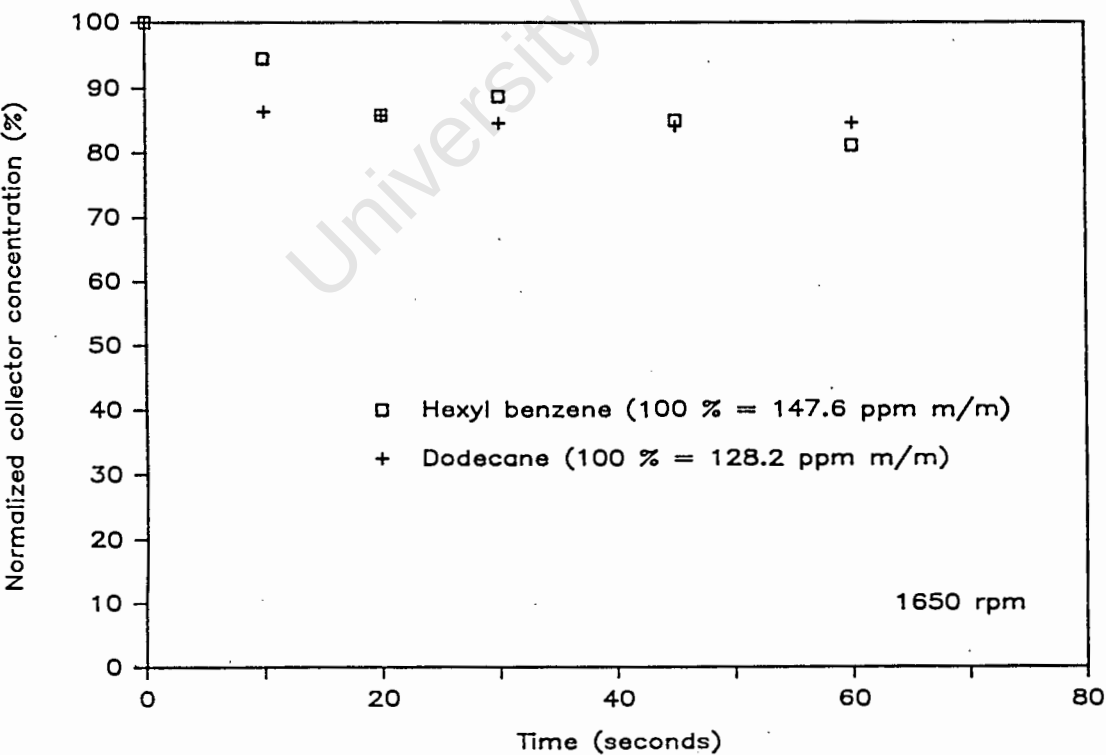


Figure 3.12 : Rate of mass loss of dodecane and hexyl benzene from the adsorption vessel during the minute prior to solids addition. 85 μ l of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

time when no solids were present. Figure 3.11 shows the decrease in the concentration of dodecane, tetradecane and hexadecane in the adsorption vessel (in separate experiments) over periods of 5 minutes. Figure 3.12 shows the drop in dodecane and hexyl benzene concentration during the first minute of dispersion. All the experiments were duplicated. The losses were reasonably consistent from run to run (average values are shown). The slightly smaller (lower) losses noted with the higher boiling point alkanes are probably due to their lower vapour pressures.

The loss in each case was very small in terms of mass (about 0.01 g) but is serious at the concentrations used if not taken into account. Serious error would be introduced if the results were normalized with the initial collector concentration value, i.e. the actual amount added, rather than the concentration in the water at the moment the solids were introduced.

Appendix 3.3 gives a detailed description of an extensive program carried out to determine the reasons for the mass loss. It was found that sampling was reliable and extraction using CCl_4 was complete. Evaporation was initially assumed to be insignificant because of the high boiling points of the oils and the comparatively short reaction (adsorption) times. Adsorption on the vessel surfaces accounted for only a small part of the mass lost. Finally, however, the loss was attributed to evaporation since the loss largely disappeared in closed vessels. Evaporation was encouraged by the oil spreading or "creeping" up the stainless steel walls of the reactor. (Oils can be assumed to wet steel since they are often used as steel lubricants). The mass loss decreased with an increase in agitation intensity, i.e. as the air-water interface was increasingly disrupted, supporting the belief that evaporation and "creep" were the mechanisms responsible for this loss.

Smitham and Firth (1982) in their work on equilibrium (final) kerosene adsorption levels (see Section 3.2.10) also encountered a collector imbalance phenomenon and were forced to normalize their results. They attributed losses to either extraction inefficiency or to variations in the original dosage. However, while considerable variation was found between duplicate experiments, duplicate extractions for individual experiments were in good agreement, so extraction inefficiency could not have been responsible. On the other hand, mass percentages of collector extracted in duplicate experiments were as low

as 47 % of the initial dosage and it is hard to imagine a 0.1 ml pipette, which they used for collector addition, being so inaccurate. The present work suggests rather that the problem may have been evaporation of collector oil encouraged by "creep", as well as loss by adsorption on vessel walls while transferring dispersions between various vessels. This source of collector loss was encountered in the technique discussed above if dispersion samples were transferred from the sampling syringes to sample bottles prior to extraction.

Although the phenomenon of mass loss is irritating, the loss was reasonably consistent. Furthermore the rate of adsorption measured once coal solids were introduced was often very rapid relative to the rate of loss. It is therefore reasonable to assume that once the initial change in concentration has been accounted for, i.e. the results normalized with the collector concentration at the moment solids were added, further mass loss has a minimal effect on the adsorption kinetics. All the results were therefore calculated on this basis.

3.3.6 Collector-coal contacting procedures

Most of the adsorption experiments were carried out by dispersing the oily collectors in water prior to the addition of a pre-wetted slug of coal. This is an approach similar to that of emulsifying the oils prior to addition to a flotation pulp. The latter is not generally done in practice despite its apparent advantages.

An advantage of pre-dispersion was emphasized by Smitham and Firth (1982) who studied the distribution of kerosene on a -0.5 mm deslimed coal. They found that :

The mass of collector adsorbed $\propto$ (average particle size)⁻²,

except if the collector was emulsified prior to contact, in which case an inverse proportionality existed, i.e.,

mass of collector adsorbed $\propto$ (average particle size)⁻¹.

Coarser particles were therefore relatively better oiled if the collector oil was pre-dispersed.

In the present testwork, pre-dispersion allowed for the removal of a sample of the water-oil dispersion immediately before coal addition. This sample was used to determine the extent to which these oils were "lost" by adsorptive and evaporative effects (as explained in Section 3.3.5 above) prior to coal addition, and hence permitted normalization of oil concentrations measured after coal addition.

Since the pre-dispersion procedure is not typical of coal flotation practice, as the oils were dispersed in a large volume of water, it was important to find out how results would differ if the oil was added directly to the coal pulp. Adding oil to water prior to the introduction of the coal ensured that the oil was well mixed on coal contact whereas adding oil to the pulp may not have permitted sufficient dispersion to take place before adsorption occurred. This could in turn affect the adsorption kinetics. Testwork was conducted to establish whether the two procedures produced different results.

Figures 3.13 and 3.14 show the results obtained on contacting hexyl benzene and dodecane (pure aromatic and pure aliphatic reagents respectively) with 500-600 μm milled Greenside No. 2 seam unwashed coal. The kinetics and degree of adsorption are very different for the two oil types. However for each oil the adsorption kinetics obtained were very similar irrespective of the mode of addition. The addition of MIBC (added mixed in each oil) also had no apparent effect on the adsorption behaviour. The influence of MIBC on oil adsorption is considered in more detail in Section 3.4.6. When oil was added to the pulp the actual initial concentration of oil available to the coal was uncertain since adsorption on the vessel walls and other avenues for "loss" were still possible. However the actual concentrations at subsequent times could be determined (by using the GLC instrument response ratio) and by careful comparison with the final adsorption levels of runs in which a sample was taken at zero time, an appropriate estimate for a normalizing concentration was derived.

The similarity of results when using the different addition procedures was a fortunate discovery in that it enabled the more convenient pre-dispersion procedure to be used with confidence in the testwork.

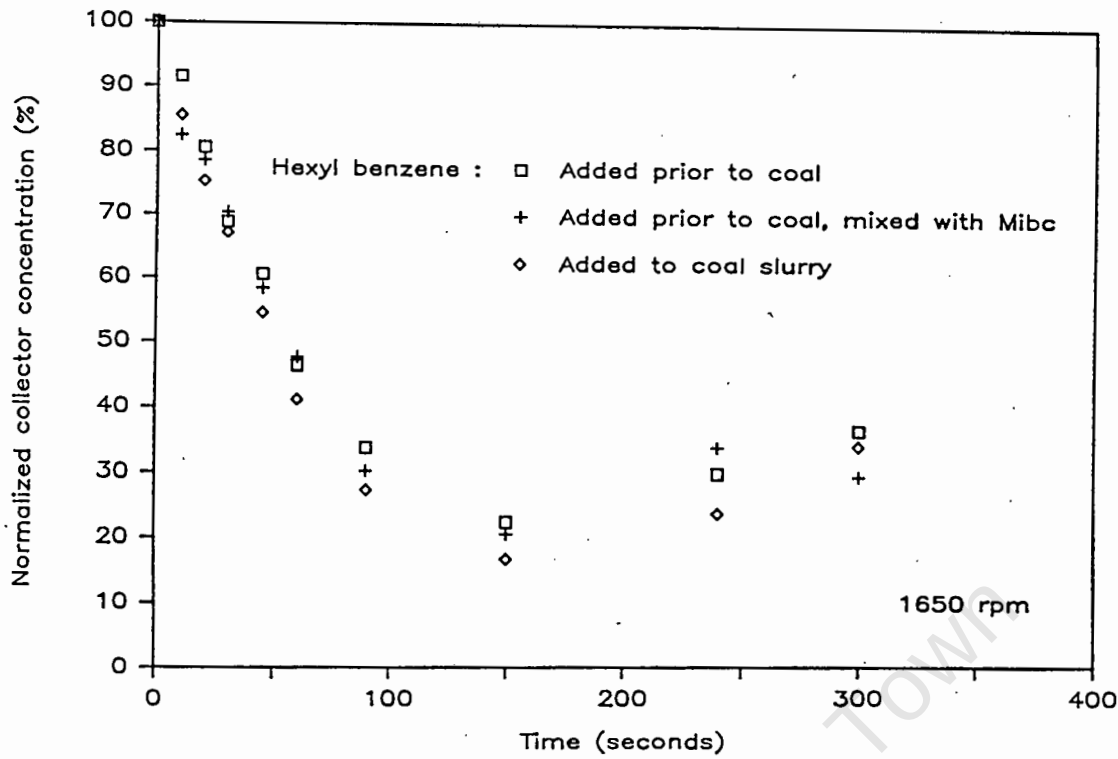


Figure 3.13 : The effect of different oil-coal contacting procedures on the rate of disappearance of hexyl benzene from the pulp water. Milled Greenside No. 2 seam unwashed coal (500-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

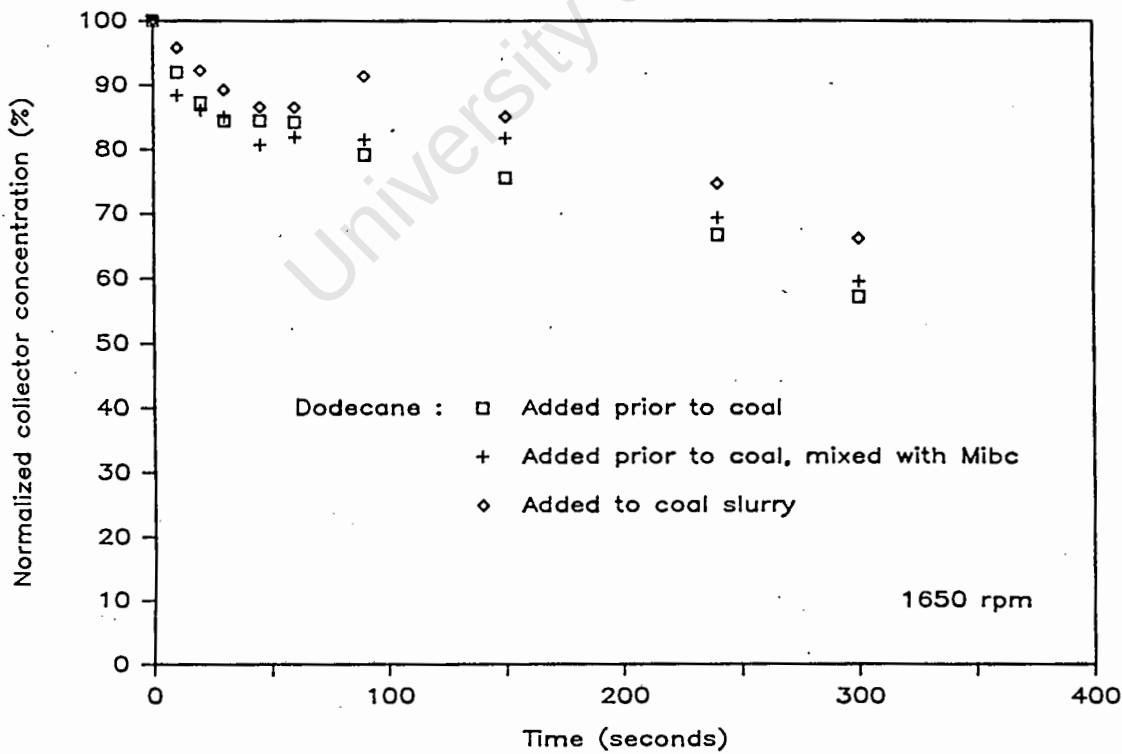


Figure 3.14 : The effect of different oil-coal contacting procedures on the rate of disappearance of dodecane from the pulp water. Milled Greenside No. 2 seam unwashed coal (500-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

Although adsorption kinetics were similar, the results do not necessarily indicate that the efficiency with which the oils were mixed within the pulp was the same. Direct addition to the pulp might result in some coal particles adsorbing a disproportionately large amount of oil in the form of large drops, and starving other particles of any. In the light of the vigorous agitation employed it is unlikely that very large droplets would remain adsorbed in totality on a coal particle surface. Pulp shear forces would ensure a fair degree of mixing, though this might not be as good as in the case of pre-dispersion prior to coal contacting. The impact of these two methods of oil addition (and by association any differences in dispersion) on actual flotation was investigated and is discussed in Section 5.4.

The apparent desorption evident in Figure 3.13 is discussed in Section 3.4.4.

3.3.7 Summary of technique

A technique to measure the kinetics of oil adsorption onto solid particles in turbulent pulps was successfully developed. The technique monitors actual oil adsorption and obviates the need to infer this from (say) static contact angle behaviour. The technique entails removing samples of oil-water dispersion at discrete intervals from a pulp containing solid particles.

The particles, which must be larger than the maximum droplet size, are excluded from the samples on the basis of their size, by using filters consisting of syringes fitted with clusters of hypodermic needles with bore sizes smaller than the minimum size of the particles. Oil is extracted from the samples using a CCl_4 liquid extraction technique within the sampling syringes. The extract is then analyzed by GLC to give the actual oil concentration for each sample. These concentrations are normalized using the concentration of oil immediately before coal addition. This concentration is not the same as that calculated from the actual oil volume added since some oil is lost by adsorption and spreading on vessel walls and by evaporation. Although oils were generally dispersed prior to coal addition to allow for efficient dispersion and the removal of a normalization sample, results were very similar to those in which the oil was added directly to the

pulp. The technique developed was readily extended for use with commercial (non-pure) oils.

3.4 ADSORPTION TESTWORK WITH MILLED COAL SAMPLES

The adsorption technique developed was implemented with the following objectives :

1. To investigate the rate and degree of adsorption of the oily collectors on both washed and unwashed coal. The collectors and the coals used in the investigation were those used in the flotation testwork described in Chapter 5. The purpose of these studies was to try to predict or explain (with hindsight) any substantial differences in batch flotation performance.
2. To determine whether the adsorption kinetics of oily collectors are sufficiently slow to have a controlling influence on the coal flotation process.
3. To investigate the effect of MIBC addition as well as of different reagent-solid contacting procedures on the adsorption behaviour of the oily collectors.
4. To quantify from a microscopic viewpoint the degree to which hydrocarbon oils are able to discriminate between "clean" coal and unwanted gangue mineral surfaces, i.e. to investigate their inherent selectivity. This in turn would provide a means of assessing the flotation washability of the oiled coal, i.e. the best concentration grades which can be produced.

3.4.1 Experimental particulars

3.4.1.1 Preparation of coal samples

Samples of washed and unwashed coal from the Greenside Colliery were used for most of the adsorption work. These samples were later used in the flotation testwork (Chapter 5). Properties of the coal samples may be found in Tables 1.1 and 1.2 in Chapter 1.

The samples were prepared by rod-milling¹⁰ 1 kg sub-samples of the respective coal "peas" for a predetermined time. The 500-600 μm size range was dry-screened from each milled batch for the adsorption work. Five 1 kg sub-samples were prepared in each session to ensure sufficient coal for each set of adsorption experiments.¹¹

Tests were also carried out on a thickener underflow sample from the same colliery. The 500-600 μm size range was dry-screened from the as-received thickener underflow material.

A sample of Vryheid Coronation Colliery unwashed coal from the flotation plant feed was used in a short series of tests. The 425-600 μm size fraction was removed by wet-screening. This fraction was split into density fractions.

The screened out coal was washed thoroughly with water to remove adhering fines and oven dried (at 80°C) overnight. Sub-samples of approximately 26 g (depending on coal S.G.) were then weighed out into sample bottles which were filled with distilled water and capped. The purpose of storing the coal under water was to reduce the chances of *in situ* oxidation prior to use.

The -500 μm size fractions arising from the milling of the Greenside washed and unwashed samples were stored in a drum under positive nitrogen pressure for later use in the flotation testwork (Chapter 5).

3.4.1.2 Oils used

The oils predominantly used were dodecane, hexyl benzene, Shellsol AB, Shellsol K and Pegasol 3745 which had been split into several boiling range cuts. Some experiments were also carried out with blends of hexyl benzene and dodecane (20 % and 40 % (v/v) of the former in the latter). Characteristics of the oils are given in Table 1.3 in Chapter 1.

¹⁰ Particulars for the milling procedure may be found in Section 5.3.2.1.

¹¹ As mentioned previously, two samples of washed coal were obtained from the Greenside Colliery at different times. Most of the adsorption experiments, and all the flotation tests, were conducted with the later sample. Figures 3.29 and 3.34 show the adsorption results obtained with the earlier sample.

3.4.1.3 Parameters investigated

In addition to the type of oil, the review of the literature highlighted several parameters that could affect oil adsorption. These are :

1. water pH and ionic strength;
2. oil droplet size;
3. the kinetic energy input to the pulp and its effect on oil droplet collisions and spreading;
4. the presence of MIBC (surfactant) and the manner in which it is contacted with the oil and with the coal, i.e. the effect of changes in the adsorption of MIBC at oil-water and coal-water interfaces.

Certain operating parameters were varied during the testwork to determine the effect of these changes on the observed adsorption rates. Impeller speeds were varied to determine how increased oil dispersion and the additional kinetic energy input would affect oil droplet adsorption. Furthermore, the sequences in which MIBC and oil were contacted with one another and with the coal were varied. A good proportion of the testwork was carried out in the absence of MIBC. This is in line with much of the flotation testwork in which the oils were conditioned with the coal for up to 5 minutes before MIBC was added.

All the raw data for the adsorption experiments are contained in Data Appendix 2 which is available on request. A summary of the raw results is included in Appendix 3.4.

3.4.1.4 Pulp regulation

Both pH and the presence of other electrolytes, especially multivalent metal ions, are known to affect interfacial electrostatic phenomena. No attempt was made to alter or control ionic strength or pH. There seemed little merit in attempting to do so since the electrochemistry is dependent on the water used, the gangue constituents and the degree of oxidation of the coal, and the type of

commercial oil impurities. A universally applicable standard set of conditions seemed impossible to formulate and control.

In unadjusted coal pulps the pH is likely to be about pH 8 which is clearly not conducive to optimum adsorption since both coal and oil particles are negatively charged (Section 3.2.2.2). However altering the pH to improve oil-coal collisions may also affect the charge on the gangue surfaces and may seriously impair oil selectivity. Since coal is so varied and any one coal so difficult to characterize, it was thought prudent not to alter pH but to rely on the molecular forces of attraction between oil and carbonaceous material to compensate, at least to some extent, for oil-coal electrical double layer repulsion. This was the approach adopted in this testwork and it seems reasonable in view of traditional (i.e. unregulated) coal flotation practice.

Interfacial tensions and hence many flotation phenomena, including oil adsorption, are somewhat temperature dependent. The effect of temperature was not investigated except for a single experiment at a very low temperature (Section 3.4.9.1). The rest of the adsorption runs were carried out at 25°C with the vessel in a water bath. The distilled water used in the experiments was left in sealed flasks in the water bath overnight to equilibrate to this temperature.

3.4.2 Adsorption of the oils onto Greenside coal

3.4.2.1 Greenside unwashed and washed milled coal

There was a distinct difference in the behaviour of the collector oils on being contacted with washed and unwashed coals. With the milled Greenside unwashed coal, the extent of adsorption of the aliphatic collectors (and the predominantly aliphatic oils) was far more limited than that of the aromatics. This may be seen from Figure 3.15. In both cases, adsorption was still taking place after 5 minutes. At this time the aromatics (hexyl benzene, Shellsol AB and the 40 % hexyl benzene in dodecane mixture) were 70-80 % adsorbed while the aliphatics (dodecane, Shellsol K and the 20 % hexyl benzene in dodecane mixture) were only 35-40 % adsorbed.

In contrast the adsorption characteristics of all the oils onto the milled Greenside washed coal were very similar. After 5 minutes, final adsorption was practically total, as shown in Figure 3.16. In fact, approximately 90 % of the mass of all the oils had adsorbed after 3.5 minutes. Some oils attained this level even earlier. The two sets of experiments were done at different impeller speeds but this was later found to have little effect on the results (Section 3.4.5).

The adsorption behaviour of the Pegasol 3745 boiling range on the washed and unwashed coals cuts are compared in Figures 3.17 and 3.18. As might have been expected, the adsorption of this largely aliphatic oil was limited on the unwashed coal (with the low boiling range cut apparently adsorbing to a greater degree). The extent of adsorption after 6 minutes varied from 25 to 40 % depending on the boiling range used. With the exception of the 180-190°C cut, the extent of adsorption after 5 minutes was somewhat poorer than obtained with the other aliphatic oils used, as evident from a comparison of Figures 3.15 and 3.17. In contrast, with the washed coal, the final adsorption level of some 90 % was essentially reached after 2.5 minutes for all the boiling range cuts. This behaviour was very similar to that of the other oils on this coal, as may be seen from a comparison of Figure 3.18 and Figure 3.16.

It is quite evident that the aliphatic oils more readily wetted washed coal than unwashed coal. The reason for this difference in adsorption behaviour must lie in differences in the surface properties of the coals. The washed coal particle surface is clearly more hydrophobic (oleophilic). Though the washed coal surface will possess a greater area of vitrinite, as indicated by the bulk composition (Table 1.3) of this coal, the difference in surface properties is more reasonably attributed to the relative proportion of surface gangue minerals. The unwashed coal surface is rendered more hydrophilic by the larger proportion of gangue minerals, with the accompanying increase in (negative) surface charge. This increases the difficulty in displacing water. An increase in the degree of surface oxidation could have had a similar effect: however, differences in the degree of *in situ* surface oxidation are probably insignificant since both samples were prepared from their respective coal "peas" in

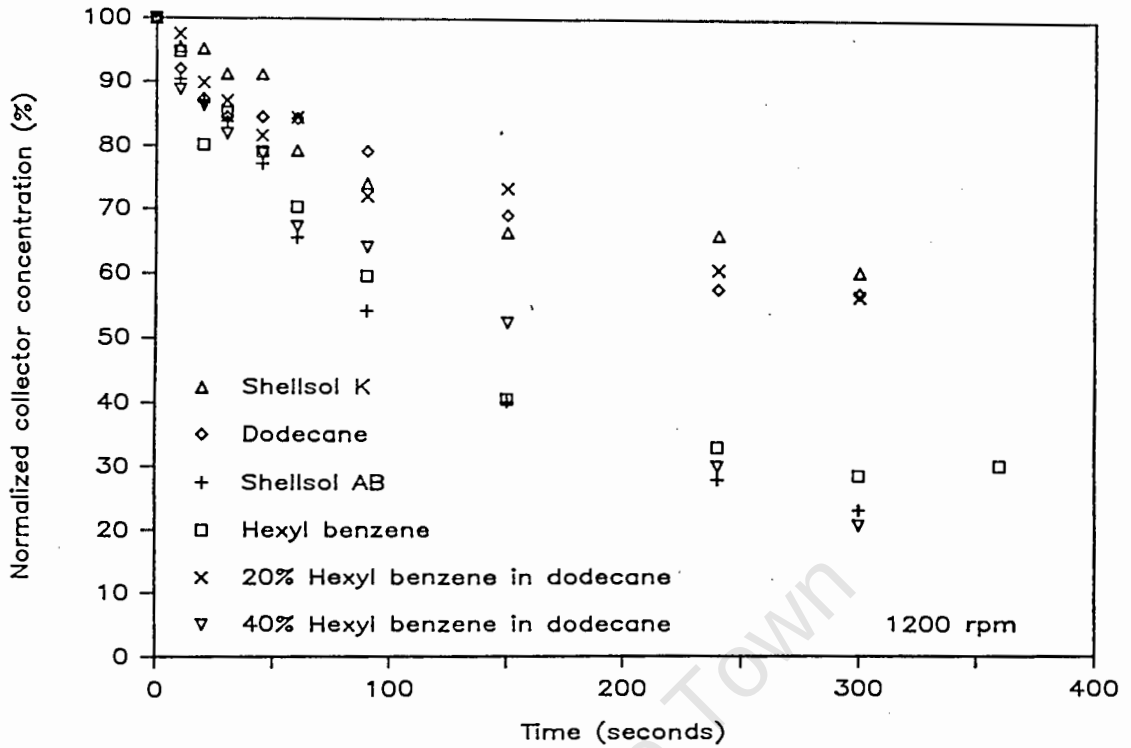


Figure 3.15 : The rate of disappearance of various collector oils from the pulp water. Milled Greenside No. 2 seam unwashed coal (500-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1200 rpm.

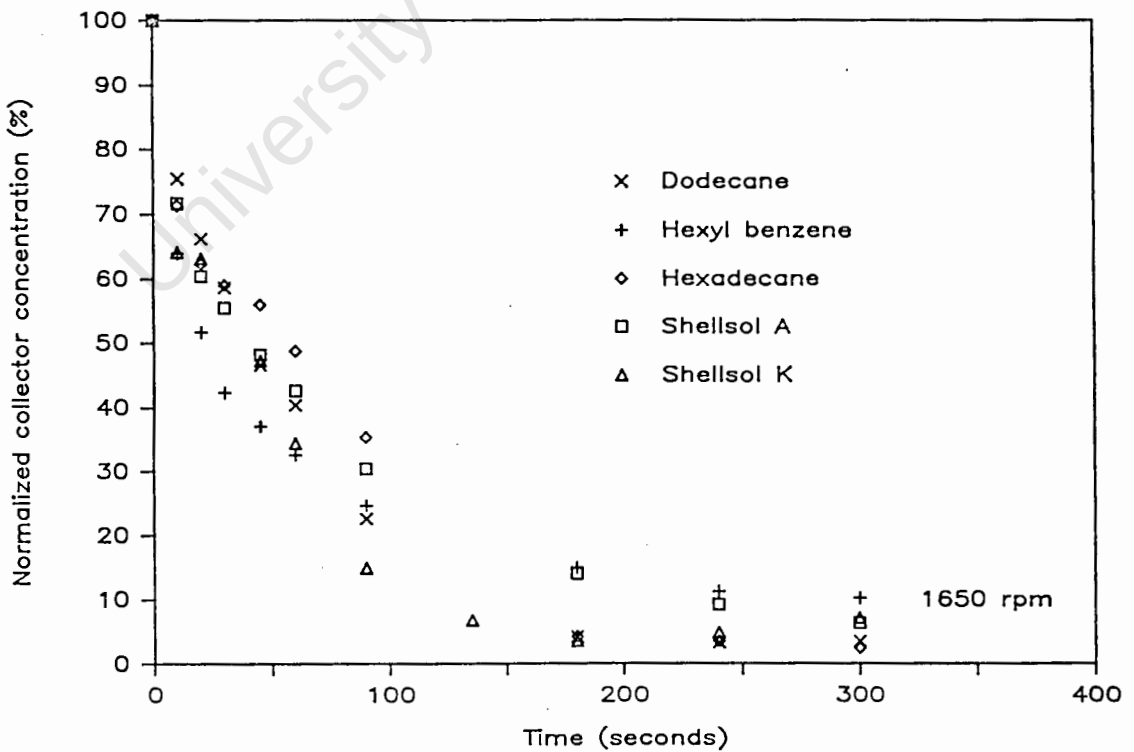


Figure 3.16 : The rate of disappearance of various collector oils from the pulp water. Milled Greenside No. 2 seam washed coal (500-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

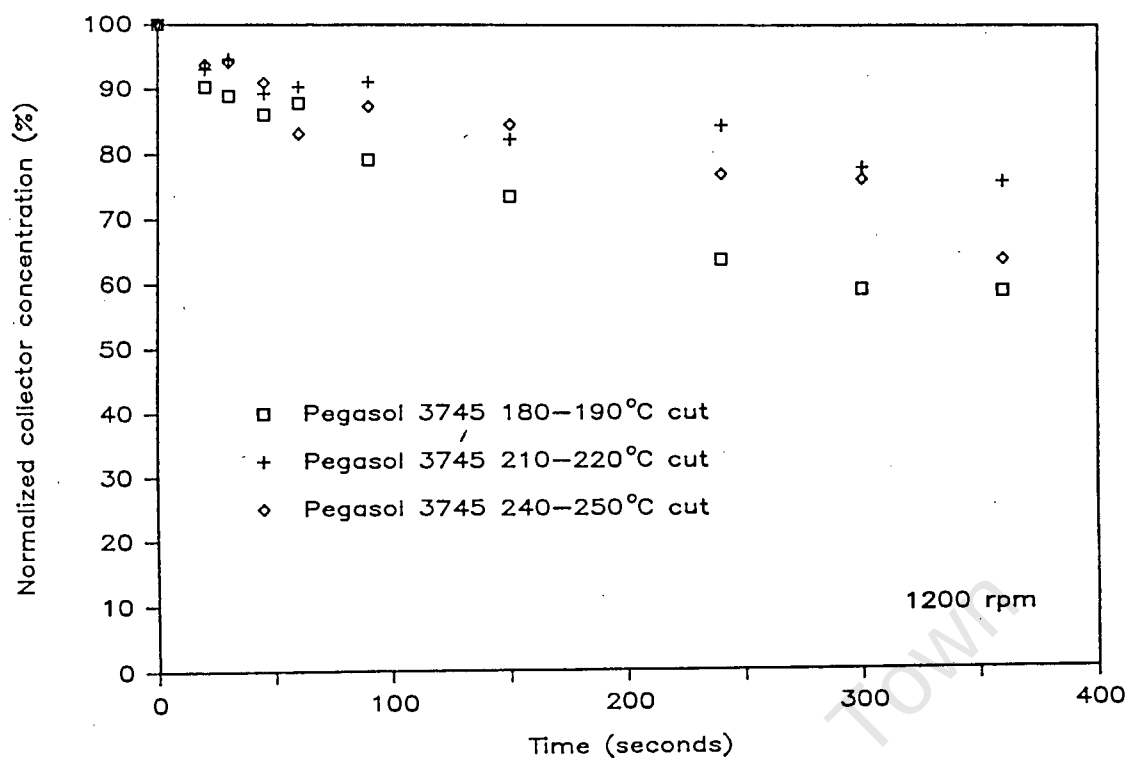


Figure 3.17 : The rate of disappearance of various Pegasol 3745 boiling range cuts from the pulp water. Milled Greenside No. 2 seam unwashed coal (500–600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1200 rpm.

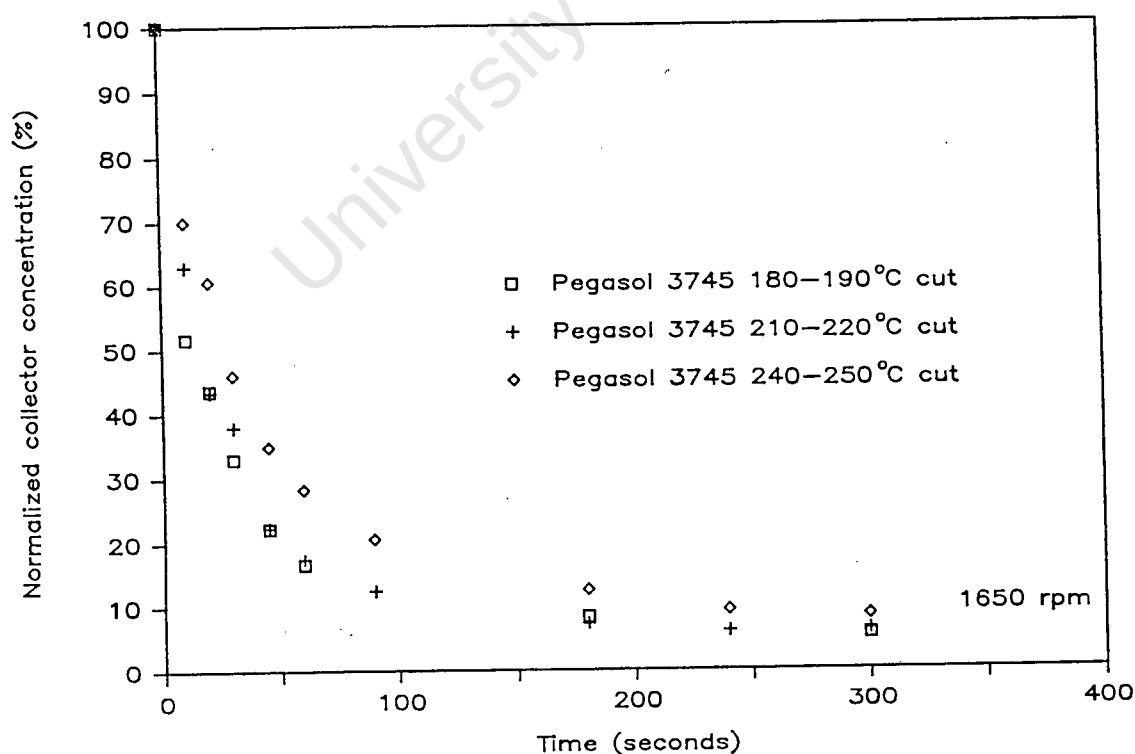


Figure 3.18 : The rate of disappearance of various Pegasol 3745 boiling range cuts from the pulp water. Milled Greenside No. 2 seam washed coal (500–600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

exactly the same manner (although it is acknowledged that vitrinite is more readily oxidized than the other macerals).

The increased negative surface charge associated with the unwashed coal will oppose the collision, film thinning and adsorption of the negatively charged oil droplets. Coal-water interfacial tension will be lowered by an increase in the proportion of surface polar and charged groups since these increase the solid surface energy. Oil adhesion and spreading will therefore be hindered. This applies to *all* the oil types and is clearly evident in the differences in *adsorption rates* found for each of the oils in conjunction with the milled washed and unwashed samples. This may be seen from a comparison of Figures 3.15 and 3.16.

However, despite the lower adsorption rate, the adsorption levels of aromatic oils on unwashed coals after 5 minutes are 10 or 15 % (of the initial concentration) higher than their equilibrium adsorption levels on washed coal (cf. Figures 3.15 and 3.16). This is not true of the aliphatic oils. The proportionately greater polarity of the aromatic oils (and the blends containing a significant aromatic content, e.g. the 40 % hexyl benzene in dodecane mixture in Figure 3.15) enhances their ability to adsorb effectively onto the surface of the unwashed coal with its comparatively larger proportion of polar functional groups. Local concentrations of negative charge associated with the benzene ring permit aromatic oils to interact with electro-positive hydrogen atoms at the coal surface. Molecular bonding mechanisms are discussed in Section 3.2.3. The polar character of the oils is inseparably associated with the interfacial phenomena of wetting and spreading. Aromatic oils have lower oil-water interfacial tensions than aliphatics (see Table 1.4 and Appendix 1) and less energy input is therefore required to spread them over a coal surface. However, none of the oils spread spontaneously.

Hydrogen bonding between products of oil oxidation (and other surface-active impurities in the oil) and the oxygen-containing coal surface groups would be expected to enhance the adsorption of commercial oils. Though this bonding mechanism undoubtedly occurs, it is not necessary for strong oil adsorption on unwashed coals as pure hexyl benzene was found to adsorb strongly on these coals.

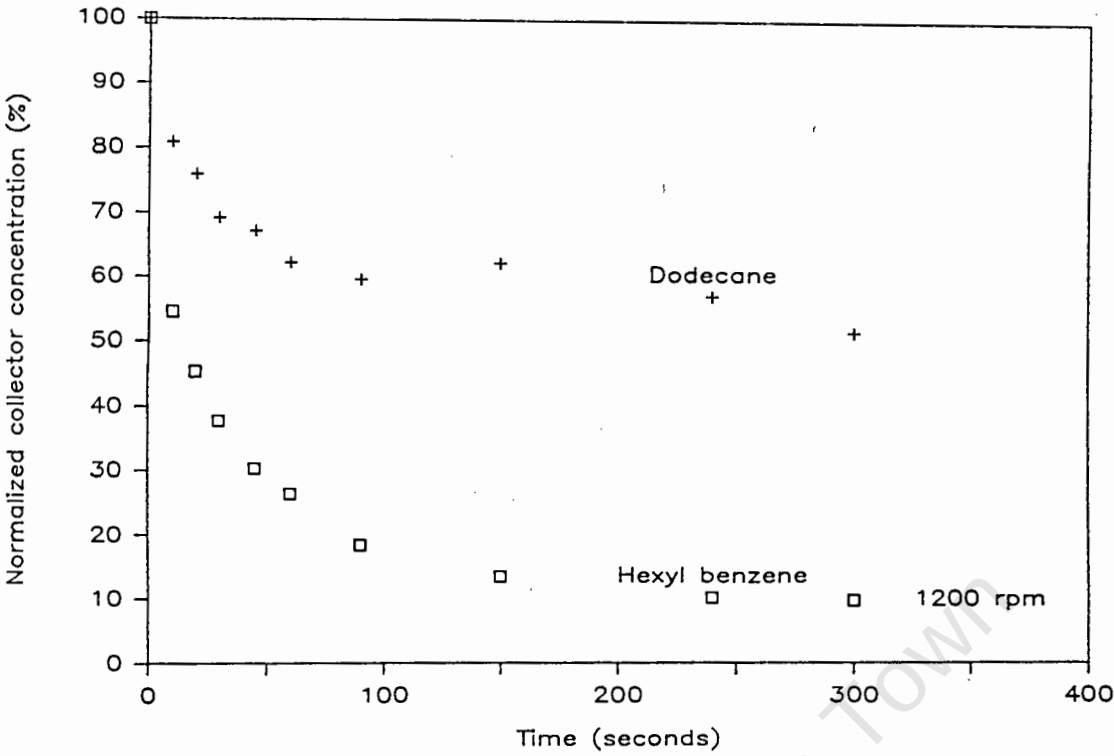


Figure 3.19 : The rate of disappearance of collector oils from the pulp water. Greenside No. 2 seam thickener underflow coal (500-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1200 rpm.

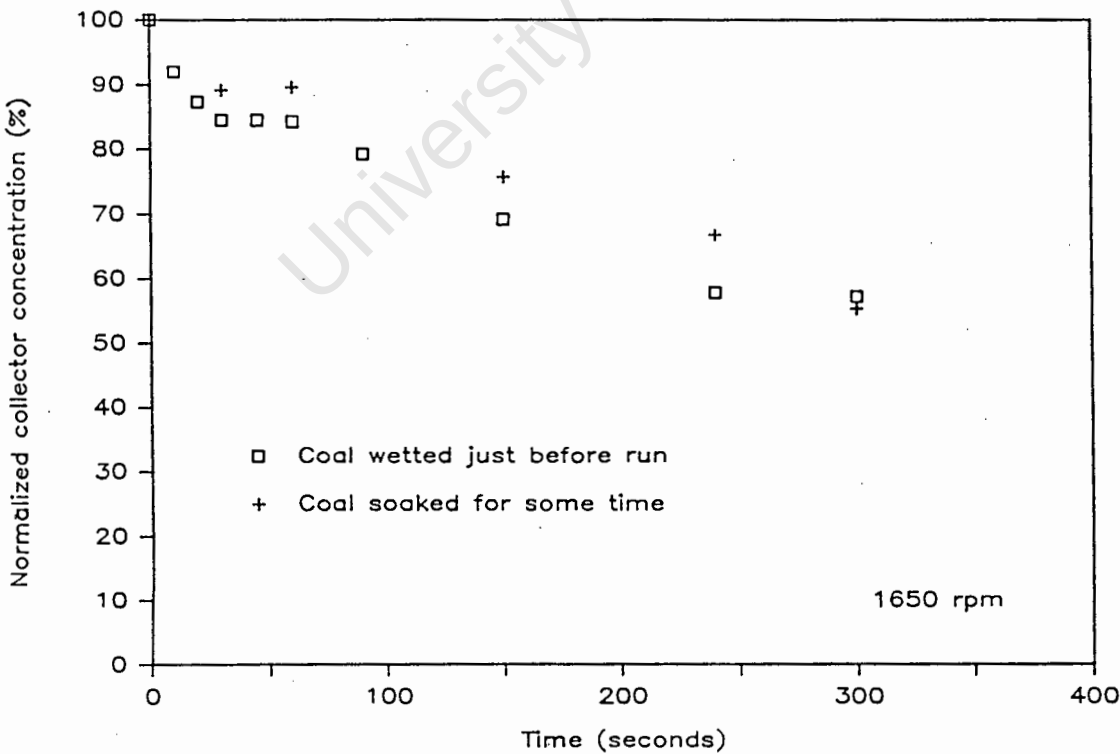


Figure 3.20 : The effect of prolonged storage under water on the rate of disappearance of dodecane from the pulp water. Milled Greenside No. 2 seam unwashed coal (500-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

In the light of the adsorption results an increase in surface oxidation of a coal and/or the proportion of gangue minerals would be expected to significantly reduce the rate and extent of adsorption of aliphatic oils onto such coal surfaces. This behaviour would support the findings of Klassen et al (1958) that at normal dosages, strictly non-polar oils cannot float coal with a high ash content or a high degree of oxidation.

3.4.2.2 Greenside thickener underflow coal

Figure 3.19 shows the adsorption of dodecane and hexyl benzene onto the 500-600 μm size fraction of the thickener underflow coal sample. Characteristics were similar to those observed with the same size fraction of the milled unwashed coal (cf. Figure 3.15), in that the aromatic oil (hexyl benzene) was readily adsorbed while the aliphatic oil (dodecane) was adsorbed to a more limited extent. Both oils adsorbed more rapidly than onto the milled unwashed coal. The final extents of adsorption were also somewhat better, being about 90 % for hexyl benzene and 50 % for dodecane. This was attributed to a lower ash content of this coal size fraction in relation to that of the equivalent size fraction of unwashed coal.

Prior to sampling, the thickener underflow coal had been passed through a classifying cyclone at the Greenside Colliery. Larger particles with a high relative density would have been removed via the underflow. The larger particles reporting to the cyclone overflow would therefore be likely to be less dense, i.e. have a lower gangue content (Table 5.2 confirms this trend). Adsorption would be expected to be better than for particles of higher ash content. This is one instance where the coarse coal size (500-600 μm) used in the adsorption testwork was less representative of the total feed coal surface.

3.4.3 The effect of prolonged storage under water

As mentioned in Section 3.4.1.1 above, all samples of coal used in the adsorption testwork were stored under water prior to use. A possibility existed that prolonged storage under water might have led to more substantial wetting of the coal by the water (through permeation

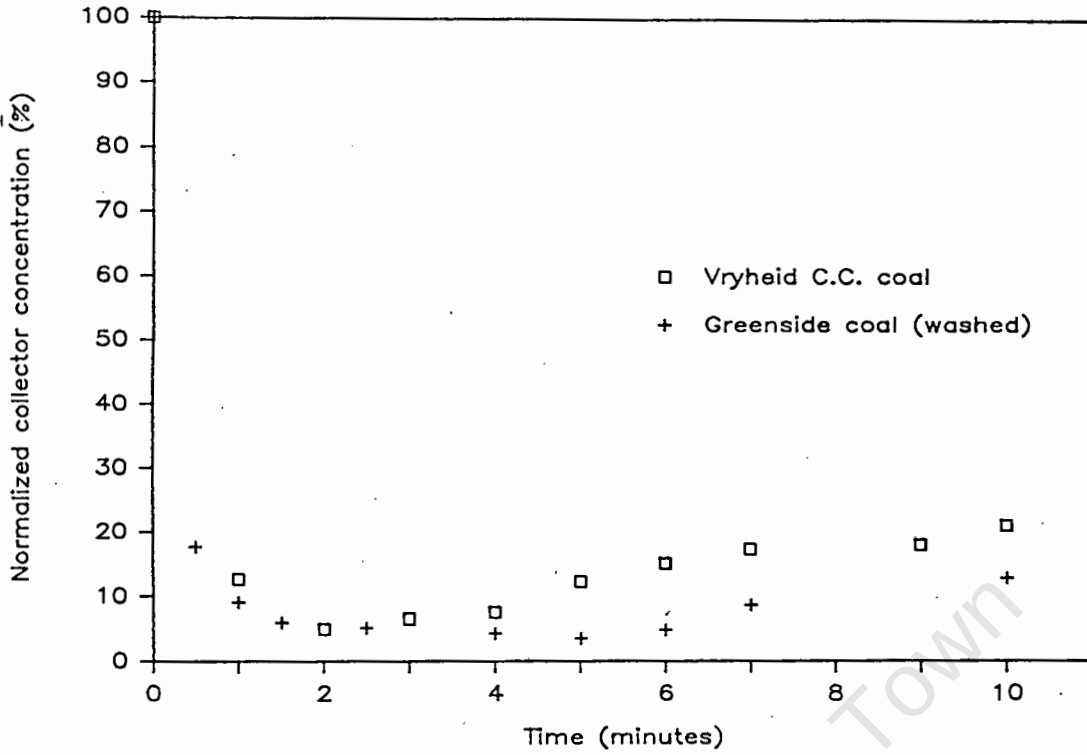


Figure 3.21 : The rate of disappearance of dodecane from the pulp water. Prolonged adsorption run to monitor a "desorption" effect. Milled Greenside No. 2 seam washed coal (500-600 μm) and Vryheid Coronation flotation feed (425-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

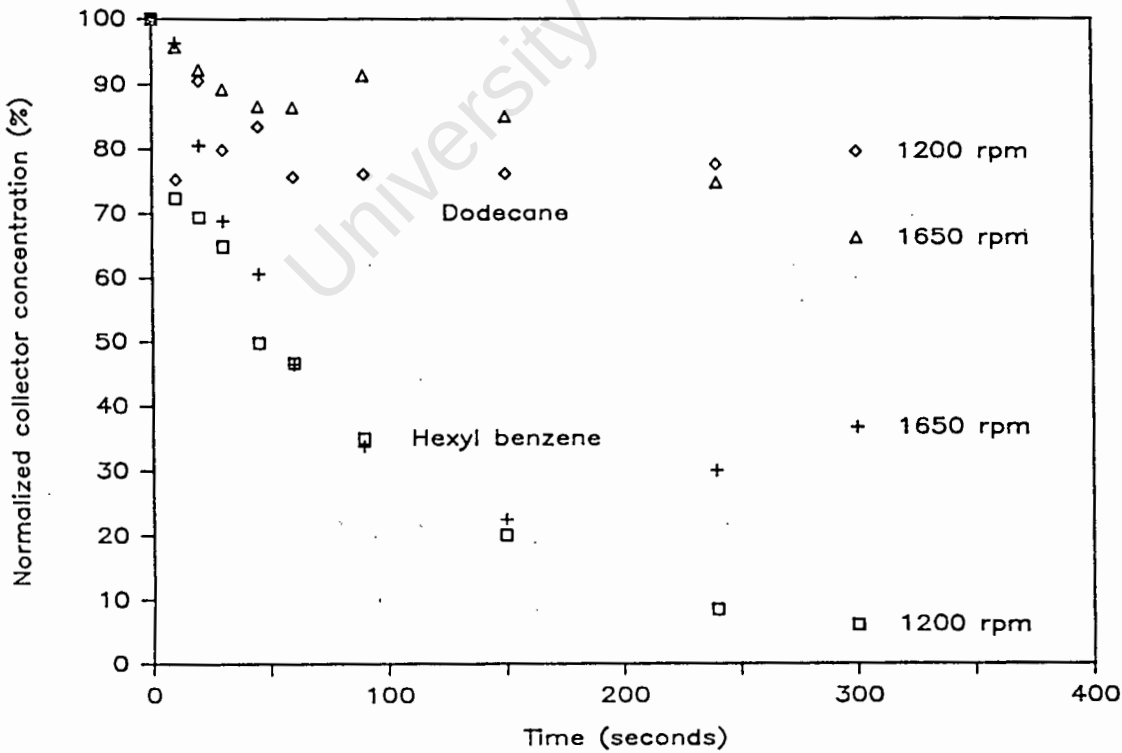


Figure 3.22 : The effect of impeller speed on the rate of disappearance of collector oils from the pulp water. Milled Greenside No. 2 seam unwashed coal (500-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C.

into coal fissures and pores with the accompanying displacement of air). Experiments were done on a coal sample wetted just prior to use and one which had been stored under water for several weeks. Dodecane, which struggles to displace water on the unwashed coal, was used as the collector. Figure 3.20 shows that adsorption behaviour with both samples was similar. Enhanced wetting of coal by water as a result of prolonged storage was therefore discounted as a possible contributory reason for variations in adsorption behaviour.

3.4.4 The effect of excessive pulp phase turbulence

Some adsorption testwork was carried out at 1650 rpm and some at 1200 rpm. The former speed was originally selected to ensure (a) good collector dispersion, (b) uniform, rapid mixing for representative pulp sampling, and (c) suspension of more dense materials such as quartz when this was used. However, testwork at the higher impeller speed, particularly with the unwashed coals, showed an apparent desorption trend, i.e. a rise in the apparent concentration of collector in the pulp water towards the end of each run (see Figure 3.13 for example).

Investigation revealed that this was the indirect result of the production of ultra-fine coal particles, caused by attrition of the larger particles within the pulp at the higher impeller speed. A Coulter Counter size analysis revealed that the ultra-fine particles were smaller than 5 μm in size. This enabled them to pass through the syringe coal filters when sampling the pulp. Being part of the original coal surface, the ultra-fine particles would have had collector adsorbed on them. Extraction with CCl_4 removed the adsorbed oils from these particles thereby boosting the concentration of the oil within the CCl_4 extract, and causing a misleadingly high pulp water concentration upon back calculation. Figure 3.21 shows that this phenomenon also occurred with the less friable washed coals during extended adsorption runs.

In a bid to overcome this misleading apparent desorption, impeller speeds were reduced to 1200 rpm. This speed still ensured dispersion of the oil and vigorous mixing of the pulp but to a large extent overcame the attrition loss experienced, especially with the more friable unwashed coals.

However, the effect of the different impeller speeds on the adsorption behaviour still needed to be examined. This was done with tests on the Greenside unwashed coal. Adsorption kinetics for hexyl benzene were unaffected by the change in speed except initially as shown in Figure 3.22. (An explanation for the more rapid initial adsorption at 1200 rpm as opposed to 1650 rpm is advanced in Section 3.6.4.2). For the dodecane runs, it is difficult to conclude much because of the initial concentration fluctuations.

It is tempting to blame the instability displayed by the dodecane on incomplete oil dispersion, but this cannot be the cause. The dispersion analyses in Chapter 2 showed that the equilibrium droplet population is approached fairly rapidly under vigorous mixing conditions in the flotation cell. Since agitation in the adsorption vessel was strongly turbulent it is reasonable to assume that droplet populations approached their equilibrium level by the time sampling commenced. As mentioned above (Section 3.3.2), a dispersion time of one minute was allowed before the addition of the coal solids. Thus good dispersion can be assumed in the much smaller adsorption vessel. Samples removed from arbitrary points within the vessel during adsorption testwork should therefore have been representative of the pulp as a whole. This conclusion is borne out by the perfectly well-behaved results obtained with dodecane onto a washed coal sample (Figure 3.16, for example).

A distinct "hump" is evident in the dodecane concentration data (at 1650 rpm) shown in Figure 3.22 about 1 or 1.5 minutes after adsorption commenced. The same phenomenon may also be observed in Figures 3.14 and 3.20 in which the impeller speed was also 1650 rpm. At 1200 rpm the "hump" disappeared. It is therefore concluded that the instability in the adsorption is a result of the difficulty dodecane (aliphatic) has in wetting an unwashed coal surface and the small likelihood of such a surface retaining larger collector droplets in their entirety. Dodecane spreads with difficulty on wet unwashed coal (see Section 3.4.2.1) and large droplets contacting the coal might be unable to expand their contact area sufficiently rapidly to ensure stable adhesion. The droplets might then become detached entirely or one or more "daughter" droplets could be torn free resulting in the dodecane concentration fluctuations in the pulp water. The shearing-off of "daughter" droplets is discussed in Section 3.6.4.2. At 1200 rpm contact

angles were apparently sufficiently large to ensure stable adsorption of even large droplets and conditions insufficiently turbulent to shear off droplets.

It is reasonable to assume that apart from some difference in initial adsorption rates there was no substantial alteration in the overall adsorption behaviour on lowering the impeller speed from 1650 to 1200 rpm. Hexyl benzene adsorption rates were found to be somewhat faster at the lower impeller speed (Figure 3.22). This trend was subsequently observed with other oils (see Section 3.4.5 below). In later work the 1200 rpm impeller speed was adopted because it became more important to determine the final degree of adsorption rather than the adsorption rate, and the former could be masked by coal breakup.

3.4.5 The effect of impeller speed

Impeller speed is expected to affect the rate of adsorption because of its effect on oil dispersion (droplet size) and in the "shearing-off" of daughter droplets from larger droplets adsorbed on the coal surfaces. Figure 3.22 shows that the reduction in impeller speed from 1650 to 1200 rpm improved the initial rate (during the first 30 s) of hexyl benzene adsorption.* Adsorption of dodecane was also more rapid though concentration fluctuations in the earlier stages of the run make this less clear.

In these experiments, which were carried out with the sample of unwashed coal, the adsorption of hexyl benzene and certainly of dodecane were comparatively slow. It was believed that the effect of varying the impeller speed would be more marked with a more rapid adsorption reaction. This hypothesis was tested using dodecane and a Pegasol 3745 240-250°C cut in conjunction with the *washed* Greenside coal sample. The impeller speeds used were 1000 and 1650 rpm.

Two approaches were used. With dodecane, the oil was dispersed at 1650 rpm in both experiments but the impeller speed was reduced to 1000 rpm on coal addition in one of the experiments. This was done in order to investigate the effect of droplet kinetic energy and pulp shear forces on the adsorption dynamics. Dodecane droplet distributions were assumed to be identical upon the addition of the coal. With the Pegasol

* Adsorption behaviour differs somewhat from that shown in Figure 3.15 for the reason given in Section 3.3.3.

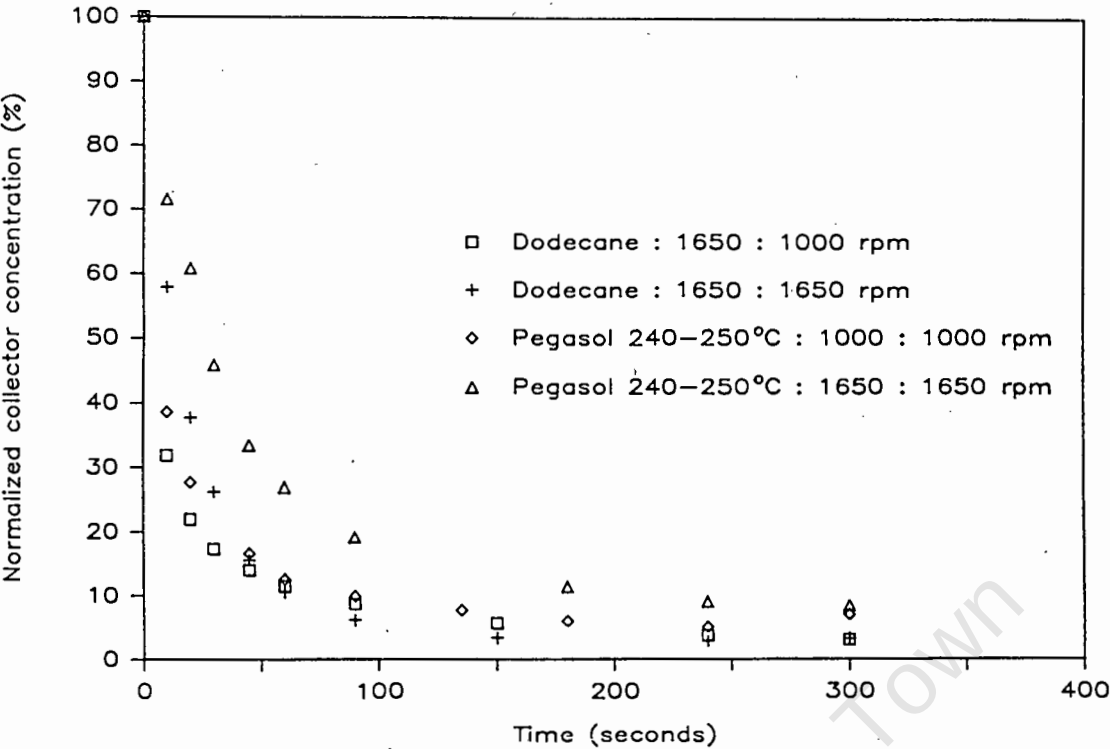


Figure 3.23 : The effect of impeller speed during oil dispersion and during conditioning on the rate of disappearance of dodecane and Pegasol 3745 240-250°C from the pulp water. Milled Greenside No. 2 seam washed coal (500-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C.

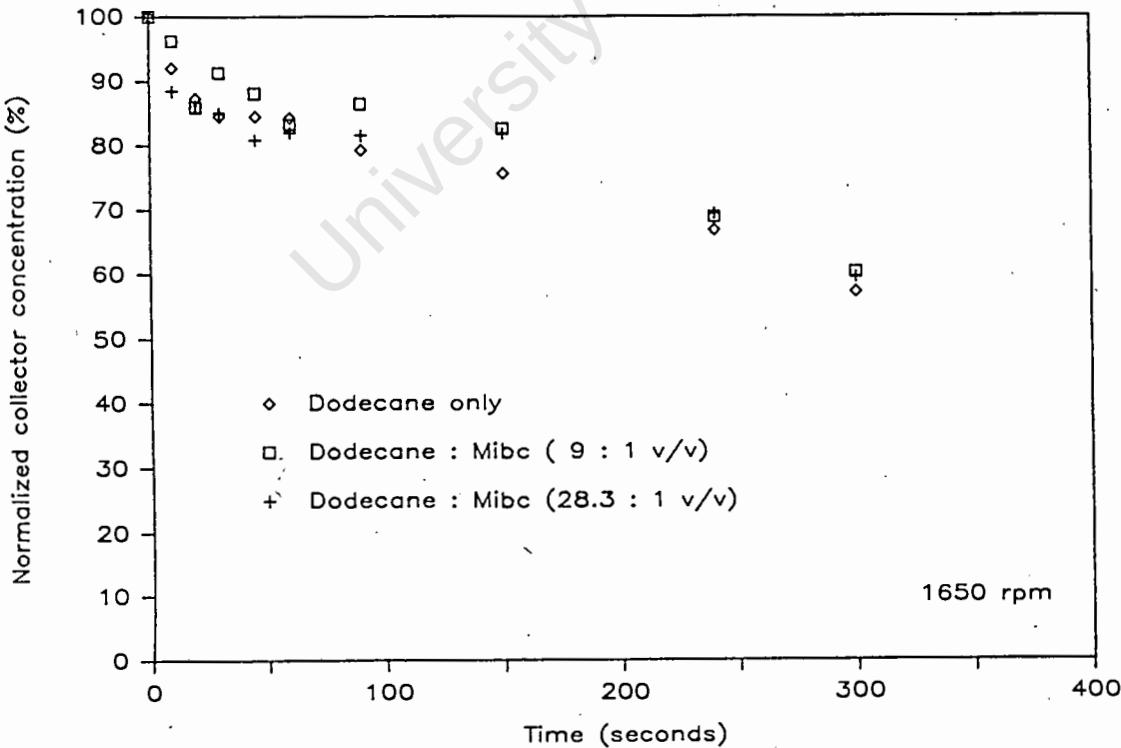


Figure 3.24 : The effect of MIBC addition on the rate of disappearance of dodecane from the pulp water. Milled Greenside No. 2 seam unwashed coal (500-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

3745 cut, one experiment was conducted at standard conditions (1650 rpm throughout) while in the other an impeller speed of 1000 rpm was used throughout. The objective in this case was to investigate the effect of an increase in droplet size on the adsorption dynamics.

With the dodecane, the decrease in impeller speed increased the rate of adsorption markedly as may be seen from Figure 3.23. As droplet size distributions were initially the same the conclusion was that at the higher impeller speed, with the accompanying higher turbulence, larger droplets were unable to expand their contact areas rapidly enough to prevent de-sorption; or else daughter droplets sheared off large adsorbed droplets. This is considered in more detail in Section 3.6.4.2 where the mechanism of droplet adsorption is considered. The extent of adsorption shows that the oil mass was eventually readsorbed (presumably following further breakup into smaller droplets); after 1 minute the extent of oil adsorption was the same at both agitation conditions. Thus it would appear that at both impeller speeds sufficient kinetic energy is available to overcome the electrostatic repulsion barrier between oil and coal surfaces.

With the Pegasol 3745 cut the adsorption at the lower impeller speed was particularly rapid. Some 60 % of the oil had adsorbed after 10 s as compared to about 30 % at the higher impeller speed. One factor contributing to this behaviour is that suggested above. Another is that oil dispersion at low impeller speed will produce larger (and fewer) droplets. The uptake of oil in terms of mass is therefore rapid as these comparatively large droplets adsorb. The milder agitation conditions ensured that they were able to do so in their entirety, that they did not desorb and no daughter droplets were torn free. Final adsorption extents were similar and were attained after about 3 minutes in both cases.

3.4.6 The influence of MIBC

Many of the adsorption tests were carried out in the absence of MIBC since in most of the flotation testwork the oils were conditioned with the coal for nearly five minutes before MIBC was added. However since some flotation testwork was done in which the MIBC was added at

the same time as the oils, some adsorption studies involving the two reagents together were undertaken.

3.4.6.1 Unwashed coal

Comparative experiments were done using dodecane and three Pegasol 3745 boiling range cuts, with and without additions of MIBC. The MIBC was added 30 s after oil addition, i.e. 30 s before coal addition. Figure 3.24 shows that the presence of MIBC had little effect on the adsorption of dodecane onto Greenside No. 2 seam unwashed coal, even at high MIBC dosages. The results of a test are included in which the MIBC concentration was trebled from about 6 μl per litre to 18 μl per litre (concentrations of 6 and 12 μl per litre were used in flotation testwork). The behaviour of the dodecane remained practically identical.

It is commonly believed that MIBC, as a frother and hence possessing surface-active properties, will enhance the adsorption of oil on the coal surface. The action of MIBC, as represented by Equation 3.11, will depend on its relative adsorption at the various interfaces and hence on its effect on the respective interfacial tensions. The reduction in oil-water interfacial tension in tandem with an unchanged coal-water interfacial tension would enhance adsorption and spreading. Since adsorption of dodecane (and by association spreading) was not influenced favourably or unfavourably by the presence of MIBC, Equation 3.15 suggests that : MIBC reduced oil-water interfacial tension by too small an extent to influence adsorption noticeably, or, the reduction in oil-water interfacial tension and to a lesser extent the coal-oil interfacial tension was accompanied by a similar reduction in the coal-water interfacial tension. This need only have been approximate since there was presumably sufficient kinetic energy available to spread the oil despite the presence of MIBC adsorbed on the coal. The former suggestion seems most probable. Furthermore, it is known that MIBC does not promote oil dispersion (Chapter 2) and that MIBC only reduces air-water surface tension by a small amount at this dosage (see Section 4.2.3).

It appears unlikely that MIBC adsorption would occur to any significant degree at the unwashed coal-water interface since this is negatively charged and the MIBC molecule is negatively polarized. However, hydrogen bonding between the hydroxyl group of the MIBC molecule and electro-positive covalently bonded hydrogen in oxygen-containing coal surface functional groups would be expected to occur to some extent.

It is probable that the hydrophobic portion of the MIBC molecule would bond (by Van der Waals forces) more strongly to a hydrophobic coal surface, i.e. that MIBC adsorption would be more pronounced on washed as opposed to unwashed coal. This supposition was tested and will be discussed in the following section.

The addition of MIBC was found to exert some positive effect on the adsorption of various Pegasol 3745 cuts on milled unwashed coal (Figure 3.25). The ratio of MIBC to oil was 1:9 v/v. A comparison of Figure 3.25 with Figure 3.17 shows that the presence of MIBC enhanced the adsorption of the lower boiling range cuts, though it had very little influence with the 240-250°C cut. MIBC was added independently of the oil (30 s after oil addition) and 30 s before coal addition in these experiments. It was therefore afforded the opportunity to adsorb at the oil-water interface.

The difference in the adsorption characteristics of the different boiling range cuts is of interest. To attempt to explain this it is necessary to consider the behaviour of MIBC at the various interfaces present in the pulp. Equation 3.15 shows that changes in oil adsorption behaviour can be a result of changes in coal-water, coal-oil or water-oil interfacial tensions. These changes follow adsorption of MIBC at one (or more) of these interfaces (Equation 3.11).

Surface tension (oil-air interface) can be assumed to vary little in a homologous series of high boiling point oils. In the absence of MIBC the water-oil interfacial tension is therefore likely to be very similar with all three Pegasol 3745 cuts, an assumption supported by their similar droplet size distributions (see Figure 2.12). There is also no reason to expect significant differences in MIBC adsorption densities at the coal-water interface

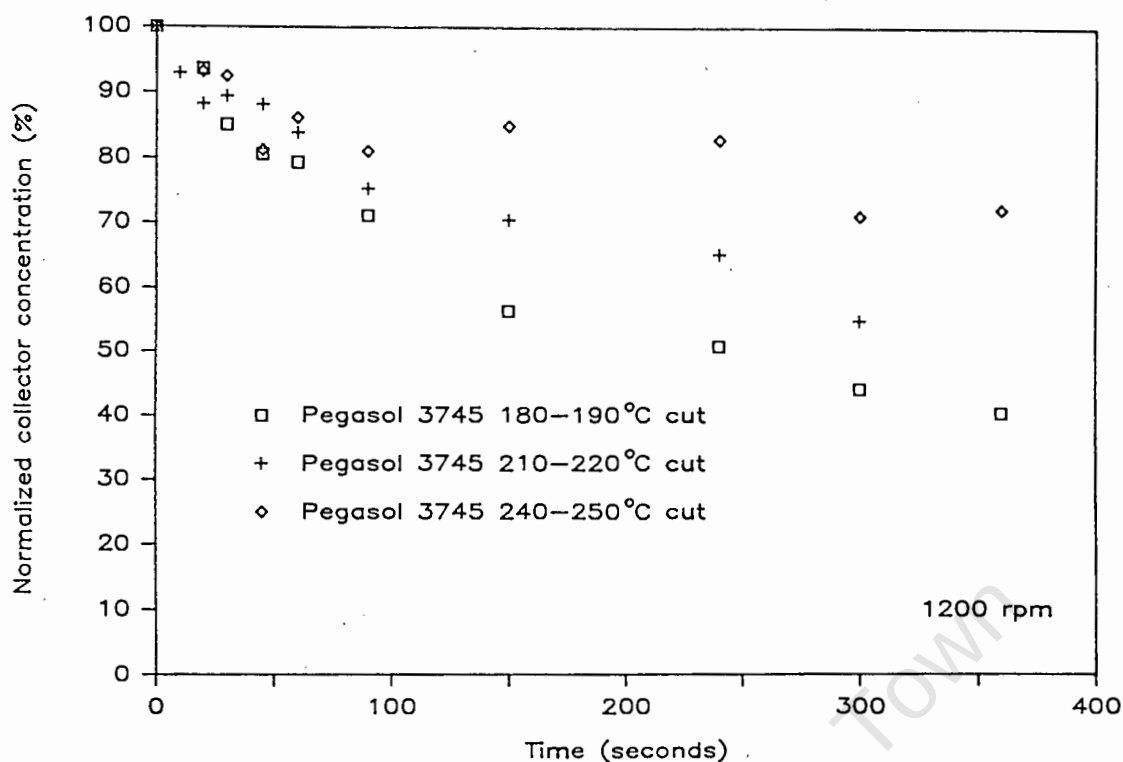


Figure 3.25 : The effect of MIBC addition on the rate of disappearance of Pegasol 3745 boiling range cuts from the pulp water. Milled Greenside No. 2 seam unwashed coal (500–600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1200 rpm.

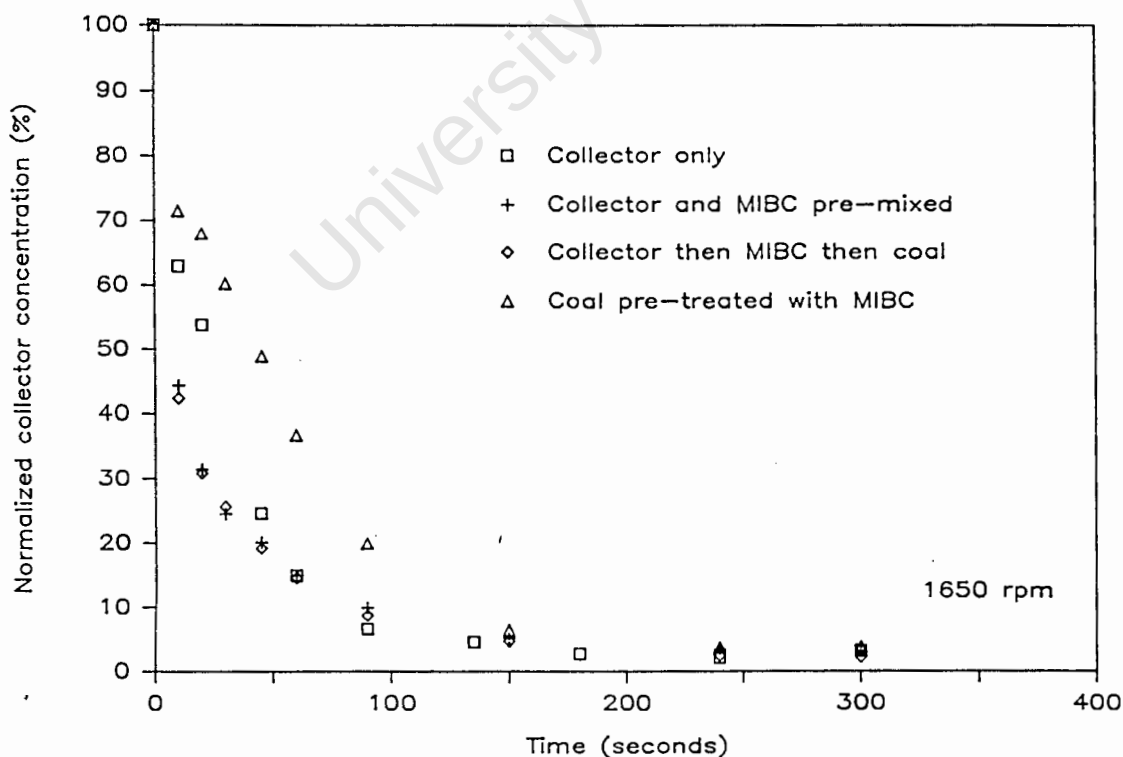


Figure 3.26 : The effect of the sequence in which coal, oil and MIBC are contacted on the rate of disappearance of dodecane from pulp water. Milled Greenside No. 2 seam washed coal (500–600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

since the coal type was the same for each experiment and MIBC adsorption is, in any event, believed to be very limited at this interface. Thus differences in the adsorption behaviour of each cut cannot be ascribed to changes in coal surface properties. It follows that the only explanation for the increased adhesion to coal by lower boiling range homologues is if MIBC is adsorbing to different degrees at the oil-water interface of each cut. Both the water-coal and coal-oil interfaces would therefore be affected though the latter would be less influenced since the MIBC can only be transferred to this interface once contact has already been established, i.e. when this interface comes into existence.

In order for the lower boiling range cuts to spread better, their interfacial tensions with water must be lowered (Equation 3.15) in relation to any reduction in coal-water interfacial tension. This seems a fair assumption as MIBC adsorption at the oil-water interface is likely to be stronger than at the unwashed coal-water interface for the reason outlined earlier. However, in order for each oil to exhibit different adsorption behaviour, MIBC would have to adsorb at the respective water-oil interfaces to different degrees. Results suggest that MIBC adsorption occurred to a greater extent at the oil-water interfaces of the lower boiling range homologues. A proposed explanation is that MIBC molecules were more closely packed at these interfaces. Since oil molecular bulk will decrease with a decrease in boiling point this could be a reasonable explanation.

3.4.6.2 Washed coal

The influence of MIBC on the adsorption of oils onto Greenside No. 2 seam washed coal was also explored, as were the effects of the sequence in which the coal, collector oil and MIBC were contacted. The manner of MIBC addition, i.e. whether mixed in the oil or added to the water, was expected to affect interfacial adsorption densities since MIBC is preferentially oil soluble. If mixed with the oil the extent of adsorption at the coal-water interface could be expected to be small.

MIBC contact with the coal prior to oil addition was achieved by conditioning the coal in 500 ml of water with MIBC (at a

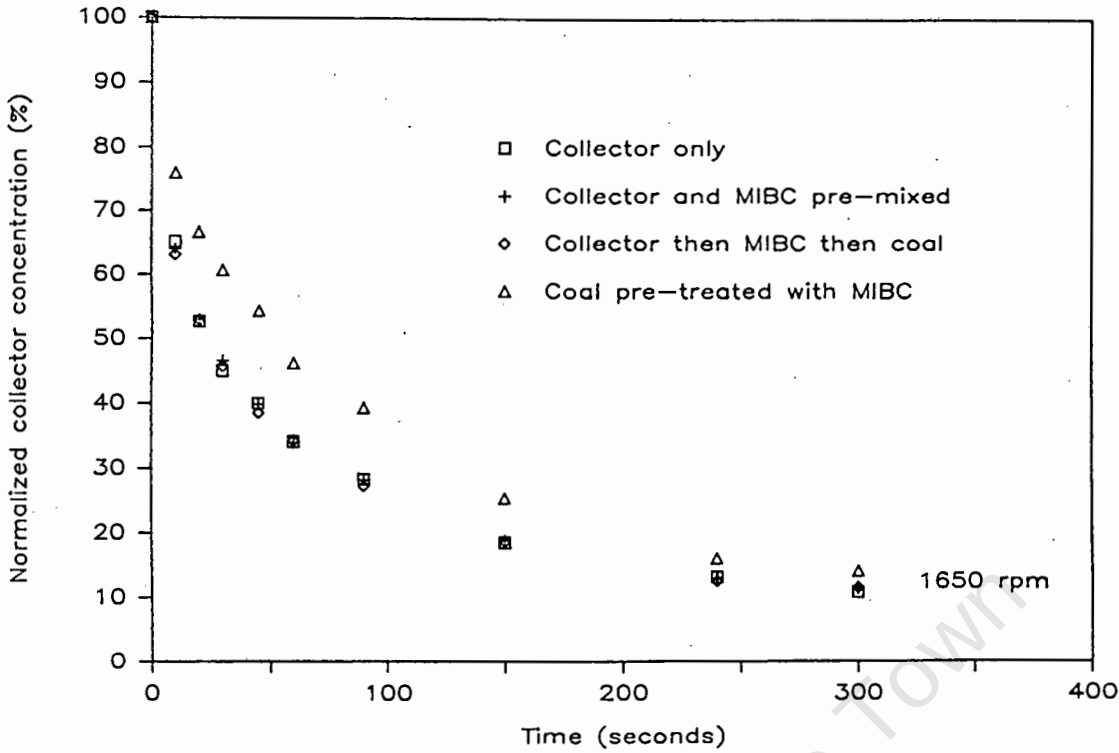


Figure 3.27 : The effect of the sequence in which coal, oil and MIBC are contacted on the rate of disappearance of hexyl benzene from the pulp water. Milled Greenside No. 2 seam washed coal (500-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

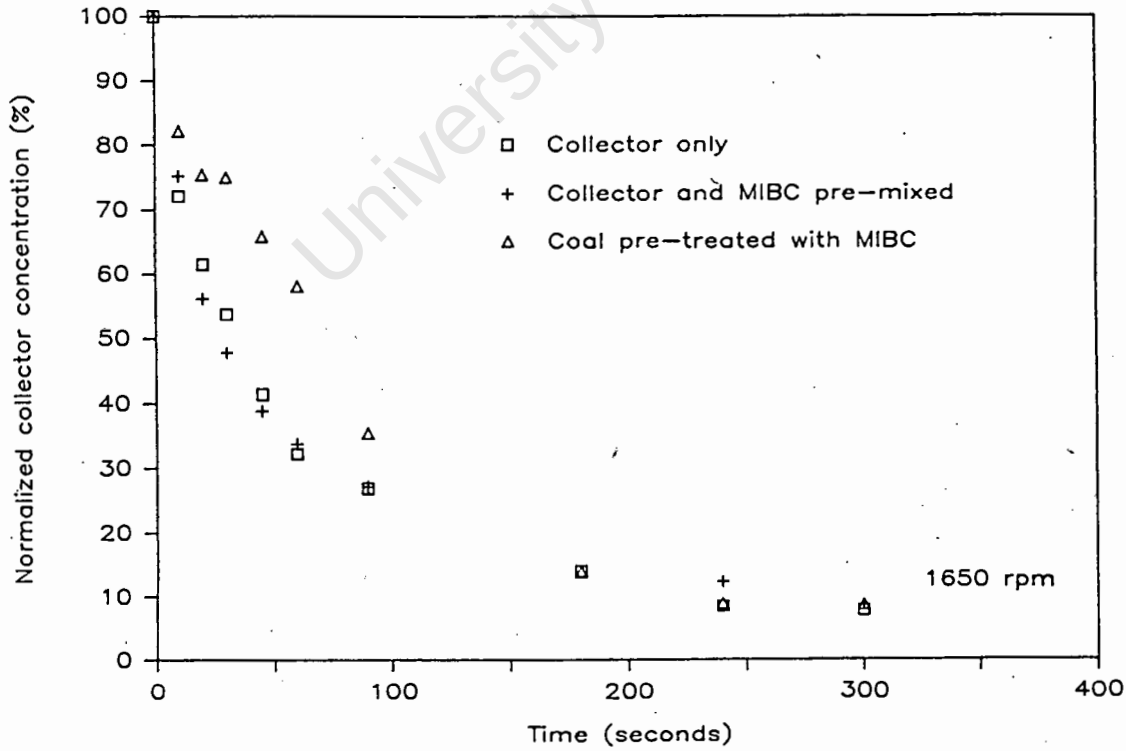


Figure 3.28 : The effect of the sequence in which coal, oil and MIBC are contacted on the rate of disappearance of Pegasol 3745 210-220°C cut from the pulp water. Milled Greenside No. 2 seam washed coal (500-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

concentration of 18 μl per litre) for 30 s and then draining away excess water in the vacuum filter-syringe device used to consolidate the coal slug. The adsorption run then proceeded as normal using this treated coal. In the other runs, MIBC was either added mixed with the collector oils or added after the oil but prior to coal addition. In this last instance it was simply added to the water in the adsorption vessel 30 s after the oil had been added (i.e., 30 s before coal addition).

The results obtained using dodecane, hexyl benzene and the Pegasol 3745 210-220°C cut as the collector oils are illustrated in Figures 3.26, 3.27 and 3.28 respectively. The same volumes of collector and of MIBC were used in each experiment. Results of experiments in which no MIBC was used are included for comparison.

The figures show that for all three collectors the initial adsorption of oil was hindered when the MIBC was contacted with the coal prior to addition of the oil. It would seem that in the absence of the oily collectors, the lipophilic portion of the MIBC molecule adsorbs onto washed (hydrophobic) coal leaving the hydrophilic end (hydroxyl group) protruding and thus hindering subsequent collector adsorption onto the coal surface, at least initially, as suggested in the previous section. This behaviour is consistent with the findings of Aston et al (1981) that MIBC rendered a coal surface somewhat hydrophilic. Unfortunately these authors did not state what type of coal was used, nor whether it had been washed (beneficiated).

The oil adsorption behaviour is also consistent with the thermodynamics of the adsorption process as represented by Equation 3.15. In the absence of an oil-water interface MIBC will adsorb to a greater extent at the coal surface and, if orientated as described above, will decrease the coal-water interfacial tension proportionately. Following the addition of oil, adsorption of MIBC at the hydrophobic washed coal-oil interface can be assumed to be negligible since both phases are hydrophobic and a surfactant would not favour adsorption at this interface. As the oil was added once MIBC adsorption on the coal had already occurred, the oil-water interfacial tension would have been comparatively high since no MIBC was adsorbed there (at least initially). The overall effect would be to lower the spreading coefficient and to hinder adsorption.

The interesting phenomenon is that this effect disappeared with time and final oil adsorption levels were unaffected by the mode of MIBC addition as may be seen in Figures 3.26, 3.27 and 3.28. Also all the other contacting methods produced practically identical results. In all the experiments (except with dodecane which is discussed below), whether the MIBC was mixed with the oil or added independently made no difference to oil adsorption, providing both reagents were dispersed prior to the addition of the coal. This was also observed with the unwashed coal sample as may be seen from Figures 3.13 and 3.14 for hexyl benzene and dodecane respectively. The only exception was that initial adsorption of dodecane was noticeably improved. Similar behaviour was noted in other experiments (Figure 3.33). Dodecane, being a pure aliphatic oil and therefore only capable of dispersion interactions, will have high oil-water interfacial tension so that a more noticeable decrease in interfacial tension in the presence of MIBC could be expected than would be the case with more polar oils. A more pronounced effect on the adsorption and spreading of dodecane in comparison to that of the other oils could thus be expected.

The following mechanism is postulated to explain the re-establishment of similar final adsorption levels in instances where MIBC was contacted with the coal prior to the addition of the oil : Upon contact of the coal with the oil a transfer of MIBC occurs to the oil-water interface or to the oil phase in which it is readily soluble. Repeated coal and oil particle collisions eventually reduce the hydrophilicity of the coal surface by redistributing the MIBC. γ_{cw} therefore increases while γ_{ow} decreases until adsorption reaches the same level as it does if MIBC is added to the system in other ways.

When oil is present, MIBC adsorption on coal surfaces can be expected to be far more limited since the oil provides a competing interface for adsorption and MIBC would rather become associated with the oil in which it is readily soluble at these dosages. Furthermore the oil itself will compete with MIBC for adsorption sites at the coal surface. The dynamics of these two effects in conjunction with the tendency of MIBC to migrate into the oil phase would substantially reduce the deleterious effect of MIBC adsorption on washed coal encountered in the absence of oil. If the MIBC is mixed in the oil

before being added to a pulp this effect will essentially be eliminated. However this procedure may have a negative influence on frothing as discussed in Section 4.2.3.1.

In any contacting scheme, MIBC does not have much influence on adsorption in terms of the final adsorption levels. The initial decrease in adsorption when MIBC was contacted with coal prior to the collector shows that addition of MIBC prior to oil is harmful. However MIBC is unlikely to contact coal much before oily collectors in a conventional flotation situation. The normal manner of adding frother is to add it to the pulp at the same time as the collector (or mixed in the collector) or just before pulp aeration begins as in the case of most of the laboratory batch flotation experiments (Chapter 5).

3.4.7 The effect of particle size

The effect of an increase in solid specific area (area per gram) on the rate of adsorption was investigated. For an equivalent mass of coal the rate of oil adsorption was expected to increase as a larger surface area was available for adsorption. This supposition was tested using dodecane and equal masses of two size fractions (250-300 and 500-600 μm) of the Greenside washed coal. Available surface area was therefore quadrupled. Results are shown in Figure 3.29. The expected increase in adsorption rate is quite clearly shown.

With feeds containing a large proportion of fine and ultra-fine coal, oil adsorption rates can be expected to increase dramatically. Predicted rates of adsorption for coal particles of any size are discussed further in Section 3.6.5. This behaviour shows that the practice of splitting flotation feeds into coarse and fine streams (e.g. Firth et al, 1982), to prevent fines "mopping up" oil so rapidly that larger particles are starved of oil, has a sound basis.

The rates of oil adsorption onto coarser fractions are nevertheless of importance since the typical flotation plant feed (or the slurry discard stream on those coal treatment plants which currently do not beneficiate fines) contains a considerable proportion of coarser material. Some typical size fractions for South African washeries are given in Table 3.1 below; and for some Canadian washeries in

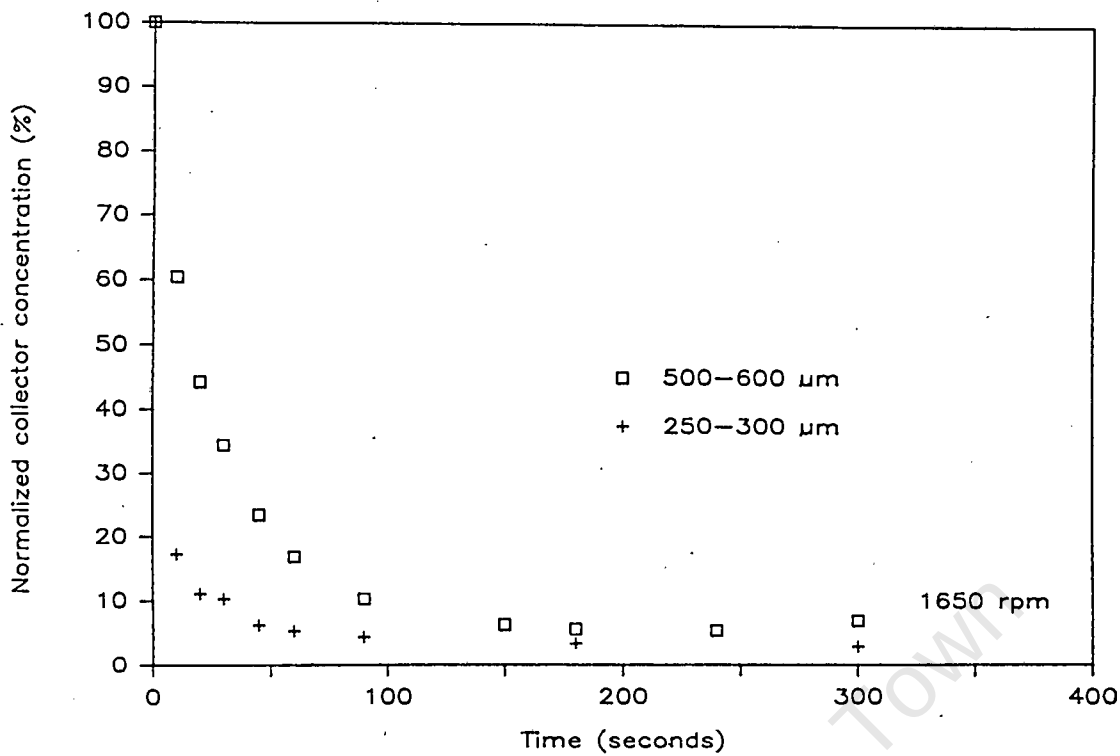


Figure 3.29 : The effect of particle size on the rate of disappearance of dodecane from the pulp water. 250-300 μm and 500-600 μm size ranges of milled Greenside No. 2 seam washed coal. 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

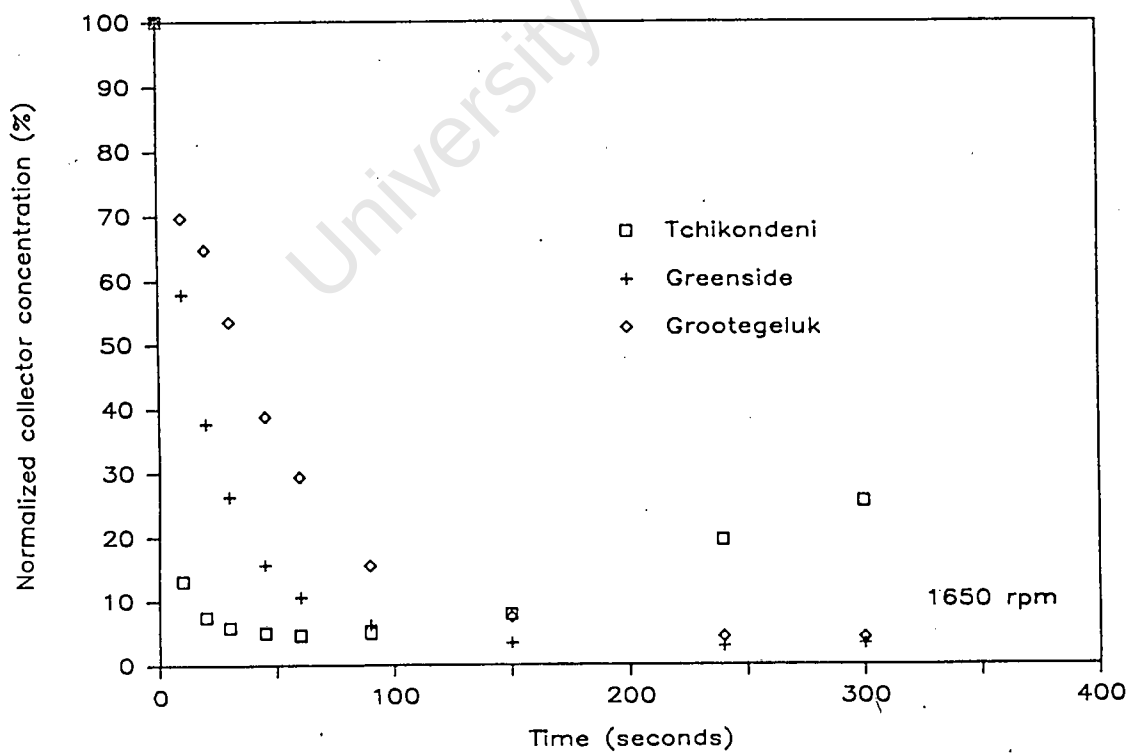


Figure 3.31 : The effect of coal rank on the rate of disappearance of dodecane from the pulp water. Milled washed coals of various ranks (500-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

Figure 3.30. This figure shows that +500 μm material may contribute as much as 20 % of some flotation feeds. The proportion of +150 μm material varies between 22 and 70 %, and of +250 μm material between 5 and 53 %.

Table 3.1 : Size fractions in flotation feed/discard streams

	+295 μm	+250 μm	+150 μm	Source
Rietspruit Colliery		35 %	46 %	Harris (1986)
Grootegeeluk Colliery	51		72	Botha (1980)
Durnacol	55		76	Botha (1980)
Greenside Colliery		19	28	Harris (1987)
Ermelo Colliery		30	44	

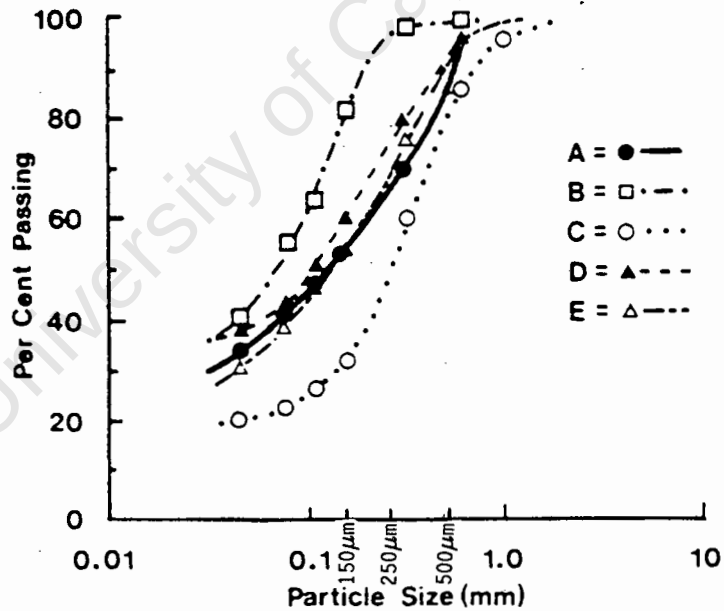


Figure 3.30 : Size distribution of froth flotation feeds in some Canadian washeries. (After Picard, 1985).

The results depicted in Figure 3.29 are for a washed coal. For the 250-300 μm fraction adsorption was essentially complete after 30 s. This would not necessarily be true of unwashed coals since adsorption rates are generally slower. The extent of adsorption is also often less. On unwashed coal feeds possessing relatively large coal particles (+250 μm)

the rates of oil adsorption are sufficiently slow to indicate the need for at least some conditioning time prior to flotation. Premature aeration of the pulp is likely to remove free oil from the pulp (as oil is highly aerophilic; see Chapter 4) before final adsorption levels are attained, and to reduce flotation performance markedly.

3.4.8 The effect of coal rank

A review of the literature (Section 3.2.2.1) suggested that the higher content of oxygen functional groups (e.g. phenol, carbonyl and carboxyl) in low rank coals would reduce the hydrophobic character of the coal surface by enhancing its (negative) surface charge and therefore its hydration by water molecules. This phenomenon and the accompanying electrical double layer development would be expected to hinder the adsorption of oil droplets, which are also negatively charged, onto the coal surface.

The presence of oxygen-containing surface functional groups is expected to have less of an effect on coal particle charge than most gangue minerals. The latter often exhibit a fixed negative charge because of isomorphous ion substitution in the solid lattice while the former are often only polarized or, if disassociated, this is to a limited extent at the mid-pH ranges typical of coal flotation. The contribution of the gangue to the surface charge on high ash (unwashed) coal particles could therefore mask the effect of rank on this and consequently on coal adsorption. It was therefore decided to investigate the effect of rank on oil adsorption using washed samples of coals of various rank. A size fraction of 500-600 μm was used in each case. The source of the coals used and their rank, in terms of RoV values (mean maximum reflectance of vitrinite), are listed below.

Source	Rank (RoV)*
Grootegeeluk washed coal	0.74
Greenside washed coal	0.85
Tchikondeni washed coal	1.21

* Source : Private communication with Mr. W. Smith of ISCOR.

It was decided to use an aliphatic oil in this work since this type of oil is most sensitive to coal surface charge. Dodecane which is pure and hence free of surfactants, was used.

As may be seen from Figure 3.31 the rate of adsorption of the dodecane decreased as the rank of the coal decreased. Adsorption of the oil on high rank Tchikondeni coal was extremely rapid, with 85 % of the oil being adsorbed in the first 10 s as compared to 30 and 40 % for the Grootegeeluk and Greenside coals respectively.

Low rank coals are known to possess a high specific surface area because of a larger number of pores. In this respect they can be expected to adsorb oil faster. As the reverse occurred it indicated that surface electrical properties control the adsorption. The results obtained conformed to the behaviour predicted by electrostatic considerations. Although electrostatic repulsion hindered the adsorption it did not prevent it since final adsorption levels for all three coals were similar. 95 % of the dodecane was adsorbed on all the coals tested. The de-sorption trend apparent with the Tchikondeni coal is a result of coal surface attrition. This effect was explained in Section 3.4.4.

3.4.9 Additional testwork

This section briefly records the results of testwork to determine the effects of reaction (pulp water) temperature and oil dosage on the adsorption behaviour. Tests were conducted with the sample of Greenside washed coal.

3.4.9.1 Temperature effects

Several decades ago, Bailey and Whelan (1953) recognized that coal flotation could be hampered by low temperature and postulated that reagent sorption could be hindered by insufficient energy being available to overcome the sorption activation energies. The effect of temperature on dodecane adsorption onto washed coal was therefore investigated in this work.

Figure 3.32 shows that very cold conditions (1°C) slowed the adsorption rate, which was as expected. Since the adsorption is a

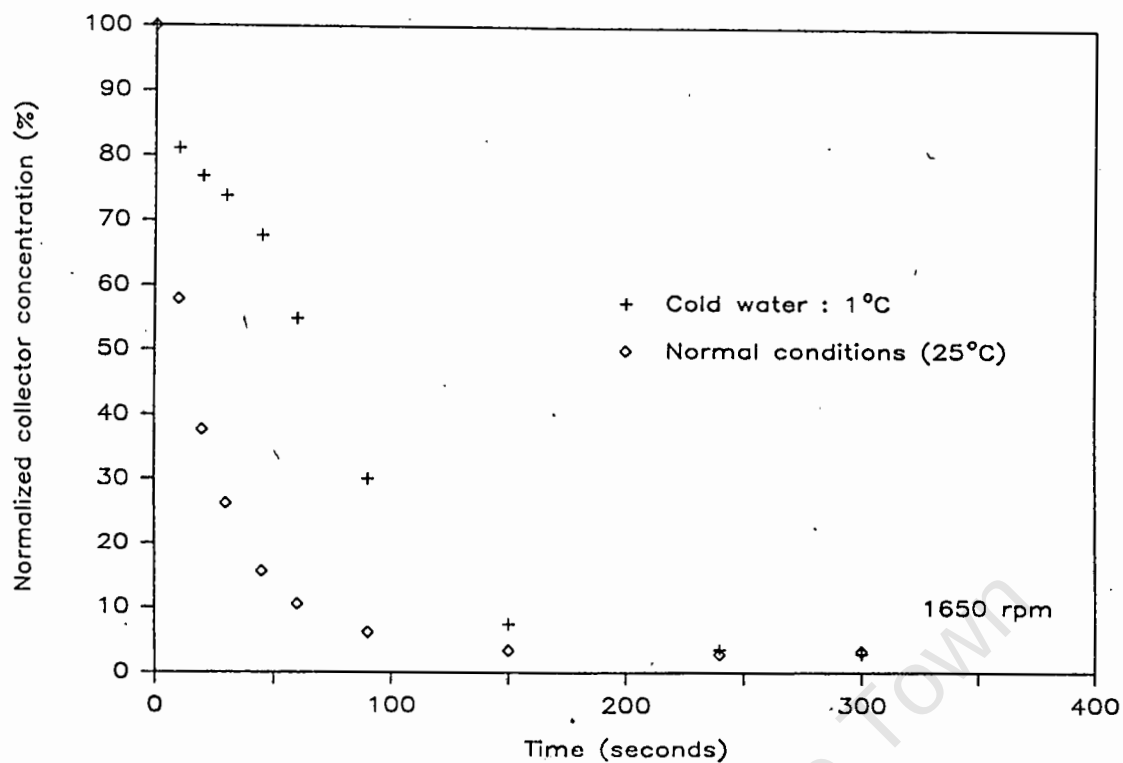


Figure 3.32 : The effect of low temperature on the rate of disappearance of dodecane from the pulp water. Milled Greenside No. 2 seam washed coal (500-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

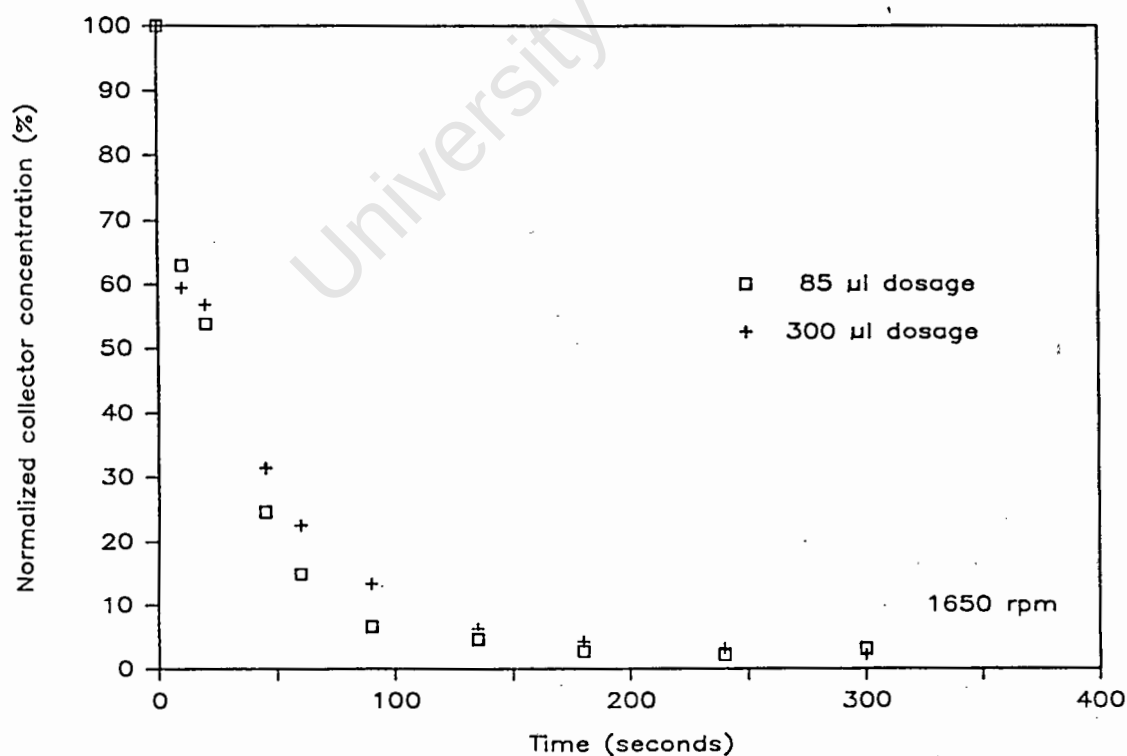


Figure 3.33 : The effect of increased dosage on the level and rate of disappearance of dodecane from the pulp water. Milled Greenside No. 2 seam washed coal (500-600 μm). 85 μl and 300 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

physi-sorption (without chemical reaction) the effect was not too pronounced. Final adsorption levels (achieved after 2.5 minutes) were identical to those measured under warmer conditions. This suggests that an adequate conditioning time could overcome the deleterious effect of a low pulp temperature. Though final adsorption levels were identical it should be pointed out that the oil may not be as well distributed amongst the coal particles since higher interfacial tensions are likely to induce larger droplets.

3.4.9.2 Capacity for oil adsorption

When reviewing the literature of reagent adsorption the term "mono-layer coverage" is commonly encountered. Mono-layer coverage is a useful concept in flotation as reagent dosages are dealt with in terms of mineral surface area rather than by mass or on some other arbitrary basis. The concept also provides a basis for assessing the maximum beneficial reagent dosage above which it becomes pointless and possibly chemically disadvantageous to add more reagent. In the latter instance over-dosage may cause a second layer of molecules to adsorb head-to-head (or tail-to-tail) with molecules already adsorbed on the mineral surface and so reinduce hydrophilicity (or hydrophobicity in the case of depressants).

However useful the concept of monolayer coverage may be when considering soluble reagents, it cannot be realistically applied to oil adsorption or be used for predicting the best oil dosage since insoluble (oily) collectors do not exist as individual molecules but rather as droplets with a range of sizes. Oils will therefore be adsorbed in layers which are possibly hundreds of molecules thick. In addition to differences in droplet size, droplets of various oil types also spread to different extents on a particular coal surface depending on their chemical properties. Following droplet adsorption the oil layers will consequently change in thickness.

The problem of trying to assess collector dosage or adsorption on the basis of mono-layer coverage is further compounded by the possibility that oil droplets which are free in the pulp may collide with oil droplets already adsorbed on a coal surface and coalesce with them rather than being adsorbed onto the coal surface itself. The

amount of oil that can be carried by an individual coal particle is impossible to quantify, being dependent on the surface area of the particle, the number and size of adsorbed oil droplets, the pulp turbulence (and the resultant shear forces) and the physico-chemical properties of the oil (amongst other factors).

Nevertheless some attempt was made to investigate how much oily collector (within the practical limits for flotation) could be adsorbed by the coal. 300 μl was added in place of the usual 85 μl in 500 ml of water, corresponding to 8825 g.t^{-1} of coal. Figure 3.33 shows the results obtained with dodecane and Greenside No. 2 seam washed coal. Oil at a dosage as high as 8825 g.t^{-1} of coal was readily adsorbed.

On the other hand the unwashed coal had a limit to how much aliphatic oil it would adsorb (refer to Figure 3.14 for instance), though this was more a function of the ability of such oils to displace water from the coal surface rather than a shortage of unoccupied coal surface. This conclusion is supported by the behaviour of the more finely dispersed aromatics. Their larger overall oil surface area at an equivalent dosage would require more solid surface area to adsorb an equivalent mass than larger (aliphatic) droplets would, yet they were more completely adsorbed by the same coal.

If one considers that a 500-600 μm coal particle size range was used in this testwork, providing a surface area more limited in relation to that arising for an equal mass of naturally arising coal fines, it can be assumed that substantial quantities of oil can be readily adsorbed by some pulps. It also again highlights the desirability of dispersing oils prior to addition to the pulp since rapid and tenacious adsorption of fairly large droplets by some particles could prevent other desired particles being oiled.

Results presented so far indicate that, generally, a greater proportion of aromatic oils is adsorbed in terms of mass than of aliphatic oils. Furthermore, since their ability to disperse is greater than the aliphatics in highly turbulent regimes (as demonstrated in Chapter 2) coal coverage is likely to be that much better. Flotation performance would therefore be expected to improve. Nevertheless the number of droplets per millilitre of even the

relatively poorly dispersing oils is very high so, that even limited adsorption of these oils may be sufficient for effective flotation. How much oil adsorption is sufficient for effective flotation is open to speculation at this stage but is considered qualitatively in Chapter 5 (e.g. Section 5.4.1.1.c).

3.4.10 Summary

The adsorption of all oil types was found to be almost complete on the washed coal sample. This was not so with the unwashed coal, onto which aliphatic or predominantly aliphatic oils were adsorbed to less of an extent than the aromatics. This behaviour was attributed to the almost complete lack of polarity of the aliphatic oils, which made a) the displacement of water from, and b) the adsorption and spreading of oil on, the more hydrophilic unwashed coal surface more difficult. The polarity of the oil affects its surface energy and by implication its interfacial tensions with other phases. Aromatic oils have lower oil-water interfacial tensions than aliphatic oils. It also determines the bonding mechanisms which occur between the oil and the coal.

Excessively vigorous conditioning of the pulp led to an apparent increase in desorption of the oil with time. It was found that this behaviour was the result of fine coal flakes, to which oil was adsorbed, being removed from the surface of the larger particles by the increased agitation intensity. This effect increased with coal friability which is often associated with increased ash content. This phenomenon is akin to true desorption in terms of its effect on flotation.

A decrease in impeller speed increased the rate of oil adsorption, even if the oil was dispersed in an identical manner prior to contacting the coal. If a low impeller speed was maintained during both the oil dispersion and coal conditioning steps the increase in the rate of oil adsorption was even more pronounced.

The presence of MIBC did not facilitate the adsorption of the oil onto washed and unwashed coal except to a small degree with the lower boiling range cuts of the Pegasol 3745 oil. MIBC enhanced the initial rate but not the extent of dodecane adsorption on the washed coal. The adsorption of oil was hindered (rates were reduced) if MIBC was

contacted with coal prior to the oil. It was found that all these effects were a consequence of the interfacial properties of the oils and the modifying effect induced by MIBC, particularly at the water-oil and coal-water interfaces.

The rate of oil adsorption increased markedly with a decrease in particle size, i.e. with an increase in the specific area of the coal. In coal pulps containing a substantial proportion of fine particles, these particles would therefore be expected to adsorb much of the oily collector before it has a chance to be properly distributed in the pulp. The adsorption kinetics of the oil on larger particles (500-600 μm), particularly of the unwashed coal, indicated that some minutes of conditioning would be required prior to flotation. A substantial proportion of the coal particles in typical flotation plant feeds are large.

Washed (low in ash and therefore more hydrophobic) coals in combination with any oil type, and unwashed coal in combination with aromatic oils were able to adsorb far larger quantities of oil than are normally used in flotation practice.

Very low pulp temperatures reduced the rate of oil adsorption but not the final extent of adsorption. With samples of washed coals, decreasing coal rank reduced the rate of adsorption while the extent of adsorption remained similar.

3.5 SELECTIVITY OF HYDROCARBON OILS

3.5.1 Introduction

Collector adsorption is a pre-requisite for effective flotation of most South African coals since they do not float adequately in the presence of a frother alone. This adsorption has been shown to occur but of equal if not greater importance is a study of the ability of a collector oil to be selective towards the desired component, i.e. the carbonaceous material. Determination of the selectivity of the hydrocarbon oils on a micro-scale was another objective of the adsorption testwork.

If the oily collector cannot distinguish between a coal-rich surface and one dominated by gangue, or is able to spread over gangue surfaces from adjacent coal surfaces, then the selectivity of this collector will be low, i.e. it will not be possible to produce a high grade (low ash content) product. The insolubility of oil means that collector is present as droplets of considerable size (in relation to its constituent molecules) and this could also have a harmful effect on selectivity.

The ability of aliphatic and aromatic oil types to discriminate between gangue minerals and coal was tested using "pure" coal and gangue solids, and on relative density fractions of two unwashed coals.

3.5.1.1 Comparison of the selectivity potential of insoluble and soluble collectors

A debateable point is just how selective an oily collector can be. It is widely believed that the selectivity of oily collectors is poor, i.e. that they tend to inadvertently adsorb onto (or "oil") unwanted gangue material. Certainly the impression gained when assessing the ash content of coal flotation concentrates is that reagent selectivity is poor. Grades are often poor despite careful adjustment of various physical flotation parameters, such as reagent dosage, aeration rate and froth height. It is difficult, if not impossible, to obtain even low recoveries of low ash coal (7 % ash content) from many South African r.o.m. coals using conventional flotation techniques. This is despite the fact that the washability curve (obtained by float and sink analysis) suggests that a considerable quantity of such material is present. By choosing appropriate flotation conditions the effects of physical entrainment can be reduced yet poor grades often persist.¹²

It is believed that soluble collectors, acting as individual molecules, are able better than insoluble collectors, which form droplets, to discriminate between small gangue and desirable mineral surfaces and less likely to coat undesired mineral surfaces. Consider the selectivity potential of droplets versus that of single molecules.

¹² Another possible reason is that the coals are simply insufficiently physically liberated and poor reagent selectivity is not the problem at all - this is discussed further in Section 5.4.7.

Hydrocarbon oils by nature are strongly hydrophobic and from this point of view should be excellent collectors for coal, providing it is not excessively oxidized. From the point of view of chemical compatibility they should be quite capable of distinguishing between hydrophobic (coal) and hydrophilic (gangue) surfaces - being attracted to the former and repelled by the latter. Thus it is possible to argue that the physical attributes of oil droplets are to blame for their apparently poor selectivity.

This issue of the size of the collector entity only becomes of importance in terms of selectivity when the mineral matter size approaches that of the collector agent. This is obviously never the case with soluble collectors, but the situation with oily (insoluble) collectors could be different. However the hydrocarbon oils, dispersed in a flotation cell, displayed a droplet size distribution in which the mean droplet size was seldom greater than 30 μm (Chapter 2). This was based on droplet volume (mass). In terms of droplet number such droplets were distinctly uncommon and most droplets were of the order of a few microns in size. They therefore had the ability in terms of size to discriminate between coal and gangue surfaces (or minute independent particles) of these minerals in almost every conceivable case. There cannot be much sub-micron gangue within the coal matrix or many sub-micron coal particles in typical r.o.m. coal. Particles of this size should be liberated and in any case, there is some doubt as to whether their tiny mass would allow them to cross the streamlines surrounding an oil droplet and so effectively contact the oil.

Providing that chemical selectivity is apparent, i.e. that the oils will not adsorb on hydrophilic surfaces, then there would be little doubt that oils should be effective collectors. The potential for a decrease in grade caused by accidental oiling of unwanted gangue by the few large collector droplets in the pulp would be likely to be minimal. None of the oils studied spread spontaneously on a coal surface and it is most improbable that they would spread onto gangue surfaces which are usually charged and therefore hydrophilic.

Collector selectivity is manifested during the adsorption step and was monitored in the testwork that is described below by using the adsorption technique developed. The advantages of using this technique

rather than other means of evaluating selectivity such as contact angle measurements have already been discussed (Section 3.1)

3.5.2 Adsorption onto coal and quartz fractions.

Before applying the adsorption analysis to actual r.o.m. coals, reagent selectivity was tested independently on samples of washed coal and gangue. Clays are the dominant gangue minerals in South African coals and therefore it was desirable to study collector adsorption onto them. However it was impossible to do so as the ultra-fine particulate nature of clays would prevent their separation from the water-oil dispersion. Clay particles are typically of the order of microns in size which is often smaller than many of the collector droplets. Separation of oil and solid particles using needle filters (or any other filter) is therefore impossible. (See Section 3.3.1.2 where the problem of separation of solids from oil droplets is described).

Quartz (99.8 % pure) was therefore selected for the preliminary testwork. The quartz was supplied by Industrial Sands, Cape Town and a 500-600 μm size fraction was used in the tests. The mass of solids was adjusted according to solid specific gravity to ensure similar solid surface area for adsorption of collector oil, as in all the other experiments. Figure 3.34 allows the comparison of dodecane adsorption onto washed coal and onto quartz.

It is obvious that dodecane can discriminate between the hydrophobic coal and the hydrophilic quartz. The oil is barely able to adsorb on the quartz. In fact adsorption may be non-existent since the decrease in oil concentration in the pulp water with time was no greater than that observed in the complete absence of solids (cf. Figure 3.11). It is reasonable to expect that other oils would behave similarly with quartz. Although aromatic oils have a somewhat lower water-oil interfacial tension than pure aliphatic oils this difference is too small to affect quartz wetting. From Inequality 3.5 it is evident that γ_{wo} could be smaller than $(\gamma_{qo} - \gamma_{qw})$ since quartz is a high surface energy solid and γ_{qo} can therefore be expected to be high and γ_{qw} low in the absence of surfactants. In this case not even partial wetting of quartz by oil would occur. Oils containing (ionic) surfactants, which reduce the oil-water and quartz-oil interfacial tensions considerably, may

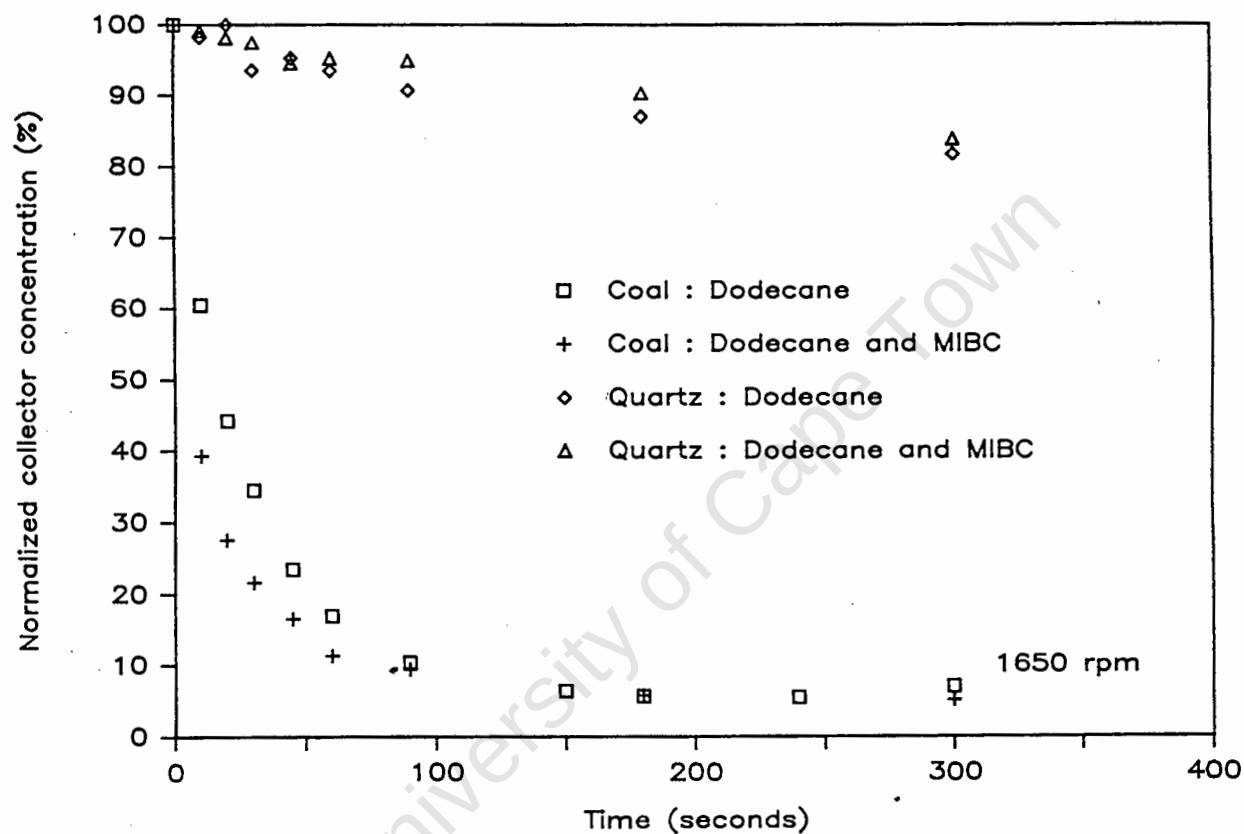


Figure 3.34 : The rate of disappearance of dodecane from the pulp water. Independent milled Greenside No. 2 seam washed coal and quartz (500-600 μm). The effect of MIBC on the rate of disappearance also shown. 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

adhere to quartz and preclude selectivity. Since reasonably pure oils show very poor adsorption on quartz it is probable that they will exhibit similar behaviour with other hydrophilic gangue minerals, particularly charged minerals like clays.

3.5.3 Adsorption onto density fractions of r.o.m. coals.

As the ash mineral content of a "coal" particle of any given size increases so (on average) the proportion of actual carbonaceous surface decreases. Most mineral impurities are high surface energy (hydrophilic) solids like oxides and silicates. Consequently the adsorption of oily collector would be expected to decrease as it is deprived of adsorption sites. Minerals have a higher specific gravity (S.G.) than the coal. So increasing ash content corresponds to an increase in S.G. Thus if coal is split into discrete S.G. fractions, adsorption would be expected to decrease with increasing S.G..

Two coals, a milled Greenside No. 2 seam unwashed coal sample and a flotation feed from the Vryheid Coronation Colliery were used to test this supposition. A 500-600 μm size fraction was removed from the former and a 425-600 μm from the latter coal (the size range was broadened in order to obtain sufficient coal from the available sample).

These sized samples were separated into various density fractions, using ZnCl_2 solutions for separations up to 1.8 S.G. and tetrabromoethane (TBE) for separations at higher densities. The fractions separated with TBE were washed thoroughly using CCl_4 and this solvent was removed entirely by applying a mild vacuum. The density fractions below 1.8 S.G. were filtered and then washed continuously with water for two hours to remove residual ZnCl_2 . Crossley (1958) reported that coal could adsorb a fair proportion of zinc from solution. To test the efficacy of the washing process a test was made by contacting a quantity of coal with ZnCl_2 and then washing with water for 2 hours and carrying out a standard adsorption test. The sample had similar adsorption characteristics to untreated coal.

As the density of the material increased so progressively greater masses of material were used in the adsorption runs to ensure that similar surface areas were available for adsorption (similar particle

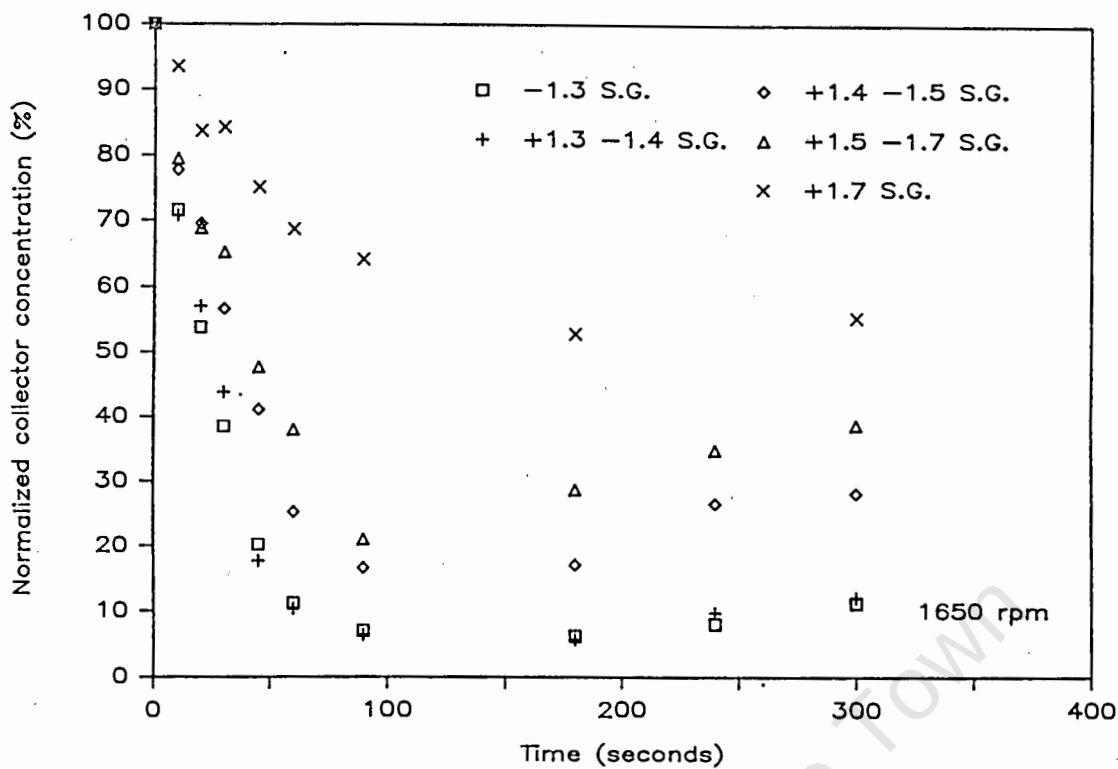


Figure 3.35 : The rate of disappearance of dodecane from the pulp water. Density fractions of Vryheid Coronation r.o.m. coal (425-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

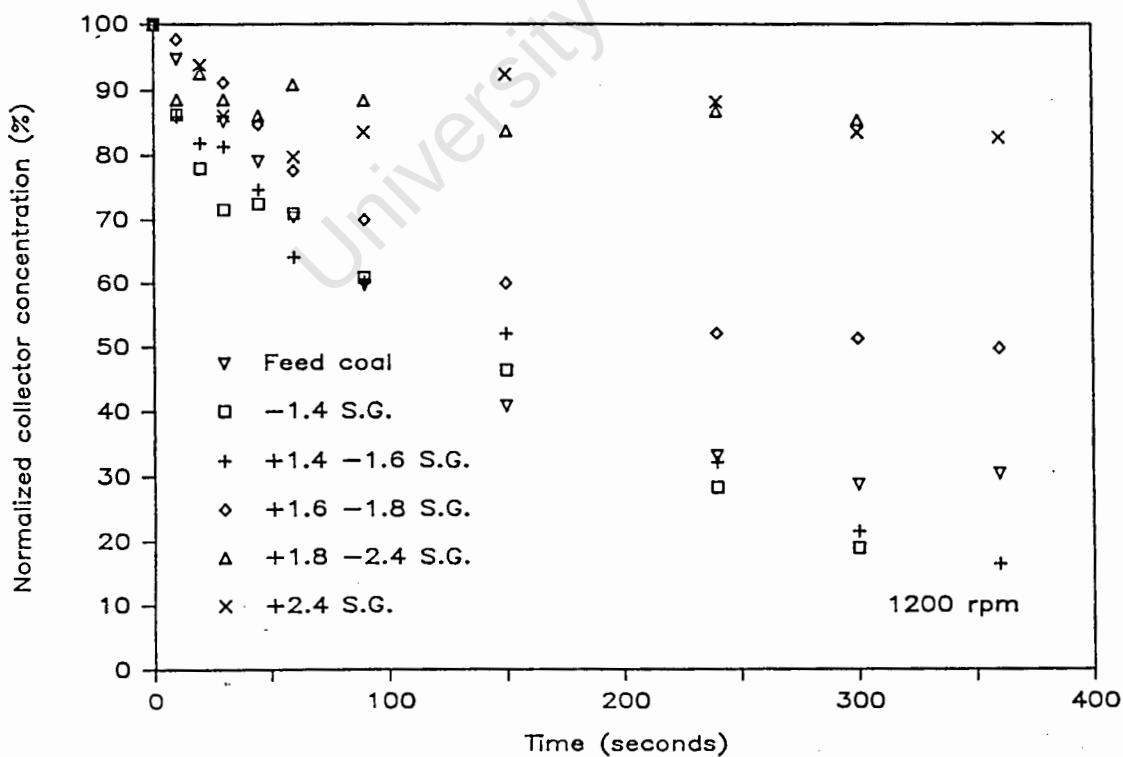


Figure 3.36 : The rate of disappearance of hexyl benzene from the pulp water. Density fractions of Greenside No.2 seam r.o.m. coal (500-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1200 rpm.

shapes and porosities were assumed). The mass of each fraction used is given in Table 3.2.

Table 3.2 : Mass of coal of each density range used in the adsorption tests

Greenside No.2 seam unwashed		Vryheid Coronation unwashed	
S.G. range	Mass (g) per 500 ml water	S.G. Range	Mass (g) per 500 ml water
		-1.3	19.60
-1.4	25.00	+1.3 -1.4	20.76
+1.4 -1.6	27.78	+1.4 -1.5	22.28
+1.6 -1.8	31.48	+1.5 -1.7	24.60
+1.8 -2.4	38.89	+1.7	27.68
+2.4	46.29		
Ratio 500-600 μm to 425-500 μm was 0.808 (m/m).			

Dodecane was used in testwork with the Vryheid Coronation coal density fractions. The kinetics of the adsorption are shown in Figure 3.35. The decrease in adsorption with an increase in density is clearly shown.¹³ The adsorption behaviour of dodecane on -1.3 and 1.3 to 1.4 S.G. fractions were virtually identical. A small decrease in both the rates and the extent of adsorption was apparent with the +1.4-1.5 and +1.5-1.7 S.G. fractions. A big decrease in these characteristics was evident with the +1.7 S.G. fraction.

Dodecane was not used with the Greenside No. 2 seam unwashed coal density fractions because this oil showed poor adsorption on even the feed material, in which the proportion of carbonaceous surface is high. (see Figures 3.14 and 3.15). Hexyl benzene was used instead. Results are depicted in Figure 3.36. The decrease in adsorption with an increase in density is again clearly evident.¹⁴ Hexyl benzene behaved very similarly

¹³ The apparent desorption trend after 1.5 minutes is explained in Section 3.4.4. The adsorption at 90 s should be considered to be the final adsorption level.

¹⁴ Note that at an impeller speed of 1200 rpm the apparent desorption trend encountered with the previous coal sample (Figure 3.35) was not evident.

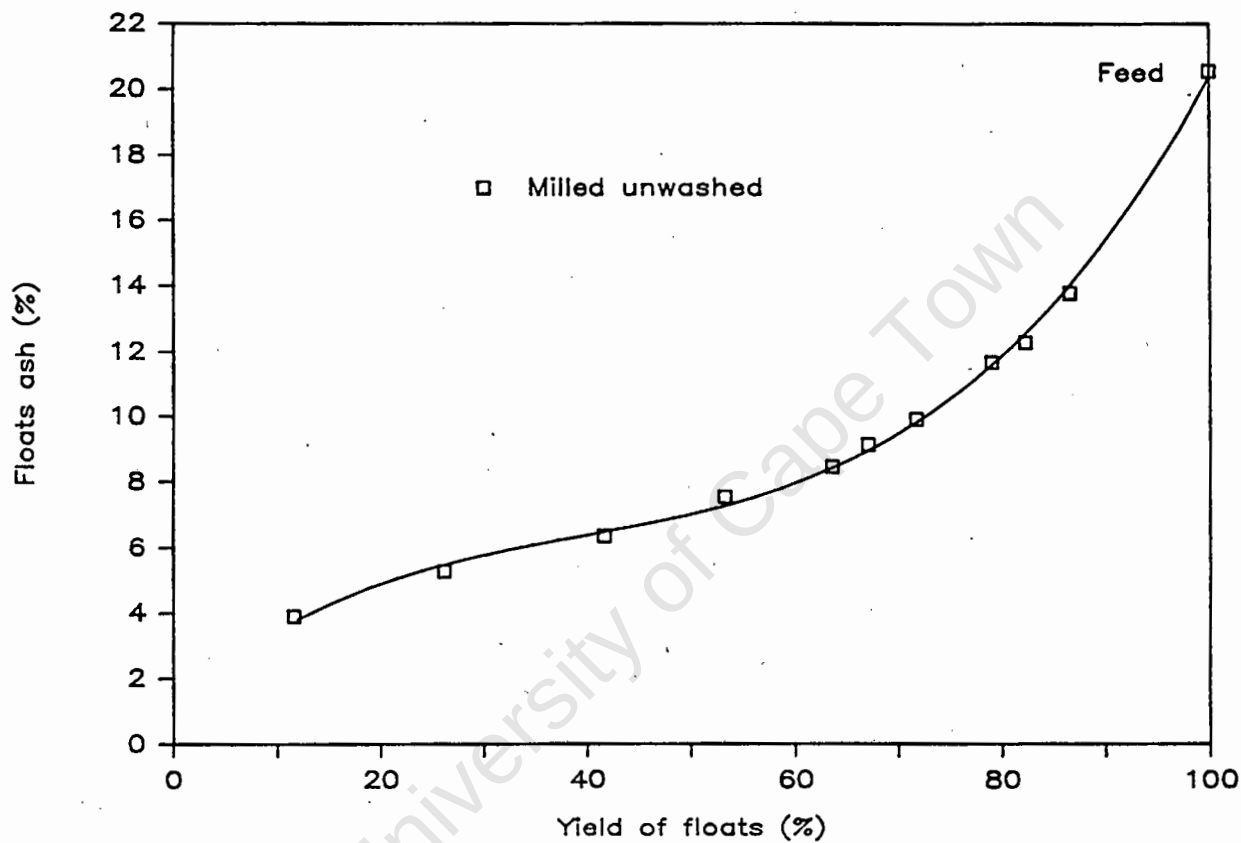


Figure 3.37 : Washability curve. Cumulative ash of floats versus cumulative yield for a sample of -500 μm milled Greenside No.2 seam unwashed coal.

with the -1.4 and +1.4-1.6 S.G. fractions. A big difference was found between its adsorption onto these density fractions and the +1.6-1.8 S.G. fraction. The extent of adsorption onto the +1.8-2.4 and the +2.4 S.G. fractions approached that of pure quartz (cf. Figure 3.34) The oil was not adsorbing to any significant degree on these fractions. The degree of adsorption may in fact have been less than that indicated by the curve because of the loss phenomenon discussed in Section 3.3.5.

Discussion

The aim of the adsorption tests on different S.G. fractions was to investigate selectivity of the oils on a microscale, i.e. to determine whether they could distinguish a coal rich surface from one dominated by gangue. The results described above appear to confirm the poor selectivity of the oils. The +1.5 -1.8 S.G. fractions of both coals displayed a significant degree of adsorption and could be expected to float, i.e. coal with an ash content of about 30 % will be floated.

However, it should be borne in mind that the adsorption tests portray the worst scenario. Firstly, in these tests collector dosage in terms of coal surface area was very much greater than that used in conventional flotation plants where the feed contains an entire range of particle sizes, dominated (in terms of surface area) by material finer than 500 μm . The high collector volume to surface area ratio in the adsorption experiments is likely to encourage adsorption. Secondly, in the adsorption tests with the high density fraction, the collector had little clean coal surface to distract it. But in reality the more dense (high ash) fractions would constitute only a relatively small proportion of the naturally arising feed. The limited extent of high ash (high density) material in the Greenside unwashed coal feed is shown in Figure 3.37. Consequently, the adsorption behaviour of the oil with a 500-600 μm size fraction of the Greenside unwashed feed coal was very similar to that of the cleaner density fractions (since they dominate the feed) as shown in Figure 3.36. It is likely that with the whole coal, adsorption onto the cleaner fractions will be more rapid, leaving little reagent to adsorb onto the higher S.G. fractions.

It should also be remembered that particles in the 1.5-1.8 S.G. range, on which the adsorption of oily collectors was significant, are still dominated by hydrophobic carbonaceous material. Assume mineral free coal to have an S.G. of 1.3. The S.G.s of some typical gangue minerals are : Clay (kaolinite), 2.61-2.68; quartz, 2.65 and pyrite, 5.02 (CRC Handbook, 1980-81). Clay minerals dominate the gangue of the coals used so it may be assumed that the gangue content of the coal has an S.G. twice that of the coal (i.e. 2.6). Now suppose a low ash coal product is desired, of say 7 % ash content (by mass). Ignoring the mass loss arising from the loss of water of hydration and combustibles in the gangue minerals during ashing, a mass balance gives the total volume of the gangue in such a low ash coal product as 3.5 %. Naturally surface area is of more importance but is not easily quantifiable being dependent on the form and distribution of the gangue in the solids.

If the coal and gangue surfaces are not independent but form part of the same particles, then no matter how the gangue is disseminated within the coal, the surface area of gangue presented to a flotation collector would be very small (not more than the volume percentage). It is very likely that such a particle would be collected, irrespective of how selective the collector is or whether it is soluble or not. It is even expecting too much from a collector to reject a particle with an ash content of 14 % (or roughly 7 % gangue by volume) . In fact it would not reject particles until the proportion of gangue was considerably higher, as shown by the density testwork results. Based on the assumption above, a coal particle which is 50 % (by volume) gangue would have a S.G. of 1.95 and one of 30 % gangue an S.G. of 1.69.

A prerequisite for successful beneficiation is that the ash minerals must be substantially (virtually practically) independent of the coal, i.e. liberated, so that particles are either mostly coal or mostly gangue. Unfortunately this is not the actual situation for the Witbank No.2 seam coal that was used in the bulk of the work in this thesis. A typical float-sink curve for the milled Greenside No. 2 seam unwashed coal (Figure 3.37) indicates that this coal is dominated by particles containing both carbonaceous material and gangue, i.e. middlings. The curve reflects the poor degree of physical liberation of the coal.

Figure 3.37 is for the entire $-500\text{ }\mu\text{m}$ size fraction. It is clear that the feed as a whole is poorly liberated. Exploring the adsorption behaviour of the oils on $500\text{-}600\text{ }\mu\text{m}$ material was in this respect reasonably representative of the $-500\text{ }\mu\text{m}$ fraction used in the flotation testwork. The density washability curve shows that there is not a high proportion of low ash material and a small clearly separate portion of high density (high ash) material. Even the best possible separation (i.e. that in terms of density) will give a yield of only 50 % at an ash content of 7 %. At best, half the feed would therefore be rejected if the target was a 7 % ash product. However in view of the discussion on the inability of the collector to disregard a composite particle dominated by the desired material, such high grades will never be achieved by flotation, i.e. the flotation washability will be considerably poorer than the density washability.

But it is both impractical and uneconomical for fine ($-150\text{ }\mu\text{m}$) coal to be separated by density (gravity) on an industrial scale and it is for this reason that flotation is used for beneficiation. What must be accepted is that it is impossible to obtain adequate yields of low ash coal from a poorly liberated feed. Any collector will only reject a particle dominated by unwanted material. Efficient beneficiation by flotation is completely dependent on adequate physical liberation.

On the basis of the adsorption results, it may be said that a lack of such adequate physical liberation and not poor reagent selectivity is the principal reason for the poor flotation grades obtained with South African coals. Nonetheless, it must be emphasised that coal fines, like those used in this testwork, do contain a significant proportion (by mass) of high ash content particles as indicated by the sharp upward trend in the floats-sink curve, shown in Figure 3.37, at higher densities (higher ash contents). This material can be effectively removed by flotation without further grinding of the coal and it is advantageous to do so. Achieving a low ash coal at reasonably high recoveries is however impossible without further physical liberation.

3.6 MODELLING THE ADSORPTION KINETICS

3.6.1 Introduction

Throughout this chapter, the adsorption of various collectors onto different coals under a variety of conditions has been represented solely by the empirical data points obtained using the adsorption technique developed. In this section attempts to model this data are discussed. The modelling exercise proved to be very useful in gaining some insight into the mechanism of oil droplet adsorption. It also revealed initially unexpected difficulties in proposing a suitable model. Unfortunately an understanding of the adsorption process is so complicated by the enormous range of droplet sizes, as well as by the ability of droplets to coalesce and break up once adsorbed, that a model based on a proposed physical mechanism could not be formulated.

Instead, simple kinetic rate equations were used to model the rate of disappearance of the collector oils from the pulp water. The motivation for this is that in many other situations such relationships, e.g. first order (exponential decay) have been found to represent experimental data well; though the representation is not necessarily based on a specific understanding of the true mechanism. The flotation process itself has often been modelled using first order kinetics (e.g. Banerjee et al, 1962; Loveday, 1966; Agar and Barrett, 1983; and Fuerstenau et al, 1983).

3.6.2 Background theory

Rate equations are derived from a proposal of the mechanism of reaction. Elementary reactions are those whose rate equations can be deduced from their reaction stoichiometry. Conversely non-elementary reactions are those whose rate equations have no obvious connection with their reaction stoichiometry. In a sense, oil adsorption is non-elementary because the insolubility of the oil makes stoichiometry irrelevant and complicates attempts at defining a mechanism. The reaction is in any event a physi-sorption and not a true chemical reaction.

A rate equation refers to a single species and the change in the number of this species with time is the basis of the relationship. The most common form, used for homogeneous reactions, is

$$-r_i = -\frac{1}{V} \frac{dN_i}{dt} = \frac{\text{Moles of } i \text{ disappearing by reaction}}{(\text{Unit volume}) (\text{Unit time})} \quad [3.19]$$

Because a rate of adsorption is of interest, this author felt that the rate equation is more appropriately re-defined in terms of unit solid surface area rather than volume. A unit surface area basis allowed the model to be applied to any particle size range. In addition, the insolubility of the oils precluded the possibility of basing the adsorption reaction on molecular behaviour and meant that the rate equation did not need to be based on moles of oil. Oil mass or more precisely relative mass was a more convenient basis for the rate equation. This basis related directly to the adsorption technique which measured collector mass concentration (mass relative to that of water) normalized against the mass concentration at zero time. At zero time the relative concentration was therefore 1 (100 %).

Equation 3.19 therefore becomes

$$-r_i = \frac{1}{S} \frac{d(M/M_0)}{dt} = -\frac{1}{S} \frac{d\delta}{dt} \quad [3.20]$$

where : $-r_i$ = Rate of disappearance of oil

S = External solid surface area

M = Mass of collector in the pulp water at time t

M_0 = Mass of collector in the pulp water at time 0

δ = Normalized oil (collector) mass = M/M_0

The use of the collector concentration in the bulk (i.e. pulp water) phase in Equation 3.20 is explained below. The adsorption systems studied were heterogeneous and involved the adsorption of a liquid phase (oil) onto a solid surface after displacement of another liquid phase (water). The difference between homogeneous and heterogeneous reaction systems concerns the number of "resistances" which must be overcome in the latter type before the actual reaction can occur. These are chiefly resistances to mass transfer.

In solid-fluid systems (with the reactant constituting part of the fluid phase) the rate of reaction is dependent on the concentration of the reactants at the actual solid surface, which is often different from the concentration in the bulk fluid because of diffusional resistance. Because the surface concentration is not measureable it is preferable to base the rate equation on the bulk concentration. Boudart (1968) and Levenspiel (1972) explain that this is often done by applying the concept of a limiting rate. The rate of chemical reaction is likely to be more rapid than (say) the rate at which the reactants can diffuse to the solid surface. The apparent rate is therefore controlled by the slowest step which in turn is dependent on the bulk fluid concentration.

The oil adsorption systems studied here have the complication of having two immiscible fluids, one of which is the reactant. This author believes that resistances to collision and film thinning, rupture and retreat can be considered resistances to the physi-sorption process in much the same way as diffusion is a resistance in a single fluid system. The rate of physi-sorption bond formation is likely to be quicker than the rates of collision and film thinning, rupture and retreat. In other words the physi-sorption step (the formation of Van der Waals and hydrogen bonds) is not likely to be rate controlling - one of the preceding steps is. Applying this assumption allows the oil concentration within the pulp water to be used in the rate equation.

The mass basis selected for the rate equation would be totally acceptable if a single species (both chemically and physically) was being studied. In terms of chemistry, the oils used were essentially single species since their insolubility allowed even the complex chemical mixtures of the commercially produced oils to be regarded as homogeneous. In this sense insolubility was particularly useful as impure oils consist of a vast range of molecular species. Unfortunately this very insolubility gave rise to a physically non-homogeneous reagent in the sense that a droplet size distribution was produced as opposed to independent molecules.

This suggests that each droplet size is analagous to a different chemical species; it is likely to have its own adsorption rate under any given set of conditions (turbulence, etc.). In other words many parallel reactions occur simultaneously, the overall apparent rate being the sum of these rates. The actual mechanism is consequently very difficult to

quantify. However, such an understanding is not essential for modelling purposes. Thus, despite the insolubility of the oils, rate equations based on elementary molecular reactions were applied.

3.6.3 Selection of data sets for modelling purposes

A number of "typical" runs of characteristic form, representing various aspects of the adsorption results, were chosen for use in the modelling exercise. The data selected were from the better, or smoother, runs to avoid complications introduced by real or sampling-induced concentration fluctuations.

Some data manipulation would be required in fitting some of the other data sets. In particular, the data points obtained towards the end of some of the runs, particularly with the friable r.o.m. coals, would have to be replaced by estimates based on earlier concentrations and these estimates would then be assumed to be the equilibrium adsorption levels. This would be necessary because of the apparent desorption effect found (Section 3.4.4).

The data sets used are tabled below. That other data sets have similar shapes may be verified by comparison of Figures 3.38 to 3.41 with the appropriate earlier Figures. As only a small number of samples were taken in each run, and these themselves were subject to inherent experimental scatter, analysis of actual system fluctuations was impossible. A smooth curve was fitted.

Table 3.3 : Data sets used for modelling

Oil	Coal	Exp No.*
Dodecane	Greenside No.2 washed	1 and 2
Hexyl benzene	Greenside No.2 washed	45
Pegasol 180-190°C	Greenside No.2 unwashed	88
Hexyl benzene	G/s No.2 unwashed +1.6-1.8 SG	81

* Experiment numbers are those of the raw test results in Data Appendix 2.

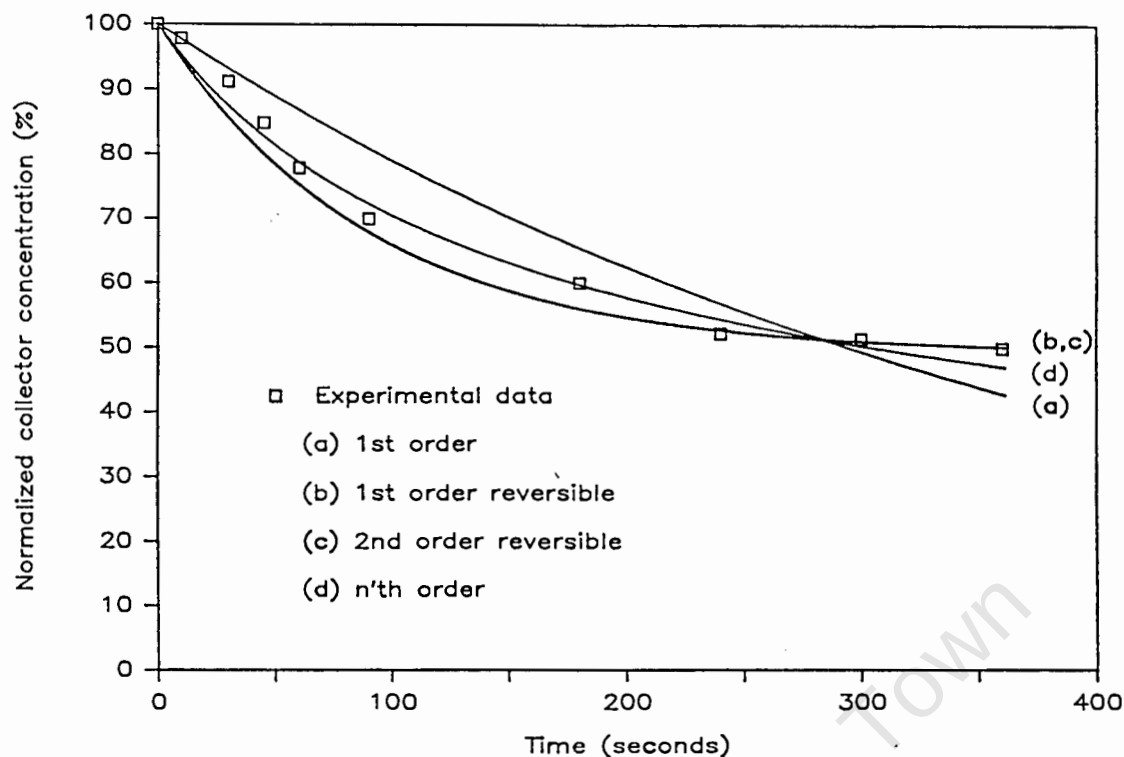


Figure 3.38 : Empirical kinetic data (discrete) and values predicted by kinetic models (continuous). Pegasol 3745 180-190°C cut and Greenside No. 2 seam unwashed coal (500-600 μm). 85 μl of oil added to 500 ml of distilled water at 25°C. No MIBC. Impeller speed 1200 rpm.

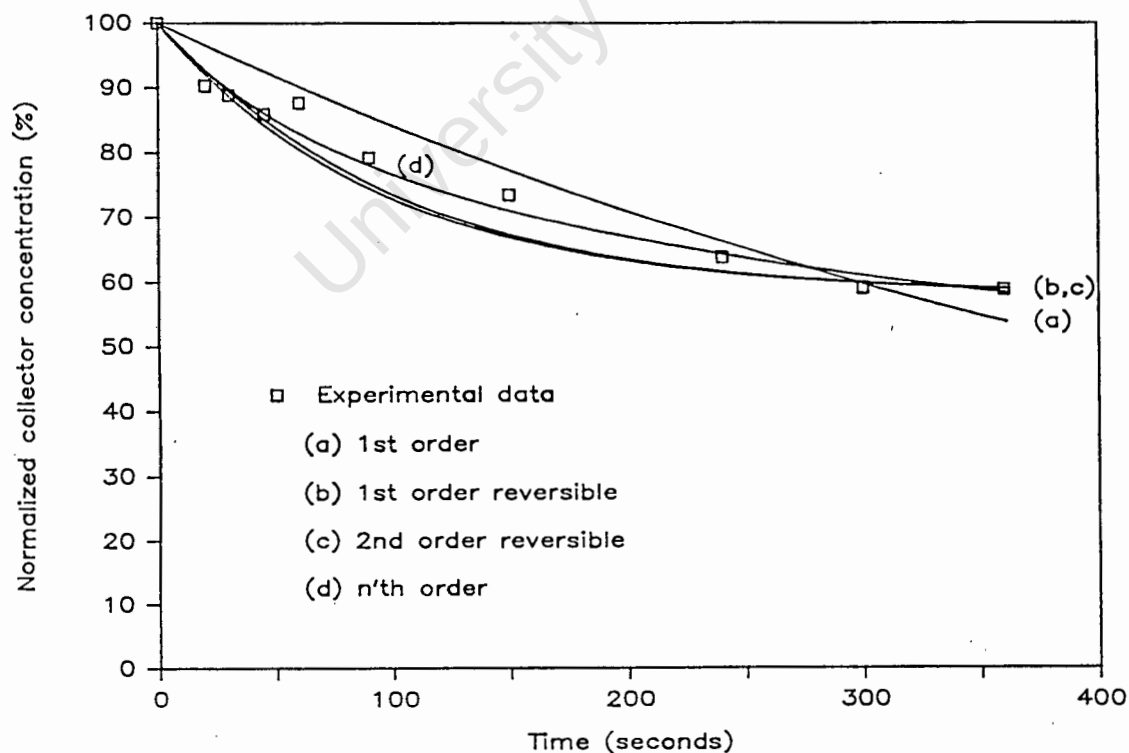


Figure 3.39 : Empirical kinetic data (discrete) and values predicted by kinetic models (continuous). Hexyl benzene and Greenside No. 2 seam unwashed coal; +1.6 -1.8 SG fraction (500-600 μm). No MIBC. 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1200 rpm.

3.6.4 Application of kinetic models to the empirical data

3.6.4.1 First order irreversible model

Initially a first order irreversible relation was tried as such a model has often proved to be a simple and reasonable approximation to empirical data in other contexts.

The rate of disappearance of the oil as defined by a first order irreversible reaction is directly proportional to the concentration of the oil :

$$-r_i = -\frac{1}{S} \frac{d\delta}{dt} = k_1 \delta$$

where : k_1 = Rate constant

Rearranging and integrating :

$$\int_1^\delta \frac{d\delta}{\delta} = -Sk_1 t$$

$$\ln \delta = -Sk_1 t \quad [3.21]$$

Equation [3.21] was fitted to each set of experimental data by a least squares linear regression, where the regression equations were defined with an intercept of zero thereby forcing the fit through the origin ($\ln \delta = \ln M_0/M_0 = 0$). A first order equation was not a good model as shown by Figures 3.38 to 3.41. Initial adsorption was too rapid to be described by this exponential behaviour and final adsorption levels were lower than those predicted. This led to the introduction of the concept of reversibility to the model.

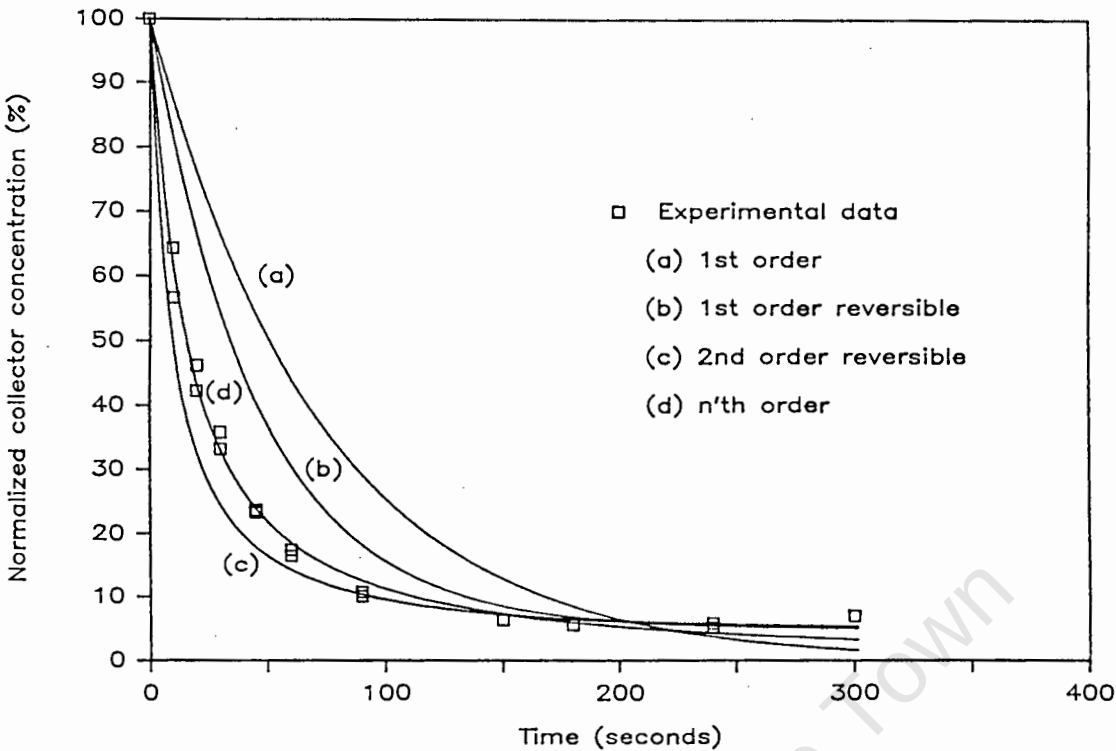


Figure 3.40 : Empirical kinetic data (discrete) and values predicted by kinetic models (continuous). Dodecane and milled Greenside No. 2 seam washed coal (500-600 μm). No MIBC. 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

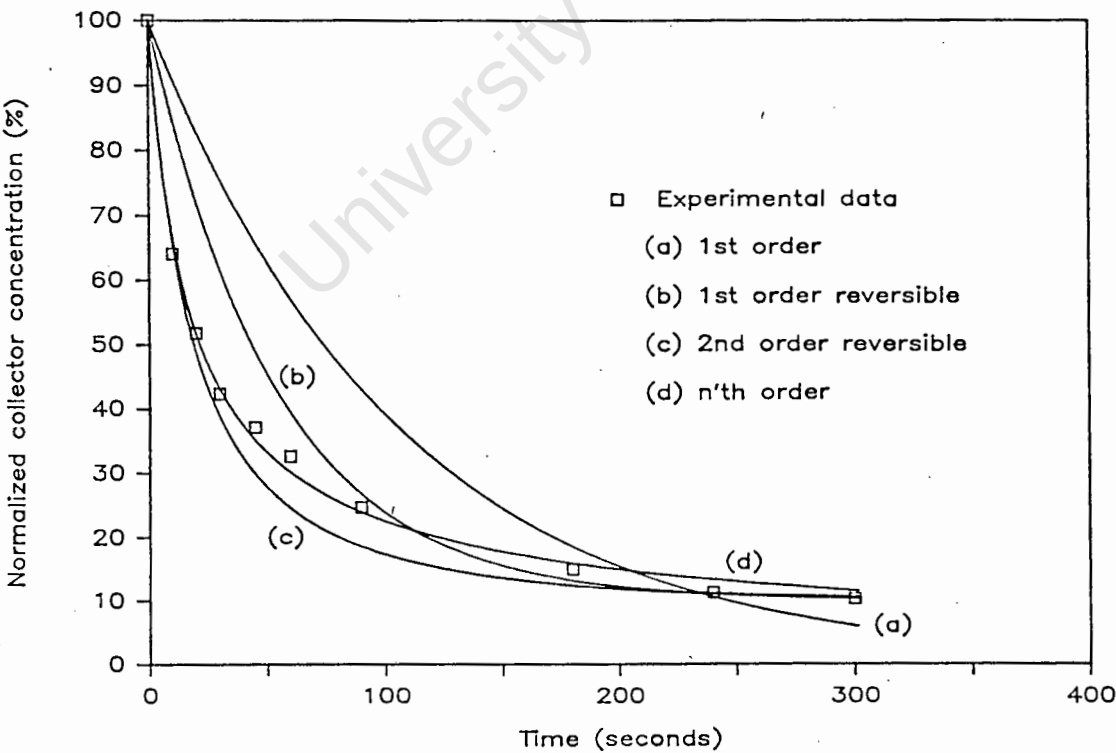


Figure 3.41 : Empirical kinetic data (discrete) and values predicted by kinetic models (continuous). Hexyl benzene and milled Greenside No. 2 seam washed coal (500-600 μm). No MIBC. 85 μl of oil added to 500 ml of distilled water at 25°C. Impeller speed 1650 rpm.

3.6.4.2 Reaction reversibility

Up to this stage, reaction reversibility has not been considered explicitly. True reversibility is a dynamic process in which competing forward (adsorption) and backward (desorption) reactions occur. A stage is reached when the opposing rates become equal and an equilibrium concentration is established.

This author believes that a dynamic adsorption-desorption scenario has limited mechanistic application in oil adsorption since adsorbed oil will in general not be displaced from the solid surface. However, while small droplets will adsorb essentially irreversibly, larger droplets could become detached if their dynamic contact angle is too small. Alternatively, they might lose a portion of themselves because of high shear forces or particle-particle impact. These droplets would once again manifest themselves in the pulp water prior to possible re-adsorption. In other words a quasi-desorption phenomenon would be apparent.

The degree to which this occurs would be dependent on pulp turbulence and droplet size as dictated by the properties of the oils. In high shear regimes the loss of daughter droplets would have the effect of slowing the adsorption rate, i.e. increasing the concentration of oil in the pulp water. Figure 3.22 indicates that such a mechanism could exist, since adsorption rate increased with a decrease in impeller speed, i.e. agitation intensity. The quasi-desorption phenomenon at the higher impeller speed suggests that the oil is being better distributed amongst the pulp solids.

The results of the dispersion study (Chapter 2) showed that most droplets were very small. Obviously this was once mixing had taken place. However generation of daughter droplets would be expected when oil was added directly to the pulp, i.e. as it dispersed within a slurry in which the coal is already present. This would explain the fluctuations in adsorption level found in the initial part of the adsorption curves (especially prevalent with the aliphatic oils which are less readily dispersed) in these experiments. Fluctuations evident in the initial adsorption of pre-dispersed oils onto unwashed coals are discussed in Section 3.4.4.

While an actual reversible mechanism will certainly prevail to some extent in the pulp it is probable that the "equilibrium" adsorption levels encountered with unwashed coal or hydrophilic solids were more a result of a shortage of suitable adsorption sites. Nevertheless the concept of reversibility is useful in modelling those instances in which only a proportion of the oil was adsorbed (Figures 3.38 and 3.39).

3.6.4.3 First order reversible model

The first order reversible reaction is obtained by introducing a rate of desorption with rate constant k_2 ; and an equilibrium mass concentration level δ_e defined as :

$$\delta_e = \frac{M_e}{M_0}$$

where M_e is the equilibrium mass of collector in the pulp water

The rate equation is :

$$-r_i = -\frac{1}{S} \frac{d\delta}{dt} = k_1\delta - k_2(1-\delta)$$

On integration this gives :

$$\ln \left[\frac{((k_1+k_2)\delta - k_2)}{((k_1+k_2) - k_2)} \right] = -S(k_1+k_2)t \quad [3.22]$$

Now at equilibrium,

$$\frac{d\delta}{dt} = 0 = k_1\delta_e - k_2(1-\delta_e)$$

$$k_2 = \frac{k_1\delta_e}{(1-\delta_e)} \quad [3.23]$$

Substituting [3.23] in [3.22] and rearranging

$$\ln \frac{(\delta - \delta_e)}{(1 - \delta_e)} = - \frac{Sk_1}{(1 - \delta_e)} t \quad [3.24]$$

It may be seen from Figures 3.38 to 3.41 that the first order reversible model provided a better fit to the experimental data than the irreversible version. The concept of reversibility was ideal for modelling the final adsorption levels but the first order model was still a poor fit to earlier data points where adsorption was rapid (as shown in Figures 3.40 and 3.41). To improve the fit to earlier data points a second order reversible model was tried.

3.6.4.4 Second order reversible model

This model implies that both adsorption and desorption are a function of collector concentration squared. Again the equation has no formal mechanistic basis with regard to oil adsorption but was a useful model.

By reasoning similar to that used in determining the first order relationship, the final integrated form of the second order reversible equation is :

$$\ln \left[\frac{(1 - \delta_e) - (2(1 - \delta_e) - 1)(1 - \delta)}{(\delta - \delta_e)} \right] = 2 Sk_1 \frac{\delta_e}{(1 - \delta_e)} t \quad [3.25]$$

This model provided a reasonable fit to all the data sets (Figures 3.38 to 3.41).

3.6.4.5 N'th order model

In an effort to obtain a still better fit to the initial data points the concept of reversibility was put aside and an n'th order equation was fitted. Fitting data with an equation of this form is often attempted when the mechanism of reaction is not known precisely - as in these cases.

The n 'th order equation is :

$$-r_i = -\frac{1}{S} \frac{d\delta}{dt} = k_1 \delta^n$$

which on integration yields :

$$\delta = ((n-1) S k_1 t + 1)^{1/1-n} \quad [3.26]$$

With an order $n > 1$ the model predicts that the reaction will never go to completion, which is useful when applying the model to data with a definite final adsorption level. On the other hand if the order is less than 1 then the concentration will become negative at some stage. This obviously cannot occur in reality and Levenspiel (1972) pointed out that the observed order will shift to unity as the reactant (oil) is depleted. Rate equations in which the order shifts with changing oil concentrations are considered at the end of this section.

Mechanistically derived orders for elementary reactions are rarely larger than two in absolute value. This of course applies to a reaction involving molecules in which the chance of simultaneous collision of three molecules is small and of four or more is unknown. In dealing with an insoluble oil the mechanistic molecular order limit is not relevant and for modelling purposes, which in this case are essentially those of curve fitting, higher orders have been used at times (see Table 3.4).

The n 'th order relation is not linear. A Nelder-Mead least squares simplex search routine was used to fit the data. The fits achieved were good as shown by Figures 3.38 to 3.41.

Within the time frame of the adsorption experiments the n 'th order model gave a better fit than the other models tried. However the second order reversible reaction fitted initial data points reasonably and modelled the final adsorption level more accurately. The model also had the distinct advantage of a fixed reaction order. The final adsorption level is of more interest in the context of this thesis though it must be empirically determined in order to model the reversible reactions.

3.6.4.6 Other kinetic models

Other kinetic models exist which can account for a restricted number of adsorption sites - the so called "active site theories" (Levenspiel, 1972). These models are perhaps better suited mechanistically to describing adsorption onto unwashed coals in which there was a definite equilibrium adsorption level for some oils; a result possibly produced by a situation analagous to a shortage of suitable "active sites". In this case "active sites" would be low surface energy areas (unoxidized carbonaceous material). Two typical simplified rate expressions of this type (from Levenspiel, 1972) are :

$$-r_i = \frac{k_1 \delta}{1 + k_2 \delta} \quad [3.27]$$

$$-r_i = \frac{k_1 \delta^m}{1 + k_2 \delta^n} \quad [3.28]$$

While the concentration of oil remains close to the initial concentration, the initial rate from equation [3.27] will be zero order, i.e. the rate is independent of the oil concentration. As the concentration level drops ($k_2 \delta \ll 1$) so the reaction rate tends to first order. An extension of the previous reasoning to equation [3.28] shows that the order shifts from (m-n) initially to m at low oil concentrations. This shift would occur when $k_2 \delta^n \approx 1$.

The active site kinetic equations were not used as good fits were obtained with the simpler equations (n'th order and 2nd order reversible).

3.6.5 Application of the models

There was no rate relationship which described the adsorption globally though this was not surprising in view of the variations encountered in the adsorption behaviour. The form of the model however remained the same. The modelling constants obtained from curve fitting

the empirical data are particular to the collector oil and to the type of coal. Values are given in Table 3.4 below.

Table 3.4 : Constants used in modelling the selected data sets

Model	Constant	Dodecane [1&2]*	Hex. benz. [45]*	Hex. benz. [81]*	Pegasol [88]*
1st order	Sk_1	0.01370	0.00938	0.00236	0.00172
1st order	Sk_1	0.02087	0.01681	0.005625	0.004368
reversible	δ_e	0.05	0.10	0.49	0.58
2nd order	Sk_1	0.1043	0.01184	0.005704	0.003943
reversible	δ_e	0.05	0.10	0.49	0.58
n'th order	Sk_1	0.05998	0.05763	0.005199	0.004354
	n	1.807	2.536	3.115	4.447

* Experiment numbers are those of the raw test results in Data Appendix 2.

The n'th order equation is a reasonable one to adopt for the rate of disappearance of the oil (adsorption) where only simple curve fitting is required. If a specific relationship is required for true modelling (predictive) purposes then the second order reversible relationship appears to be a reasonable choice. By using the second order reversible model, for example, it was possible to predict the effect of particle size on the rate of adsorption. The predicted rates were compared with the observed rates, as described below.

The rate of adsorption of dodecane onto Greenside washed coal was studied. This oil and coal were selected since experimental data was available for both a 500-600 and a 250-300 μm size fractions. Duplicate experiments were conducted with both size fractions so the data was known to be reliable. The constants for the model were obtained by linear regression using the data from the 500-600 μm runs (Figure 3.40). The constants are listed in Table 3.4 above. The constants were then

substituted into Equation 3.25 and the rates of flotation for 250-300 and 62.5-75 μm size fractions predicted. The surface areas increased by factors of 4 and 64 respectively. The dodecane was assumed to be 95 % adsorbed at equilibrium in all cases. The actual and predicted results are compared in Table 3.5 below.

Table 3.5 : Comparison of experimental data with that predicted by a second order reversible model

Time (s)	Particle size ranges				
	500-600 μm		250-300 μm		62.5-75 μm
	Exp.	Pred.	Exp.	Pred.	Pred.
0	1.00	1.00	1.00	1.00	1.00
1	-	0.91	-	0.71	0.13
10	0.60	0.49	0.17	0.20	0.05
20	0.44	0.32	0.11	0.11	0.05
30	0.34	0.24	0.10	0.08	0.05
60	0.17	0.14	0.05	0.06	0.05
90	0.10	0.10	0.04	0.05	0.05

The model provides a good fit to the experimental data for the 250-300 μm size fraction. It also predicts that dodecane adsorption onto a 62.5-75 μm size fraction is essentially complete after 2 seconds. The model is expected to become unreliable as coal particles become ultra small since their tiny mass will lower their chances of crossing fluid streamlines and of overcoming electrical double layer repulsion and hence contacting the oil droplet. However, the adsorption on small particles is sufficiently fast for the rate to be unimportant in terms of conditioning time. This is clearly not true of larger particles.

3.6.6 Modelling : conclusions

This author believes that oil droplets effectively behave as different species depending on their size. There are probably many parallel (size-dependent) adsorption reactions occurring simultaneously, each with its own rate constant. Furthermore the adsorption mechanism is not a simple adsorption-desorption reaction but is complicated by the fact that portions of droplets may desorb, and that droplets may also coalesce with adsorbed droplets rather than being adsorbed onto solid particles directly. Once adsorbed, smaller droplets are likely to be retained on the solid surface. In addition, the equilibrium adsorption levels shown particularly by aliphatic oils in conjunction with unwashed coal are believed to be a result of a shortage of suitable sites for oil adsorption rather than to a dynamic process of droplet adsorption-desorption. For these reasons the compound effect on the loss of oil mass from the pulp water was not of an elementary form, e.g. first order. A proposal of the mechanism of adsorption is difficult and was unnecessary for an understanding of overall flotation behaviour, so no further attempts were made at elucidating it and simple, commonly used kinetic expressions were applied instead.

There was no rate relationship which described the adsorption globally though this was not surprising in view of the variation in the adsorption behaviour encountered. The form of the model however remained the same. The modelling constants obtained from curve fitting the empirical data are particular to the collector oil and to the type of coal. The n 'th order equation is a reasonable one to adopt for the rate of disappearance of the oil (adsorption) where only simple curve fitting is required. If a specific relationship is required for true modelling (predictive) purposes then the second order reversible relationship appears to be a reasonable choice. In contrast to the n 'th order relation the order is fixed and therefore not dependent on empirical curve fitting though the equilibrium level is still required, and must be determined from experiment.

3.7 CHAPTER SUMMARY

The aim of the adsorption studies was to measure the rate and extent of adsorption of various hydrocarbon oils onto coal and gangue surfaces. This was in order to determine the importance and the influence of the adsorption sub-process on the overall flotation process. A literature review was carried out and is summarized in Section 3.2.9; only a brief recap is included below. The remainder of this section is devoted to a summary of the experimental results.

The oil-coal bond is in all cases a physi-sorption predominantly by London-Van der Waals forces. The presence of oxidized hydrocarbons in commercial oils allows for hydrogen bonding between the oil and oxygen-containing surface functional groups on the coal. The absence of polar interactions with saturated aliphatic oils limits their adsorption on comparatively high energy, i.e. relatively high ash or oxidized coal surfaces. This is a result of a limited ability to displace water from such surfaces.

Both the oil droplets and the coal particles are likely to possess negative charges in unregulated pulps where the pH is about 8. Sufficient kinetic energy must therefore be available during mutual collisions to overcome electrostatic repulsion and allow for the two particles to approach sufficiently closely for molecular forces of attraction to come into play. The thermodynamic possibility of oil droplets adhering to the coal exists if the aggregate possesses a lower free energy than the individual constituents. However prior to actual adsorption, the thin aqueous film separating the two particles must be thinned to such an extent that it ruptures and retreats, thereby permitting the adsorption of the oil droplet. The higher the surface energy of the coal, which corresponds to an increase in gangue mineral content and/or oxidation, the more stable the disjoining aqueous film and the less readily oil is adsorbed.

Following aqueous film retreat, a contact angle will be established since none of the oils studied will completely wet coal. Mechanical work is required to enhance spreading. This highlights the importance of coal pulp conditioning.

Oil droplet adhesion is adequately modelled by Young's equation. However the contact angle established usually displays hysteresis since the advancing angle is numerically greater than the receding angle. This hysteresis is generally attributed to surface roughness and surface chemical heterogeneity. The term "equilibrium contact angle" is misleading since either contact angle (receding or advancing) may retain its value for some time. These are static contact angles. Dynamic contact angles will be prevalent in a flotation pulp and are likely to be quite different to their static counterparts, which can be measured.

Surfactants change surface tensions by adsorbing at various interfaces and they may hence affect the contact angle and the spreading of oil on coal. Qualitative predictions of their effect in dynamic situations may be made using Young's equation in combination with the Gibb's adsorption equation. The effect of surfactants on contact angle increases with increasing coal hydrophilicity, i.e. increasing gangue content or oxidation. Most coals have some hydrophilic character and oil adsorption will therefore be affected by the presence of surfactants.

The oil-coal-water interfacial behaviour is not fully understood and is further complicated by the impossibility of categorizing the coal surface which has widely varying properties within any one coal. The three most important factors influencing the coal surface properties are the carbonaceous organic skeleton, the quantity and type of inorganic impurities and the existence of oxygen containing surface functional groups. These factors together determine the electrostatic properties of the coal (which in turn influence its interfacial tensions).

3.7.1 Experimental observations

A technique to measure the kinetics of oil adsorption onto solid particles in turbulent pulps was successfully developed. A summary of the technique is given in Section 3.3.7.

All the oils investigated adsorbed readily onto washed coal (l.a.c.). Onto unwashed (r.o.m.) coals, however, aliphatic oils adsorbed to a more limited extent than aromatic oils. In this context aromatic oils are expected to induce better flotation performance. However, the

extent of adsorption of the aliphatic oils may still be sufficient for flotation.

The degree of adsorption is controlled by the respective interfacial characteristics. The fact that adsorption does occur satisfies at least one precondition for effective flotation. Selectivity is another prerequisite for beneficiation. All the oils tested were found to be highly selective towards coal as shown by the results of the micro-scale adsorption studies.

The low final adsorption levels observed with unwashed coal and aliphatic oil combinations were not a result of the establishment of an adsorption-desorption equilibrium since oil is essentially irreversibly adsorbed, but were rather the consequence of a shortage of suitable adsorption sites (which in turn was a reflection of the selectivity of the oils for carbonaceous surfaces). Limited adsorption may be sufficient for effective flotation, though there is probably a minimum quantity of oil which must be adsorbed to ensure effective flotation. The very small amounts of the oils adsorbed by pulps consisting only of gangue minerals are probably insufficient for their flotation.

The kinetics achieved when the oils were added directly to the coal pulp were similar to those measured when the oils were predispersed. However the oil distribution efficiency of the two contacting procedures is not necessarily the same. Milder agitation conditions were found to increase the rate of oil disappearance from the pulp, suggesting that comparatively large droplets were being adsorbed (by comparatively fewer particles). Oil distribution would therefore be poorer. Pre-dispersion of the oils should improve flotation performance. This is a better option than violent conditioning from both a power-saving point of view and because excessive agitation may effectively de-condition some coals. Excessive pulp phase turbulence was found to lead to harmful particle attrition which in turn caused an apparent desorption of oil as a result of fine particles sloughing off the larger ones. This produces the same effect as actual oil desorption.

Oil droplets are essentially adsorbed irreversibly though large adsorbed drops may spawn daughter droplets especially in high shear regimes. These droplets are released back into the pulp water and may be re-adsorbed. The result of this behaviour is that high turbulence

results in a decrease in the apparent adsorption rate; though it also emphasizes the importance of pulp conditioning for the distribution of the oils.

MIBC (the frother) does not usually promote oil adsorption. It may promote adsorption if it is used in conjunction with an ionic surfactant. Final adsorption levels were not related to the manner in which the MIBC and oil were contacted with the pulp; nor indeed to the presence of MIBC. Oil adsorption rates were reduced if MIBC was contacted with coal prior to the oil but the deleterious effect disappeared as adsorption progressed, presumably because MIBC was removed from the coal surface by repeated contact with the oil.

The rate of adsorption of all oils on unwashed coal feeds, to which beneficiation by flotation would be aimed, was slow on coarse size fractions (e.g. 500-600 μm). Several minutes were often required for the oils to achieve their final adsorption extents. This emphasized the necessity for conditioning prior to flotation, as the slurry streams of coal washing plants often contain a significant proportion (by mass) of coarse material. On the otherhand, fine coal particles were able to adsorb oil very quickly because of their high specific surface area. Adsorption may occur in a matter of seconds. This behaviour will starve larger particles of oil since the oil is essentially irreversibly adsorbed. It will therefore not be distributed thoroughly within the pulp. These observations support the claimed advantages of split conditioning or flotation (coarse and fine fractions) which have been proposed for coal flotation plant flowsheets.

A postulation of the mechanism of oil adsorption is complicated because of the insolubility of the oils. Deriving an appropriate kinetic model from simple mechanistic postulates was not possible. However the relatively simple, empirically derived, n 'th order rate equation was suitable for describing the decrease in collector oil concentration levels in the pulp water (adsorption). For predictive purposes a second order reversible model is suggested since reasonable fits were obtained with this model and reaction order is not a variable. Both procedures still require empirical adsorption testwork with the particular oil and coal combinations envisaged, though with the latter model only final adsorption levels, which are readily determined by a variety of simple methods, are needed.

3.8 CONCLUSIONS

1. Both aromatic and aliphatic oils adsorb extensively on washed (comparatively hydrophobic) coal surfaces and flotation yield is expected to be excellent with both oil types.
2. Aliphatic oils adsorb to a more limited extent on unwashed coal (r.o.m), i.e. coal with an increased hydrophilic character. Thus, aromatic oils are expected to be better collectors of unwashed coal, though the extent of adsorption of aliphatic oils may be sufficient to induce floatability.
3. Hydrocarbon oils are highly selective towards carbonaceous material. Aliphatic oils appear to be more selective than aromatic oils, judging by their more limited adsorption onto unwashed coal. Nevertheless, aromatic oils are very selective and will not adsorb on particles which are dominated by hydrophilic gangue minerals. Their tolerance of some hydrophilic character is expected to make them a better choice of collector than aliphatic oils: aromatic oils will adsorb on somewhat oxidized coal surfaces thereby allowing for greater operational flexibility in flotation.
4. Collector oils should be predispersed (in water) prior to addition to the coal pulp. The presence of fines, as well as mild conditioning procedures, contribute to very rapid oil adsorption. Since oil is essentially irreversibly adsorbed, addition of oil directly to the pulp, under these conditions, will limit oil distribution within the pulp. Flotation performance (grade and yield) is therefore expected to be significantly reduced, especially at lower oil dosages.
5. Excessive pulp phase turbulence is expected to de-condition friable coals as a result of particle attrition and the consequent loss of oil from the particle surface when small flakes of the particle (on which the oil is adsorbed) slough off. The deleterious effects of this phenomenon on flotation performance is expected to be particularly prevalent at low oil dosages.

6. Oil adsorption onto coarse size fractions (e.g. 500-600 μm) of unwashed coal, which often constitute a significant proportion of a washery slurry stream, will take several minutes before the final extent of adsorption is reached. This emphasises the importance of an adequate conditioning time prior to flotation. The very rapid adsorption of oil by fine particles, in contrast to that of coarse particles, supports the use of split conditioning or split flotation of these particle size fractions.
7. MIBC does not promote oil adsorption. However, the use of additional and more powerful (ionic) surfactants, such as "promoters", is expected to have a strong influence on oil adsorption, and in consequence on flotation performance; especially with coals of increasing hydrophilic character.
8. A kinetic adsorption equation based on a postulated mechanism of oil droplet adsorption onto solids is precluded by the large range of droplet sizes. However, to predict the rates of oil adsorption onto size fractions of any one coal, a simple second order reversible kinetic equation can be used. This model requires that the final extent of oil adsorption be empirically determined.

CHAPTER 4

ANALYSIS OF BUBBLE SIZE DISTRIBUTIONS

4.1 INTRODUCTION

The dispersion of air, leading to the creation of air bubbles within the pulp, was the third pulp phase sub-process through which the oily collectors were postulated to have an influence on flotation behaviour. At any given volumetric air flowrate, the size of the bubbles formed will determine factors such as their collision and collecting efficiency and the rate at which solid material can be transported through the pulp to the froth phase. In addition, the size of the bubbles created within the pulp will dictate to a very significant degree the form and stability of the overlying froth.

The influence of hydrocarbon oils (the coal collectors) on bubble size is seldom considered. These reagents are often assumed to be relatively inert in respect to air-water interface chemistry, and the frother alone is assumed to control bubble size within the pulp. However, Glembotskii et al (1970) reported that some Soviet researchers have found that the oil influences the dispersion of air and as this improves so flotation performance increases.

In this part of the work, an investigation of the influence of various oily collectors on the formation of air bubbles was undertaken. Preliminary visual observations revealed that some of the oils indeed have a dramatic effect in reducing bubble size at dosages of similar magnitude to those normally employed in flotation; more so than the MIBC (frother) in some instances. These visual observations were subsequently quantified with an optically based bubble-sizing device. The impact of frother-collector joint action on the bubble size was also investigated.

Bubbles were sized in the absence of solids since the presence of bubble-oil-solid particle aggregates, and the comparatively large size of the coal particles used (up to 500 μm), would otherwise have made bubble sizing very difficult. The degree to which the presence of solids

influences bubble creation is open to conjecture. While fine solids are well known to stabilize the froths by hindering the coalescence of bubbles within the froth phase, their influence on bubble creation within pulps of fairly low solids content could well be comparatively small since they cannot have much influence on air-water interfacial chemistry. The congregation of fine solids at the air-water interface could assist in physically stabilizing the bubbles against coalescence in the pulp. However agitation conditions and the presence of surface-active agents, together with the nature of the oil being used, would be expected to be the dominant factors determining bubble size. In this respect sizing results obtained in the absence of solids would be quite a reasonable reflection of the bubble distributions which are actually produced in a pulp.

The results of the bubble sizing testwork are discussed in Section 4.4. The bubble sizing equipment is described in Section 4.3. A review of the literature and theory concerning the interaction of air, solid and oil is the subject of Section 4.2. The role of non-ionic surfactants in this process is also considered.

4.2 LITERATURE REVIEW

4.2.1 Introduction

This review is aimed specifically at evaluating the current understanding of the influence of oil and non-ionic surfactants on the formation and subsequent behaviour of air bubbles in the absence of solids. In so far as the factors which influence bubble behaviour in the pulp influence the overlying froth phase, the froth phase is considered; but an indepth review of froth phase behaviour is beyond the scope of this thesis. A survey of the understanding of the interactions of bubbles and solids and their effect on flotation performance is included in the literature review of Chapter 5 (Section 5.2).

4.2.2 Bubble electrostatic properties

It is generally accepted that air bubbles are somewhat negatively charged in aqueous systems *free of surfactants* (Dibbs et al, 1974; Ralston, 1983). Dibbs et al (1974) reported that the excess negative charge arises at the interface because cations are generally more strongly hydrated than anions and tend to be drawn into the bulk aqueous phase, leading to a deficiency at the interface. This is the same mechanism by which charge is postulated to develop at a non-polar oil surface in the absence of surfactants (Shaw, 1985).

Dibbs et al (1974) reported that the presence of electrolytes in the region of the interface, particularly multi-valent inorganic cations which are strongly hydrated, encourages the formation of ordered water molecule dipole arrays. These, apart from influencing bubble polarity, significantly increase the water viscosity in the region of the interface. The increased viscosity opposes film draining, which must take place between two bubbles in contact if coalescence is to occur, and hence retards this latter action. The effects of hydration as well as of electrostatic repulsion in reducing coalescence (of oil droplets) are discussed in more detail in Section 2.2.4. Much of this discussion is directly relevant to the coalescence behaviour of air bubble dispersions.

In actual flotation systems the pH, the presence of other electrolytes in the pulp water (from plant water and/or emanating from the solid) and the type of surfactants all contribute to determining the bubble charge (sign and magnitude) through their influence at the interface and in the electrical double layer which develops in the aqueous phase adjacent to the bubble. The specific adsorption of typical non-ionic frothers at the bubble surface leads to the formation of a dipole array with negative polarity. Other (ionic) surfactants induce different behaviour but this is not considered here since only MIBC, which is non-ionic, was added (consciously) to the system. Bubble behaviour is similar to that of strictly non-polar oil droplets in that no electrical double layer develops within the bubble, though in this case the reason is that this is not possible in a gaseous phase. Double layer formation is reviewed in more detail in Section 2.2.5.

As bubbles course through the pulp the fluid flowing around them tends to "sweep" back surfactant molecules so that these tend to congregate at the rear pole of the bubble. This behaviour leads to a non-uniform charge or potential distribution at the bubble interface. Individual bubbles may consequently assume dipolar characteristics. This phenomenon is influenced by the type and concentration of surfactant. The higher the concentration, the greater the molecular packing at the interface and the more immobile the interface becomes.

4.2.3 The action of frother

The passage of an air cavity (bubble) from the pulp to the froth entails the formation of a second air-water interface. The thin aqueous film so formed tends to drain rapidly, in the absence of surfactants, leading to the rupture of the bubble. Collected solids will then be lost back to the pulp. The primary purpose of a frother is therefore to produce a transient froth capable of supporting the hydrophobic coal until it can be removed from the cell. Klimpel and Hansen (1987, p.83) pointed out that the froth must be sufficiently stable to allow gangue drainage but must still break readily to permit concentrate treatment. In general, the smaller the bubbles formed, the smaller their size in the froth and the greater the stability of the froth (Harris, 1982, p.241).

The choice of commercial frothers is guided by several considerations. They should be relatively inexpensive, safe to use and have a low sensitivity to pH and dissolved salt concentrations (Klimpel and Hansen, 1987, p.83). In addition Harris (1982, p.237) stated that they must possess the ability, at low concentrations, to generate a froth of sufficient volume and stability to act as a medium for gangue and [coal] separation.

Non-ionic surfactants like MIBC and polyglycol ethers generally satisfy these criteria and are commonly used in coal processing as "frothers" and oil "emulsifiers". Another important property of a frother is that it should have no collecting properties of its own. Non-ionic surfactants are incapable of chemical bonding with the solid surface and are therefore poor collectors (at normal dosages where "oiling" does not occur). MIBC has long been acknowledged to have no

collecting properties for coal at typical flotation dosages (Horsley and Smith, 1951).

Frothers function chiefly by their ability to adsorb at the air-liquid interface thus lowering interfacial tensions. They may also adsorb at liquid-liquid and solid-liquid interfaces. Their specific influence is dictated by their molecular structure and by the presence of other associated species which are commonly found in industrial grade surfactants like MIBC. The basic theory behind the action of surfactants is discussed in Section 3.2.7. The influence of frothers on overall flotation performance is discussed in Chapter 5 (Sections 5.2, 5.4 and 5.5).

Frothers are used to inhibit bubble coalescence, chiefly by reducing interfacial and surface tensions and hence the free energy of the system. They also increase interfacial viscosity which in turn retards coalescence. In addition, the potential induced by their charge or polarity at the two air-water interfaces of the froth bubble discourages film thinning because of the increasing electrostatic repulsion as the film thins and the two interfaces approach one another. The non-polar portion of the surfactant is capable of Van der Waals interactions which further stabilize the froth. Excessive hydrocarbon chain lengths with the associated increase in Van der Waals bonding, can lead to excessively stable and therefore undesirable froths.

Whelan (1953) drew the general conclusion that a good frother is one which produces small air bubbles within the pulp phase. This highlights the point that the action of the frother is not merely to stabilize the froth by preventing coalescence but also to control air bubble size and behaviour within the pulp.

Klassen and Mokrousov (1963) reported that small amounts of frother (10 to 40 mg.l^{-1}) drastically reduce the size of bubbles created in the pulp by improving air dispersion and reducing bubble coalescence. Swanson et al (1984) noted additionally that the frother also narrows the bubble size range created. Suitable frothers, like MIBC, are understood to stabilize the bubbles to the extent that coalescence times increase beyond the residence time of bubbles in the pulp. This precludes any significant coalescence and therefore restricts the spread in bubble size distributions (in the pulp). As the dosage of frother is

increased however so its concentration at the air-water interface increases, until a saturation level is reached, after which no further decrease in bubble size, and no further increase in the strength or life of the froth can be expected.

Aston et al (1981) studied the effect of non-ionic surfactants in coal preparation (flotation and oil agglomeration). Their study included a brief investigation of the relationship between MIBC concentration and air-water surface tension. They observed no obvious micellization, i.e. no aggregates of MIBC molecules were formed by Van der Waals attraction between the hydrocarbon chains (up to concentrations of $5 \times 10^{-3} \text{ mol.dm}^{-3}$ [about $630 \mu\text{l.l}^{-1}$]). This dosage is at least an order of magnitude greater than that normally used in flotation. MIBC was also found to have an unexpectedly lower degree of activity at the air-water interface than comparable non-ionic surfactants (polyglycols) as shown in Figure 4.1 below. Aston et al (1981) found that the surface tension of clean water was only reduced from 72 mN.m^{-1} to about 50 mN.m^{-1} at a concentration of MIBC as high as $5 \times 10^{-3} \text{ mol.l}^{-1}$. Typical MIBC dosages used in the flotation testwork are $12 \mu\text{l.l}^{-1}$ or $9.4 \times 10^{-5} \text{ mol.l}^{-1}$, so air-water surface tension will be lowered to a limited extent (to about 65 mN.m^{-1} according to the results given in Figure 4.1).

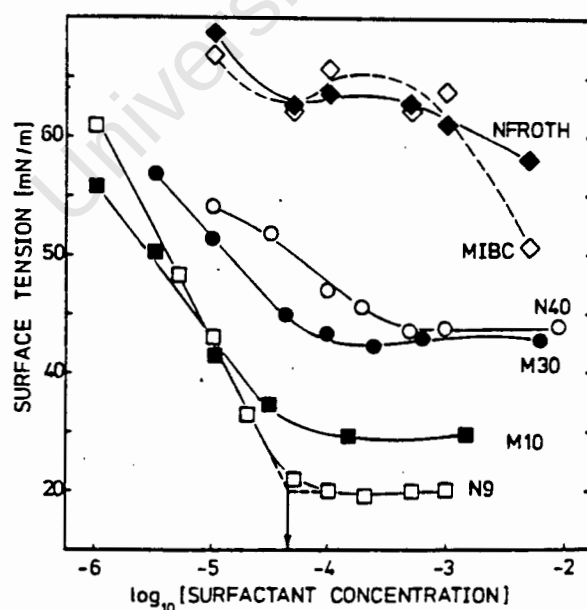


Figure 4.1 : Surface tensions of MIBC and some typical polyglycols in aqueous solution. (After Aston et al, 1981).

Froths are thermodynamically unstable systems and they tend to collapse, as coalescence of the bubbles brings about a decrease of the free surface energy of the system. The destruction of the liquid film as a result of the collapse of individual bubbles consequently leads to a change in the surface tension (Equation 2.2). The tendency to coalesce, particularly with small bubbles, is reduced by the use of frothers since the interfacial tension and hence the bubble capillary pressure is reduced. From visual observations it was anticipated that bubble sizes would not be nearly as small as the oil droplets sized in the experimental work discussed in Chapter 2. Most bubbles appear to be at least an order of magnitude greater. Excess pressure with the air bubble will be comparatively small. A reduction in capillary pressure helps to counteract the decrease in bubble numbers within the *froth*. This decrease may occur without coalescence as the air diffuses from the high pressure zone within small bubbles, through the bubble film, into adjacent larger bubbles or into the atmosphere (Davies and Rideal, 1961).

It is interesting to note that Lekki and Laskowski (1975) established that many flotation frothers do not produce substantial froths in the absence of collectors. Surface activity is therefore not a pre-requisite for frothing ability though it is essential for the creation of two-phase froths (no solids). Froths consisting of only two components (air and water) are entirely unstable and rely on a third component for stability (Lekki and Laskowski, 1975; Harris, 1982, p.238). This component need not necessarily be surface-active; a finely divided solid will also stabilize the froth. Lekki and Laskowski (1975) found that non-surface active reagents such as short chain alcohols (which are highly water soluble and therefore not surface-active) do produce adequate froths in the presence of partially hydrophobic solids, which compensate for the deficient surface-active character of the reagent. An optimum particle size exists for the solids, with coarse or very fine particles having a reduced stabilizing effect. Klassen and Mokrousov (1963) believed the optimum range for coal to be about 50 to 200 μm .

4.2.3.1 The importance of frother addition procedures

Aston et al (1981) confirmed that non-ionic surfactants, which include MIBC, display finite solubility in oil as well as the ability to adsorb at interfaces. Phase partitioning between water and oil will therefore affect the concurrent interface adsorption process. The relative affinities for aqueous and oil environments can be determined by calculating the hydrophile-lipophile balance (H.L.B.) value of the surfactant (see Section 2.2.4).

The tendency of MIBC to migrate into the oil phase highlights two important dosing considerations :

1. The manner in which MIBC is added, and,
2. The timing of MIBC addition.

If MIBC is added in the oil phase, in which it is preferentially soluble, limited accumulation at the water-oil interface or transfer to the aqueous phase can be expected. Frothing will therefore be adversely affected. If MIBC is added to the aqueous phase independently of the oil, it will tend to migrate to the water-oil interface and into the oil itself. However a significant proportion will remain in the aqueous phase in which it is soluble at typical flotation dosages, though this concentration will diminish with time as transfer to the oil phase ensues. It is clearly best to add MIBC to the pulp independently of the oil and as late as possible to ensure optimum frother performance.

4.2.4 The influence of hydrocarbon oils

In order to affect bubble size the oil must be present at the air-water interface. This necessitates its presence on a basis approaching molecular levels, say, as a monolayer or a thin film. All the oils used in this testwork programme are extremely insoluble. Only a minute portion of the oil would dissolve and migrate to the air-water interface. However, some of the oils can spread at the interface sufficiently thinly to influence its chemistry and so affect bubble size.

By spreading at the air-water interface a film of oil is formed which engulfs the bubble. Two accompanying interfaces, water-oil and oil-air, are consequently formed. These interfaces together have a lower interfacial tension than the air-water interface (which is why the oil spreads spontaneously) and the bubble size is consequently reduced. Glembotskii et al (1970) reported that petroleum have surface tensions of $25\text{--}30\text{ mN.m}^{-1}$, which are largely independent of the composition and nature of the oil. However while the oil-water interfacial tensions are typically $25\text{--}32\text{ mN.m}^{-1}$, impure oils may produce interfacial tensions as low as 12 mN.m^{-1} (as confirmed by Ng, 1982) while highly refined and pure oils have interfacial tensions of up to 50 mN.m^{-1} . Pure alkanes and cyclo-alkanes typically have interfacial tensions of about 50 mN.m^{-1} ; and pure aromatics interfacial tensions from $35\text{--}38\text{ mN.m}^{-1}$.

By spreading over the air-water interface the oil will influence the size of bubbles created, while this would not be so to any extent with an oil which forms a lens at the interface. On the other hand oils which form a lens on the interface may promote froth stability by an analagous mechanism to fine hydrophobic solids, i.e. by inhibiting bubble coalescence. Glembotskii et al (1970) believed that the existence of such a lens reduces the chance of the interfaces of bubbles coming into contact and coalescing. However reduction in bubble size also improves froth stability. At this stage it is open to speculation as to which type of behaviour (spreading or non-spreading) of the oil will best enhance flotation performance.

Brown et al (1958) found that commercial paraffin fractions, as well as decane and hexadecane, do not spread spontaneously on a water-(air) surface whereas benzene and p-xylene do. Glembotskii et al (1970) substantiated this behaviour, finding that the paraffinic hydrocarbons have the lowest coefficient of spreading over a water-air interface and do not spread over a bubble surface.

Brown et al (1958) also observed that commercial oils do not always conform to expected spreading behaviour, which they attributed to the existence of surfactant impurities. Klassen et al (1958) noted that industrially produced "paraffins" contain surfactant impurities like naphthenic acids which considerably influence flotation performance. Surfactant impurities in commercial oils will reduce bubble size and quite probably contribute to the success of these oils as collectors.

The impurities are likely to contain oxygen or sulphur polar groups. Sulphonic acids, for example, are neutralized by the alkali "sweetening" processes used in refining, and may remain in trace quantities as sulphonates which can be powerful surfactants (detergents). Glembotskii et al (1970) reported that when kerosenes are treated with aqueous alkali to remove acids present in the crude oil, substances are always formed with high emulsifying power. These are believed to be sodium salts of the organic acids.

Furthermore, Glembotskii et al (1970) believed that commercial hydrocarbon oils will always contain a proportion of products of their oxidation, e.g. acidic compounds like phenols, naphthenic and fatty acids as well as neutral compounds such as alcohols, ethers, ketones, etc. These compounds often exhibit surface-active behaviour and will thus have an influence on the frothing characteristics of the oil.

Clearly, impure oils often behave in contrast to their single components, because of the way surfactant impurities influence the spreading (of the oil) at an air-water interface. In this regard pure oils either spread or remain as a lens while impure oils usually remain as a lens; possibly because surfactant emanating from the oil and congregated at the air-water interface reduces the surface tension sufficiently to prevent the oil spreading over it (Inequality 2.6). However the presence of these surfactants will itself influence bubble size, i.e. oil spreading is not necessary.

4.2.5 Oil-frother joint action

The existence of oil-frother joint action is widely acknowledged. For example Whelan (1953) reported that in coal flotation using mixtures of creosote and cresylic acid (a phenolic frother), the creosote is added in order to "stiffen" the fragile froth. Nearly two decades ago, Dmitrieva et al (1970) stressed that one urgent problem in coal flotation was to determine the influence of the oils on frothing in the presence of frothers. Klimpel and Hansen (1987) noted that little specific research into the combined effects of oil and frother has yet been conducted. However various Soviet researchers have studied the oil-frother joint action experimentally and this work was reviewed by Glembotskii et al (1970).

The frothing effect is influenced by the type of oily collector selected and Dmitrieva et al (1970) showed that these should be matched to the frother to give the optimum flotation performance. They found that, in general, hydrocarbon oils decreased the stability of *two-phase* froths (no solids), the degree varying according to each particular frother-collector combination. Glembotskii et al (1970) concurred and believed that the instability might be caused by the oil displacing polar molecules (surfactants) at the bubble interface. They found that non-polar collectors do influence the surface tension and that they often increase it (though to varying degrees) which they believed accounted for the decreased froth stability.

This would be true of non-spreading oils and is quite evident from the interfacial and surface tensions given above. An increase in surface tension can be expected to accompany the displacement of ionic or polar molecules (surfactants) from the interfacial area occupied by the oil lens as shown by Equations 3.9 and 3.10. However some oils spread spontaneously at an air-water interface. This implies that interfacial tensions are lowered (as discussed above). In this case it is suggested that the coalescence of oil films on adjacent bubbles contributes to bubble rupture and thereby to froth instability.

Unfortunately Glembotskii et al (1970) could not find a definite relationship between the surface tension and the froth stability with any particular oil. They studied the joint action of collector and frother on frothing performance with a range of frothers and a range of hydrocarbon oils. The oils were individual paraffins (alkanes), naphthenes (cyclo-alkanes) and aromatics, petroleum cuts, diesel fuel and kerosene. They listed the combinations of frothers and oils which gave the best froth height and stability. They found that for any particular frother there is, in terms of frothing performance, a particularly effective hydrocarbon fraction.

Two-phase froths with oils and a frother containing a polar hydroxyl group (such as MIBC and other related alcohols) were found to give a large volume of froth and a reasonably long froth life. With collectors of broad composition such as the petroleum distillation cuts, the paraffins and iso-paraffins within these fractions gave good froths. The single component (pure) hydrocarbons produced no froth on their own but they did stabilize frothing; the extent of this depending on their

molecular structure and the particular frother used. Longest froth lifetime occurred with the high molecular weight pure hydrocarbons, i.e. those with longer hydrocarbon chains, presumably because of increased Van der Waals interactions.

Klassen et al (1958) confirmed that non-polar oils are not frothing agents. Surface-active agents either present as impurities in the oils or added to the system are therefore necessary for frothing when oils are used as collectors. Glembotskii et al (1970) proposed that the linear structure of the paraffins (alkanes) allows them to wedge more freely between the non-polar groups of frother molecules adsorbed at the bubble surface. As a result the non-polar groups of the frother become elongated and the difference between the polarities at either end of the frother molecule increases and so froth stability increases.

They also came to the general conclusion that the greatest decrease in the quality of the froth is caused by either the most viscous oils or the least viscous oils. However, viscosity was insufficient to determine the frothing effects of the oil. The oil composition was evidently of more importance. They studied the oil composition by IR spectroscopy and deduced that the presence of carboxylic and hydroxyl groups in the oil itself improves frothing. These substances were presumably oxidation products of the oils.

They also found additional chemical structures present when some frothers and oils were mixed together, i.e. these structures were not evident with the individual compounds. Apparently interactions between the molecules of the frother and the various surface-active groups present in the non-polar collectors may arise. These can lead to structural changes in the hydrated layer of the bubble. If such oily collectors are co-"adsorbed" on the bubble surface and the resultant new collector-frother chemical structures increase the strength of the adsorption layer, then froth stability is increased and vice versa.

These findings are in accordance with the results of Leja and Schulman (1954) on the penetration of somewhat soluble surfactants in interfacial films. Adsorption and interactions between metal ions and the polar groups of surfactants were also observed. They stated that if interaction occurs between both the polar and hydrophobic portions of adjacent surfactants (frother and surface-active oil constituents in

this case) complexes are formed. These are not necessarily true chemical compounds (they separate upon crystallization for instance) but are stable in an orientated state in interfacial films.

4.2.6 Summary

Bubbles are negatively charged in aqueous systems free of surfactants because of a migration of hydrated cations from the interface. Their electrostatic properties are analagous to those of strictly non-polar oils since no internal double layer can form (as the internal phase is gaseous). In actual flotation systems, pH, water quality (electrolyte concentration) and the type of surfactant present will control bubble charge. Bubbles can display dipolar behaviour at low surfactant concentrations as surfactants tend to congregate at the lower pole of a rising bubble. Non-ionic surfactants, of which flotation frothers are typical examples, contribute to surface potential but not to surface charge.

Only small concentrations of frother are needed to reduce bubble size in the pulp dramatically and to promote the stability of the froth phase which develops above the pulp. Froths are thermodynamically unstable because of their high interfacial area. Temporary stability is however essential for the recovery of solids. Strictly 2-phase (air-water) froths are entirely unstable and are dependent on surfactants and/or finely divided hydrophobic solids to achieve some stability. Frothers stabilize froths by reducing the tendency of bubbles to rupture and to coalesce. This is achieved by lowering bubble surface tension, promoting electrical double layer development and consequently repulsion of adjacent bubble films, and by retarding film drainage.

MIBC shows relatively low surface activity in comparison to typical polyglycol frothers, with an interfacial tension of 50 mN.m^{-1} only being attained at high MIBC dosages. In addition, MIBC is preferentially soluble in oil. In the interests of frothing (air-water interfacial activity) it should be added independently of the oil and shortly before aeration commences.

Oils can also influence bubble size if they spread spontaneously at the air-water interface. Oils which remain as a lens do not, but may

stabilize the froth in an analogous manner to small hydrophobic solids. Non-spreading oils may increase surface tension by displacing surfactants at the interface. Oils which spread spontaneously must lower the cumulative interfacial tensions. Impure oils may show anomalous behaviour to that expected after consideration of their aliphatic/aromatic constitution if the impurities are surface-active.

The joint action of oil and frother is widely acknowledged to influence frothing. Chemical and physical structures which are not apparent when either reagent is used in isolation have been observed. Two-phase froths (without solids) formed with oils and frothers containing a hydroxyl group (e.g. MIBC) have been found to give large froth volumes and a reasonably long froth life. For a given frother, a particular oil type or fraction generally offers better frothing performance than others do.

4.3 BUBBLE SIZING EQUIPMENT

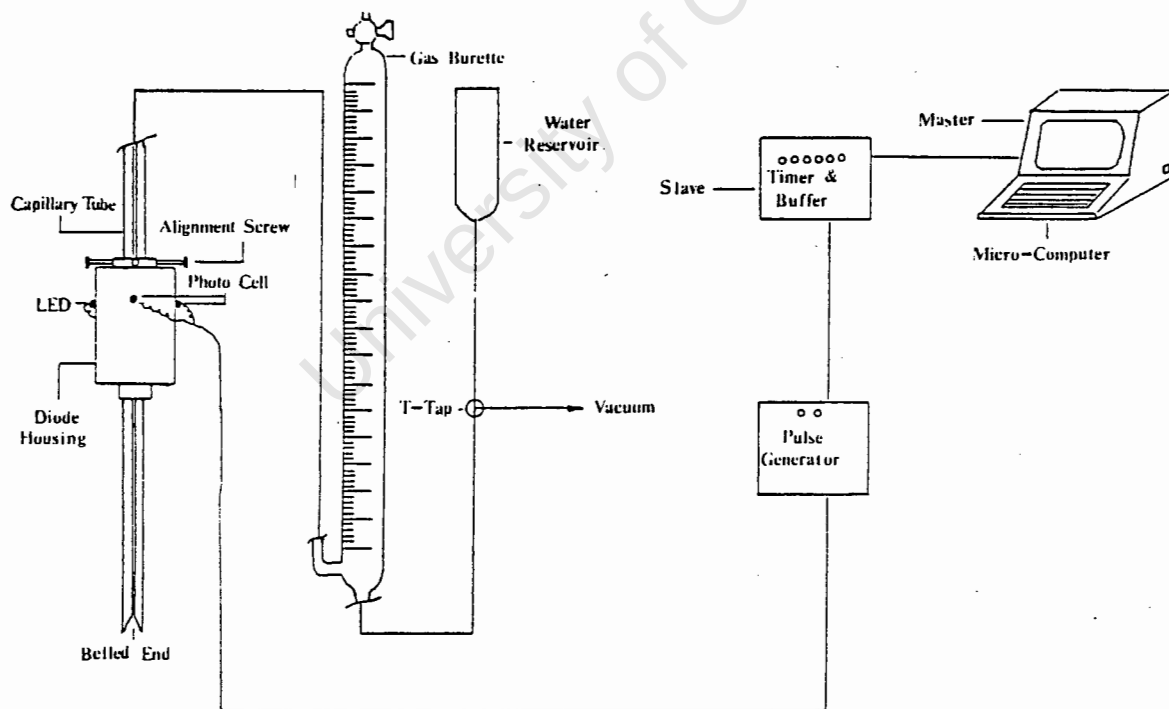


Figure 4.2 : Air bubble sizing system

Initially bubble distributions were investigated qualitatively, using ordinary photography. Later the bubble size distributions induced by the presence of various oils (with and without MIBC) were quantified

using a special bubble sizing device similar to a prototype developed at MINTEK.¹ Figure 4.2 shows the apparatus. Its operation is discussed below.

4.3.1 Theory of operation

The bubble sizing device consists in part of a glass capillary, one end of which is immersed in the liquid within a flotation cell. The other end passes through a detector. This detector consists of two UV LEDs (ultra-violet light-emitting diodes) and two UV-sensitive photocells. Each LED is mounted opposite a photocell and the two pairs are mounted exactly 5 mm apart. The glass capillary passes between the LEDs and the photocells.

The photocells are sensitive to the changes in the UV intensity which occur when bubbles are drawn through the light path by application of a controlled vacuum to the end of the capillary passing through the detector. Bubbles drawn into the capillary are deformed into cylinders which travel up the capillary past the detectors. When the two diode-photocell pairs detect the passage of the air-water interfaces, the appropriate signals are relayed through an interface to a data capturing computer. Individual bubble volume is determined by the duration between successive interfaces.

The minimum size of bubble that can be counted is dependent on the bore of the capillary, which is itself reduced by an internal liquid film. The applied vacuum also has a small influence. The bore of the finest capillary was 0.5 mm (nominally) so the smallest detectable bubble would be of a similar but slightly smaller diameter (because of the liquid film). Any bubbles much smaller than 0.5 mm in diameter would not be deformed into cylinders suitable for accurate detection. Naturally these small bubbles could not be excluded from the capillary but their impact in terms of contribution to the total volume was negligible and the photocell detection threshold was generally too high for their detection as insufficient light was blocked from the photocell by their passage up the tube. Furthermore the presence of such small bubbles was rare with most of the oils used.

¹ The Council for Mineral Technology, South Africa.

The bubble sizing procedure outlined so far has assumed a constant velocity for all bubbles. However velocity within the capillary is affected by the proportion of air and water within it. To be rigorous the velocity of each bubble should be used to correct its size as determined by its time to pass the detector. By using two diodes the velocity of each individual bubble can theoretically be determined. In practice however, the number of bubbles detected by each LED often differs by a few percent, making it impossible to associate a particular velocity with a particular bubble. This offset phenomenon is small with fairly large bubbles, where each bubble is readily deformed into a suitable cylinder within the capillary, but the presence of very small bubbles does lead to some variation.

The corrections for changes in bubble velocity were ignored in instances where the average bubble size was small, i.e. where most of the discrepancy crept in between the counts of the two diode-photocell pairs. This simplification is believed to have had only a small influence on the distribution. Distributions induced by any one oil and measured by capillaries of different bores (0.5 and 1 mm) were found to be similar under identical experimental conditions, although fluctuations in bubble velocities in each capillary can be expected to be considerably different.

All the bubbles drawn through the sampling capillary are collected by a gas burette. The volume collected during any run is recorded (at atmospheric pressure), i.e. the total volume of the collected bubbles is known. By applying the duration of the passage of each bubble past one diode-photocell pair together with the total number of bubbles counted and the total air volume collected it is possible to calculate the bubble size distribution. The diameter of the equivalent spherical volume of each bubble was calculated. The assumption of bubble sphericity is reasonable as most bubbles were smaller than 2 mm in diameter, as shown in Table 4.2 below.

4.4 REAGENTS TESTED

The oils used were dodecane, hexyl benzene, Shellsol K, Shellsol AB, and Pegasol 3745 boiling range cuts. Details of the properties of these oils may be found in Table 1.3 and Table 1.4. These oils were tested in isolation and in conjunction with MIBC. Dosages in all cases were identical to those used later in the batch flotation testwork (Chapter 5). Collector dosages were typically 200 or 400 μl in three litres of water (i.e. a full flotation cell). These are equivalent to oil dosages of 950 and 1900 g.t^{-1} of coal in a 5 % (m/m) pulp respectively. MIBC dosages were either 6 or 12 μl per litre of water and again typical of flotation dosages used in later testwork.

4.5 EXPERIMENTAL PROCEDURES

4.5.1 Dispersion of the oily collectors

A Leeds-type 3 litre batch flotation cell, the same one used for preparing the oil dispersions (Chapter 2) and later for the flotation testwork (Chapter 5), was used to disperse the oils prior to aeration.

The oily reagents were dispersed in filtered tap water in the cell. No air was introduced at this stage. The oils were added to the water in the cell using a Gilson Pipetteman and always released below the water surface. When used, MIBC was introduced separately using a microsyringe.

The volumes of water in which the oils were dispersed were similar to those used in the flotation testwork. The oils were dispersed either in a full cell or in a cell one-third full (1 litre of water). In the latter case, the cell was filled prior to commencing aeration. Oils were dispersed in an identical manner to that employed in the experimental oil dispersion work reported in Chapter 2.

Dispersion time (prior to aeration) was 3 minutes in total in all cases. Where oil was mixed in a partially filled cell this was done for 2 minutes followed by another minute during which the cell was filled. Thus bubble sizing was always carried out with the cell full - only the

method of oil dispersion was altered. Impeller speed was generally 1200 rpm, though the effect of changing this (agitation intensity) was investigated. These conditions are in accordance with those used in the droplet sizing experiments (Section 2.3.4.1).

4.5.2 Analysis of the bubble distributions

Flotation cell operating parameters were the same as those used in the batch flotation testwork programme (Chapter 5). Aeration rate was 4 l.min^{-1} . Bubble sizing was undertaken in the absence of solids. The sizing device can detect bubbles in an actual pulp, but the procedure is much more complicated (the UV blocking phase is reversed from the air to the pulp phase). For purposes of reagent comparison using a coal pulp was not warranted for the reasons outlined in the introduction to this Chapter. The adsorption of oil by the solids could have an indirect influence on bubble size by restricting oil availability at the air-water interface. This is discussed in Section 4.7.3.

The sizing system has the capability of counting about a hundred bubbles per second, though rates used in practice were never this high. Typically several thousand bubbles were collected over a period of a minute or so. Short collection times are important as bubble size was found to change quite noticeably with time as oil was removed from the pulp by the bubbles collected and, more importantly, by being brought to the water surface by other bubbles and subsequently lost by spitting, spreading and evaporation. The increase in bubble size would be expected to occur in actual batch flotation situations since the concentrate and the associated oil are removed and not replenished.

The sized and counted bubbles were grouped, according to size, into 50 size intervals between the largest and the smallest sizes measured. The number of bubbles in each size range was associated with the arithmetic mean of the range. A higher order (volume) mean would be strictly correct (Section 2.4.3) but because the size ranges were narrow the simple arithmetic mean (diameter) was adequate. Size distributions were based on the number (frequency) of bubbles within a particular bubble diameter range. Volume and surface area based distributions were not considered as the distributions based on frequency conformed to useful theoretical distributions (normal-type distributions). Unless

distributions are log-normal they will not have the same form when based on other orders of dimension, as discussed in detail in Section 2.6.2.1.

4.6 MODELLING THE DISTRIBUTIONS

All the bubble distributions investigated could be modelled by a normal distribution in either its arithmetic or geometric (logarithmic) form. In this discussion reference to a "normal" distribution refers to the arithmetic form and "log-normal" to the geometric form. The position and spread of the distributions are characterized by their mean and standard deviation statistics respectively. The theoretical basis for both these distributions and their applicability to empirically determined distributions are discussed in Section 2.2.7. Though that discussion concentrates on oil droplet distributions it is equally applicable to the bubble size distributions.

The grouped experimental data points for each experiment were fitted to the appropriate distribution function using a Nelder-Mead non-linear optimization technique. The data was fitted to the function

$$Y = \frac{K_1}{\sqrt{(2\pi) \cdot K_2}} \cdot e^{(-\frac{1}{2}(X - K_3)^2 / K_2^2)}$$

where : Y is the differential bubble frequency percent
 K_1 is a y-axis scaling factor

For a normal distribution :

X is the bubble diameter
 K is the standard deviation in bubble diameter (s)
 K_3 is the mean bubble diameter ($\bar{x}$)

while for a log-normal distribution :

X is substituted by $\ln X$
 K_2 is the natural logarithm of the geometric standard deviation ($\ln s_g$)
 K_3 is the natural logarithm of the geometric mean ($\ln \bar{x}_g$)

The sample means, $\bar{x}$ and $\bar{x}_g$, for normal and log-normal distributions respectively, are used to represent the (unknown) means μ and μ_g of the theoretical distributions. Similarly, the sample standard deviations, s and s_g , are used to represent the (unknown) standard deviations σ and σ_g of the theoretical distributions.

The K - variables were optimized to give the best function fit to the data points. The "best fit" criterion was based on least squares error estimation. K_1 , the y-axis scaling factor, has no influence on the mean and standard deviation and was calculated to enable the distribution to be drawn quickly and to the correct scale in the Figures.

No data points were rejected except those lying well below the bore size of the capillary used. These percentages were small and the normalized distributions were not readjusted following this data rejection. The mean and deviation statistics would be virtually unaffected though the y-axis scaling (interval percentages) would increase slightly. Rejection of data for small bubble diameters was necessary when using the numerical search technique in order to avoid weighting the distribution incorrectly.

In general the calculated mean and standard deviation were in close agreement with those found using the Nelder-Mead simplex search technique since most of the distributions were symmetrical and clearly normal in appearance. The equations used for the analytical solutions were :

$$\text{Mean} = \frac{\sum x_i f_i}{N}$$

$$\text{Std. dev.} = \left[\frac{\sum (x_i f_i)^2 - (\sum x_i f_i)^2 / N}{N - 1} \right]^{0.5}$$

where x_i is the value of the property, f_i is the frequency that this value is encountered and N is the total number of observations.

The numerical search technique was valuable for determining a suitable Y-axis scaling factor for drawing the distribution; and also for use with skewed distributions and in the rare instances where part

of the bubble distribution was obviously missing (bubbles well below the capillary bore size). The calculated mean and standard deviations were used to generate the starting simplex of the search procedure.

4.6.1 Goodness-of-fit tests

Goodness-of-fit statistics are discussed in detail in Section 2.5.2. For the bubble distributions statistical goodness-of-fit of the theoretical models was tested on the more obviously deviating distributions using Stephens' test, in which an adaption of the Kolmogorov statistic is used.

One aspect of Stephens' test can be used to determine goodness-of-fit between an experimental distribution and a theoretical normal distribution whose mean and standard deviation are derived from the experimental data. This was applicable to the experiments undertaken. In applying the test the standard deviation and mean generated by the Nelder-Mead optimization technique were used.

The visually better fitting bubble distributions were implicitly accepted as being statistically well fitted by the theoretical distribution, following the acceptability (at the 5 % significance level) of the more obviously deviating distributions. Examples of statistical goodness-of-fit calculations for the bubble size distributions are given in Appendix 4.1.

4.7 RESULTS AND DISCUSSION

The effect of the oils on the sizes of bubbles generated in the flotation cell was first investigated qualitatively (by photography) and then quantitatively (using a sampling capillary and the electronic sizing and counting system described in Section 4.3). Experimental data may be found in Data Appendix 3.

4.7.1 Qualitative bubble size distribution comparisons

In this section photographs are presented to show the impact of the presence of various oils on the size and number of air bubbles generated in water within the flotation cell.

Figure 4.3 shows the bubbles produced in water in the absence of any reagents. The size distribution was influenced solely by the aeration rate (4 l.min^{-1}) and the agitation conditions (1200 rpm). These conditions were also used in the tests involving the reagents. It is evident that comparatively few bubbles were produced. These were large, most being several millimetres in diameter (compare sizes with the ruler on the right-hand side of the flotation cell).

Figure 4.4 shows the impact on bubble formation of the addition of MIBC at a dosage of $12 \mu\text{l.l}^{-1}$. A characteristic of the use of a frother was the production of a narrow size range of small bubbles (clearly evident in the photograph). This is consistent with the observations of other workers and supported by the underlying theory as discussed in Section 4.2.3 above. The accumulation of MIBC at the air-water interface lowers the interfacial tension, thereby reducing bubble size. It also stabilizes bubbles against coalescence by developing bubble electrical double layers which repel one another, and by increasing interfacial film viscosities.

It is of interest to note that MIBC reduced the size of the air bubbles, as would be expected, yet it did not improve oil droplet dispersion (Chapter 2). The latter phenomenon has been explained in terms of the H.L.B. value of MIBC (Section 2.2.4.1). H.L.B. values are not relevant to water-air partitioning since frothers have a limited uptake in air since this is a gaseous phase. MIBC is therefore forced to congregate at the air-water interface and does not transfer to any significant extent into the air; unlike the situation with an oil phase.

Figures 4.5 and 4.6 show the very considerable influence of two aromatic oils, Shellsol AB and hexyl benzene respectively, on the size of the air bubbles formed in the batch flotation cell. It must be stressed that no MIBC (frother) was used. Oil dosage was $400 \mu\text{l}$ per three litres of water and the oil was added to a full flotation cell. Some extremely fine bubbles were produced, though a number of large



Figure 4.3 : Bubbles produced in the batch flotation cell in the absence of any reagents. Aeration rate was 4 l.min^{-1} and impeller speed 1200 rpm.



Figure 4.4 : Bubbles produced in the batch flotation cell in the presence of MIBC (a frother) at a dosage of $36 \mu\text{l}$ ($12 \mu\text{l/litre}$). Reagent added to a full cell. Aeration rate was 4 l.min^{-1} and impeller speed 1200 rpm.



Figure 4.5 : Bubbles produced in the batch flotation cell in the presence of Shellsol AB at a dosage of $400 \mu\text{l}$ (in 3 litres of water). No MIBC. Reagent added to a full cell. Aeration rate was 4 l.min^{-1} and impeller speed 1200 rpm.



Figure 4.6 : Bubbles produced in the batch flotation cell in the presence of hexyl benzene at a dosage of $400 \mu\text{l}$ (in 3 litres of water). No MIBC. Reagent added to a full cell. Aeration rate was 4 l.min^{-1} and impeller speed 1200 rpm.

bubbles are also evident. The narrow size range produced by MIBC (Figure 4.4) did not occur with these oils. Bubble distributions were considerably more spread.

In contrast to the behaviour of the aromatic oils Figures 4.7 and Figure 4.8 shows that both dodecane and the largely aliphatic Pegasol 3745 (210-220°C cut), had little influence on bubble size. Bubbles produced were similar in size to those shown in Figure 4.3 where no collector oil was used. This is in agreement with the fact that neither of these oils spread at an air-water interface. In addition it is clear that no significant surface-active agents were present in the Pegasol 3745 oil. This confirms that ionic surfactants are not found in largely aliphatic commercial oils. They have a very limited solubility in these oils. Weak surfactants such as oxidation products of the oil may however occur. Their concentration in the Pegasol 3745 oil appeared to be low since bubble size was not noticeably altered. Bubble size reduction is not dependent on oil surfactant impurities since pure hexyl benzene reduced bubble size considerably (Figure 4.6).

4.7.2 Quantitative bubble size distributions

4.7.2.1 Repeatability of quantitative bubble size analyses

Figure 4.9 shows that duplicate bubble size distribution analyses, performed with both dodecane and hexyl benzene, were found to be in good agreement. Figure 4.9 shows the results of four separate experiments. The experimentally obtained frequencies for each bubble size range are represented by the symbols in the figure. The solid lines represent the theoretical distribution functions which were fitted to the experimental data. A normal (arithmetic) distribution function was fitted to the dodecane data and a log-normal function to the data obtained using hexyl benzene. The results of further repeatability testwork are given in Table 4.1.

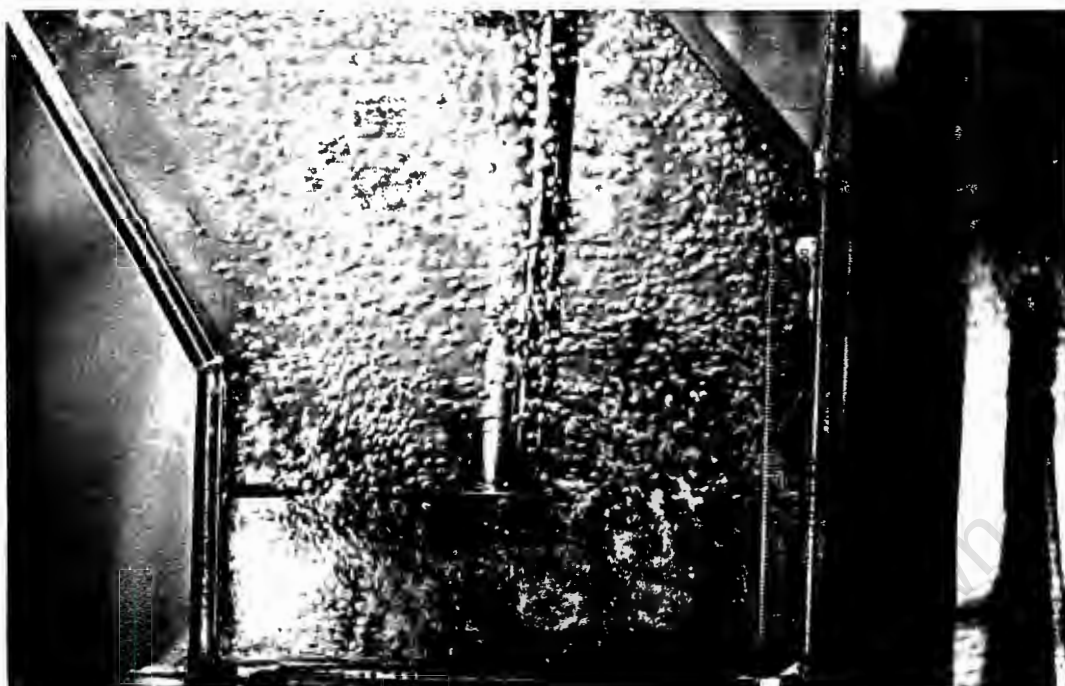


Figure 4.7 : Bubbles produced in the batch flotation cell in the presence of dodecane at a dosage of $400\ \mu\text{l}$ (in 3 litres of water). No MIBC. Reagent added to a full cell. Aeration rate was $4\ \text{l}\cdot\text{min}^{-1}$ and impeller speed 1200 rpm.



Figure 4.8 : Bubbles produced in the batch flotation cell in the presence of the Pegasol 3745 210-220°C cut at a dosage of $400\ \mu\text{l}$ (in 3 litres of water). No MIBC. Reagent added to a full cell. Aeration rate $4\ \text{l}\cdot\text{min}^{-1}$ and impeller speed 1200 rpm.

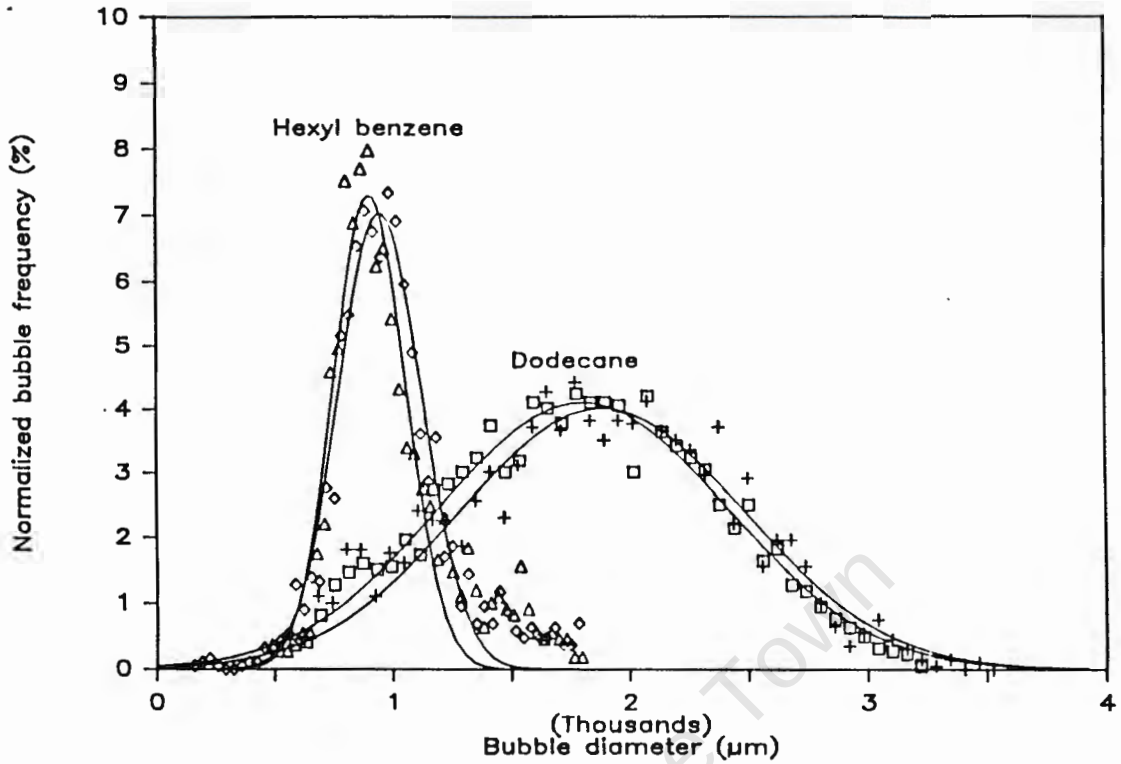


Figure 4.9 : Repeatability testwork. Bubble size distributions produced in the batch flotation cell in the presence of dodecane and hexyl benzene (independently) at dosages of 200 μl . No MIBC. Aeration rate was 4 $\text{l}\cdot\text{min}^{-1}$ and impeller speed 1200 rpm.

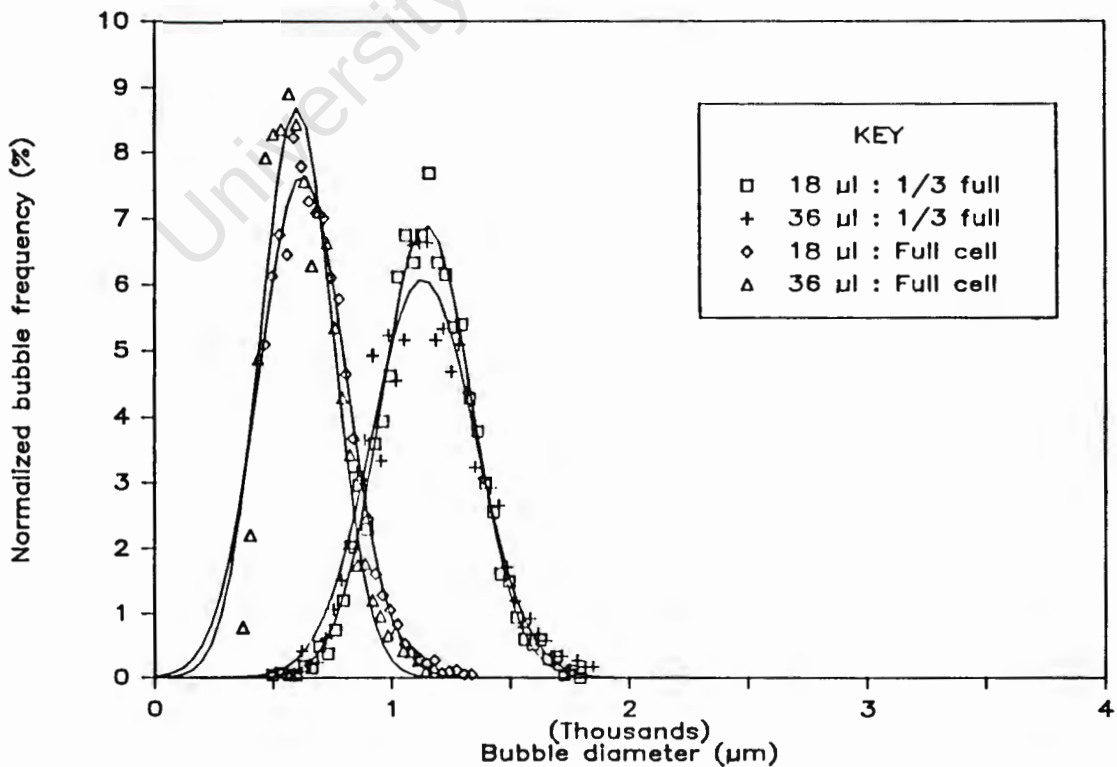


Figure 4.10 : Bubble size distributions induced in the batch flotation cell in the presence of MIBC only. Dosages were 18 and 36 μl . The MIBC was dispersed in both 1 litre of water prior to filling the cell and in a full cell before beginning aeration. Aeration rate was 4 $\text{l}\cdot\text{min}^{-1}$ and impeller speed 1200 rpm.

Table 4.1 : Repeatability testwork results

Reagent	Oil dosage (μl)	MIBC dosage (μl)	Test 1		Test 2	
			μ (μm)	σ (μm)	μ (μm)	σ (μm)
Dodecane (800rpm)	200	--	1762	578	1780	497
Dodecane	200	18	1100	331	1145	230
MIBC	--	18	1183	249	1142	243
MIBC	--	36	624	182	632	174
			μ_g	σ_g	μ_g	σ_g
Shellsol AB	200	--	812	1.260	809	1.252
Hexyl benzene	200	18	632	1.285	663	1.304
Pegasol 3745 (210-220°C)	200	18	707	1.512	742	1.461

4.7.2.2 Summary of quantitative results

Results of the quantitative bubble sizing experiments (no solids present) are summarized in Table 4.2 below. Bubbles were sized at atmospheric pressure. These results are discussed in the sections which follow.

4.7.2.3 Bubble sizes induced by MIBC alone.

Figure 4.10 shows the bubble distributions induced in the presence of MIBC alone (no collector oils). Doubling the MIBC dosage from 18 to 36 μl (per 3 liters of water) reduced the mean bubble size considerably; from 1.2 ± 0.2 mm to 0.6 ± 0.2 mm. Distributions were normal in character. The frother produced a narrow bubble size distribution at both dosages indicating that it stabilized the air-water interface against coalescence. In comparison, bubble distributions produced by the aromatic oils were considerably more spread, with many fine bubbles as well as several large ones (cf. Figure 4.4 and Figure 4.6). Bubble coalescence was apparently more prevalent in the presence of the aromatic oils. The dynamics of bubble formation could also imply that the oil does not always have

Table 4.2 : Characteristics of the bubble size distributions induced by the presence of collector oils.

Reagent	Oil dosage (μ l)	Impeller Speed (rpm)	MIBC dosage (μ l)	Arithmetic mean size (μ m)	Arithmetic std. dev. (μ m)	Scaling factor
<i>One litre of water for mixing. Two litres added later.</i>						
Dodecane	200	1200	-	1804	600	6177
Dodecane	400	1200	-	1701	577	6327
Dodecane	1000	1200	-	1674	517	5592
Dodecane	200	800	-	1762	578	6710
Dodecane	200	1600	-	1842	620	6755
Dodecane	200	1200	18 (early)	1214	401	4059
Dodecane	200	1200	18 (late)	1100	331	3904
Shellsol K	200	1200	-	1815	629	6384
Peg. 180-190°C	200	1200	-	1735	511	6314
Peg. 210-220°C	200	1200	-	1648	477	6136
Peg. 210-220°C	400	1200	-	1434	501	5745
Peg. 240-250°C	200	1200	-	1598	579	6749
-		1200	18	1183	249	3880
-		1200	36	624	182	3491
<i>Three litres of water for mixing.</i>						
Dodecane	200	1200	-	1806	612	6367
Dodecane	400	1200	-	1797	579	5898
Peg. 180-190°C	400	1200	-	1591	465	3532
-		1200	18	1134	218	3318
-		1200	36	600	152	3304
Log-normal distributions						
<i>One litre water for mixing. Two litres added later.</i>						
				Arit/Geo. mean size (μ m)	Geometric std.dev. (μ m)	
Hexyl benzene	200	1200	-	903/890	1.190	
Hexyl benzene	200	1200*	-	691/668	1.294	
Hexyl benzene	200	800	-	883/867	1.207	
Hexyl benzene	200	1600	-	793/768	1.228	
Hexyl benzene	200	1200*	18 (1)	652/632	1.285	
Shellsol AB	200	1200	-	834/812	1.260	
Peg. 180-190°C	200	1200	18 (1)	804/747	1.470	
Peg. 210-220°C	200	1200	18 (e)	749/682	1.540	
Peg. 210-220°C	200	1200	18 (1)	797/742	1.461	
Peg. 240-250°C	200	1200	18 (1)	859/767	1.610	
<i>Three litres of water for mixing.</i>						
Hexyl benzene	400	1200	-	842/818	1.268	
Shellsol AB	200	1200	-	948/917	1.296	
Shellsol AB	400	1200	-	853/827	1.285	
Peg. 240-250°C	400	1200	-	1413/1342	1.379	

* : New batch of reagent. Not used in any other testwork in this thesis.

sufficient time to spread at the developing air-water interface and so affect bubble size. It is reasonable to expect that individual surfactant molecules adsorb faster than oils can spread at the interface, so that the action of MIBC would be less affected by the dynamics of bubble formation. Furthermore, the coalescence of the oil films upon bubble collision can be expected to encourage rather than to deter bubble coalescence.

It made no significant difference whether the MIBC was initially vigorously dispersed in one litre of water prior to filling the cell or added directly into a cell full of water. This is not unexpected behaviour for a soluble reagent, which MIBC is at these dosages. The influence of the degree of mixing of the insoluble oils on the bubble size distribution induced by their presence is discussed in Section 4.7.2.5.

4.7.2.4 General oil comparisons

Initial testwork centred on a comparison of the effect of the various oils on the formation of bubbles in the absence of MIBC. In each experiment 200 μl of the oil was mixed in 1 litre of water within the cell for 2 minutes. Two litres of water were then added to the cell, and this was followed by a further 1 minute of mixing.

Figure 4.11 compares the bubble size distributions induced in the cell by the presence of the oils. The bubbles produced in the presence of largely aliphatic oils were well modelled by the normal distribution. Dodecane (pure) and Shellsol K (commercial) produced virtually identical distributions; 1.8 ± 0.6 mm. These two oils have already been found to exhibit very similar dispersion and adsorption characteristics (Chapters 2 and 3). Their respective interfacial properties must therefore be very similar. No surface activity of possible impurities or oxidation products was evident with the Shellsol K oil.

The Pegasol 3745 cut of similar boiling range (210 - 220°C), which consists of about 20 % aromatics, produced slightly smaller and less widely distributed bubbles; 1.6 ± 0.5 mm. It is therefore slightly more active at the air-water interface, probably spreading to

more of an extent, though this was still limited. Surfactant impurities may also be responsible, though if present these are clearly only weakly surface-active.

The aromatic oils, hexyl benzene (pure) and Shellsol AB (commercial), produced considerably smaller bubbles (0.8 to 0.9 mm) than the other oils. These were concentrated in a much narrower size range than bubbles produced in the presence of the aliphatics though some large bubbles still existed. Bubble distributions induced by the aromatic oils were well modelled by the log-normal distribution function. In the presence of aromatics bubble distributions tend to be log-normal in form because of the need to accommodate the presence of some large bubbles as well as very fine bubbles, i.e. positive skewing of the distributions. Even smaller bubbles were visually evident but could not be detected by the bubble sizing device.

The difference in mean bubble diameter between the aromatic and aliphatic oils is expected to have a pronounced effect on flotation since the difference in air-water surface area and bubble number follow a square and cube relationship respectively. Even relatively small changes in bubble diameter would have a dramatic effect on flotation performance.

There is some evidence supporting the existence of a second population of ultra-fine bubbles when the aromatic oils are used. Although these very small bubbles might constitute the left-hand side of the log-normal distribution, experimental results (e.g. those shown in Figure 4.11) suggest that the means of such distributions are too far from the origin to accommodate sufficient numbers of these minute bubbles within the same distribution as the larger bubbles. Many of the small bubbles were scarcely visible. They are responsible for the milky appearance of the water as shown in Figure 4.6. Such minute bubbles were initially encountered in the oil dispersion investigations (Chapter 2) whilst sizing aromatic oil droplets using a Coulter Counter. Bubbles as small as 30 μm in diameter were measured, as shown in Figure 2.7.

Further qualitative evidence of a very fine bubble population was obtained by conducting turbidity measurements on a sample of water removed from the cell during aeration. A HACH turbidimeter was used to

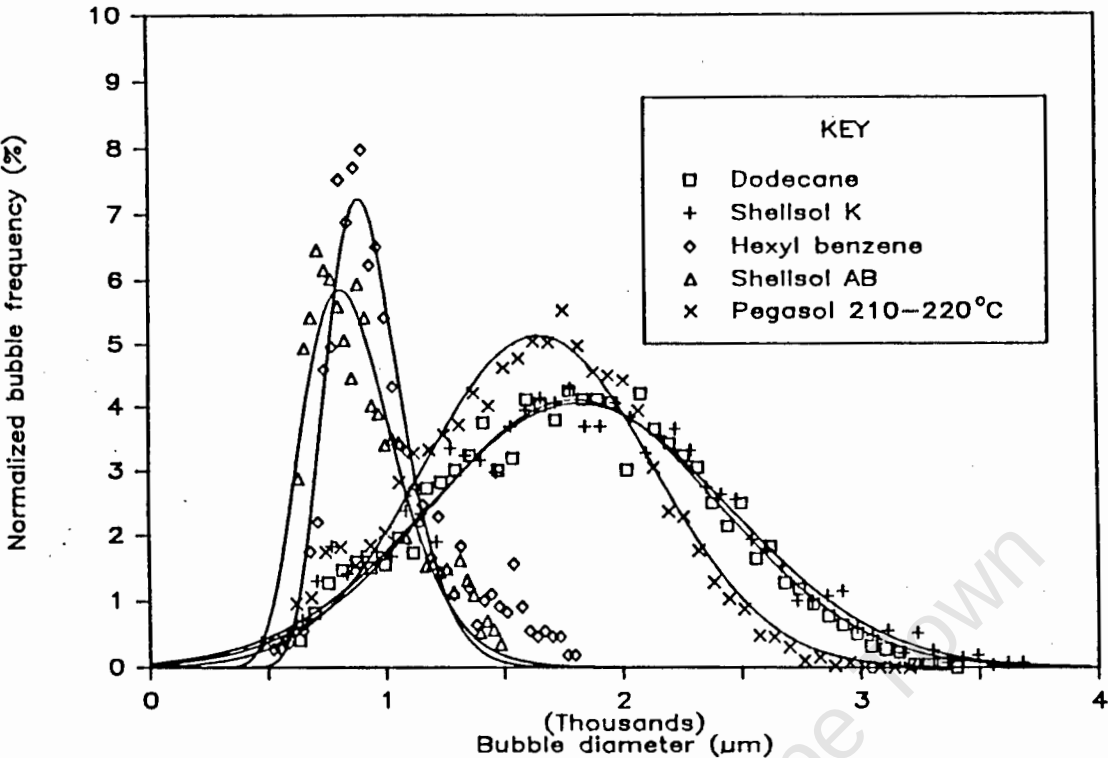


Figure 4.11 : Bubble size distributions induced in the batch flotation cell in the presence of various hydrocarbon oils. Dosages were 200 µl. No MIBC. The oils were dispersed in 1 litre of water prior to filling the cell and beginning aeration. Aeration rate was 4 l.min⁻¹ and impeller speed 1200 rpm.

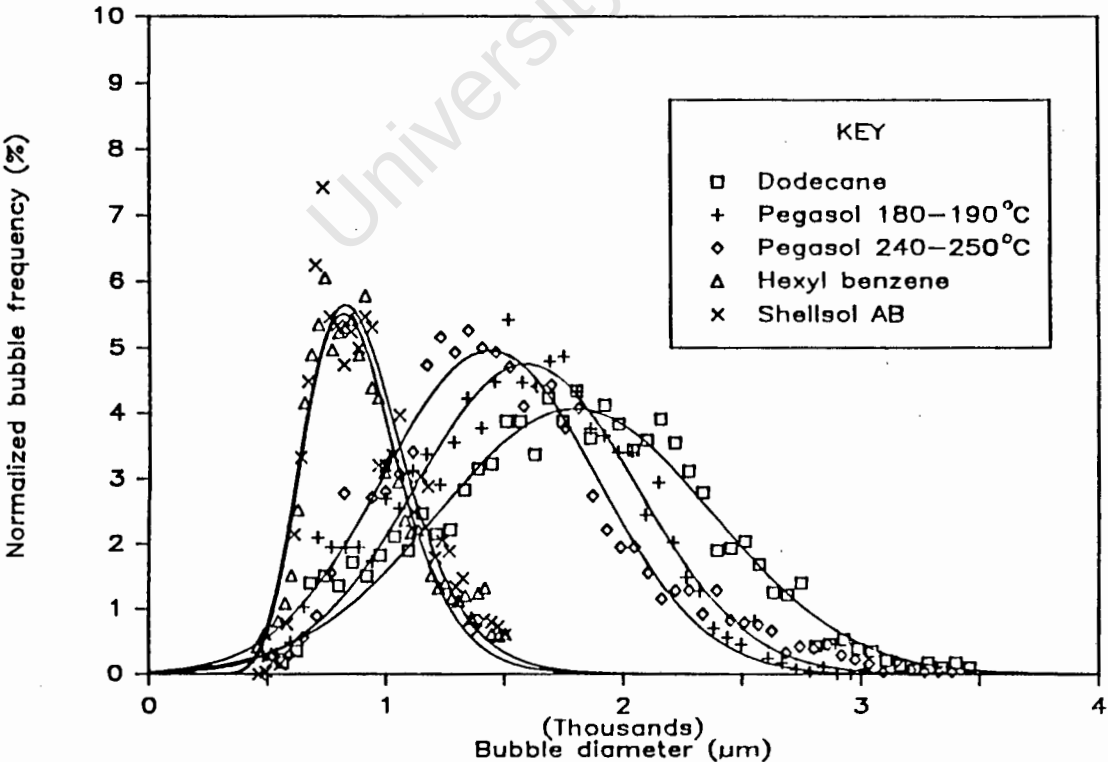


Figure 4.12 : Bubble size distributions induced in the batch flotation cell in the presence of various hydrocarbon oils. No MIBC. Dosages were 400 µl. The oils were dispersed in a full cell (3 litres of water). Aeration rate was 4 l.min⁻¹ and impeller speed 1200 rpm.

analyze the turbidity of solutions containing air bubbles after aeration in the presence of the oils and MIBC. The instrument measures the proportion of light deflected sideways from a beam passed through the solution. The amount of light deflected by standards of known turbidity were used to calibrate the instrument.

Oil dosages were 200 μl per three litres (18 and 36 μl for MIBC) and the reagents were all mixed for 2 minutes in 1 litre of water within the cell before the addition of another 2 litres and extraction of a sample for turbidity measurements. Table 4.3 summarizes the results.

Table 4.3 : Turbidity measurements of dispersions of air and oil

Reagent	Dosage (μl)	Turbidity (FTU)*		
		after 30 s	after 90 s	after 150 s
Water only		0.48	0.39	0.35
MIBC	18	0.48	0.39	0.35
MIBC	36	0.39	0.30	0.26
Dodecane	200	2.1	1.9	1.8
Shellsol K	200	2.2	2.0	1.9
Peg. 180-190°C	200	3.1	2.9	2.7
Peg. 210-220°C	200	4.1	3.8	3.5
Peg. 240-250°C	200	6.5	6.1	5.9
Shellsol AB	200	9.5	7.1	4.3
Hexyl benzene	200	22.0	18.5	18.0

* : FTU = Formazin Turbidity Units

Normally, the density difference between air and water would imply a very rapid separation of these two phases under quiescent conditions, yet turbidity remained fairly high after two or more minutes in some cases indicating that some of the air bubbles were extremely small. The turbidity measurements were decidedly qualitative since the oil droplets themselves contribute to the turbidity. The turbidity measurements obtained with MIBC were virtually identical to those of water. This was expected since MIBC dissolves at these dosages and a true solution is therefore formed.

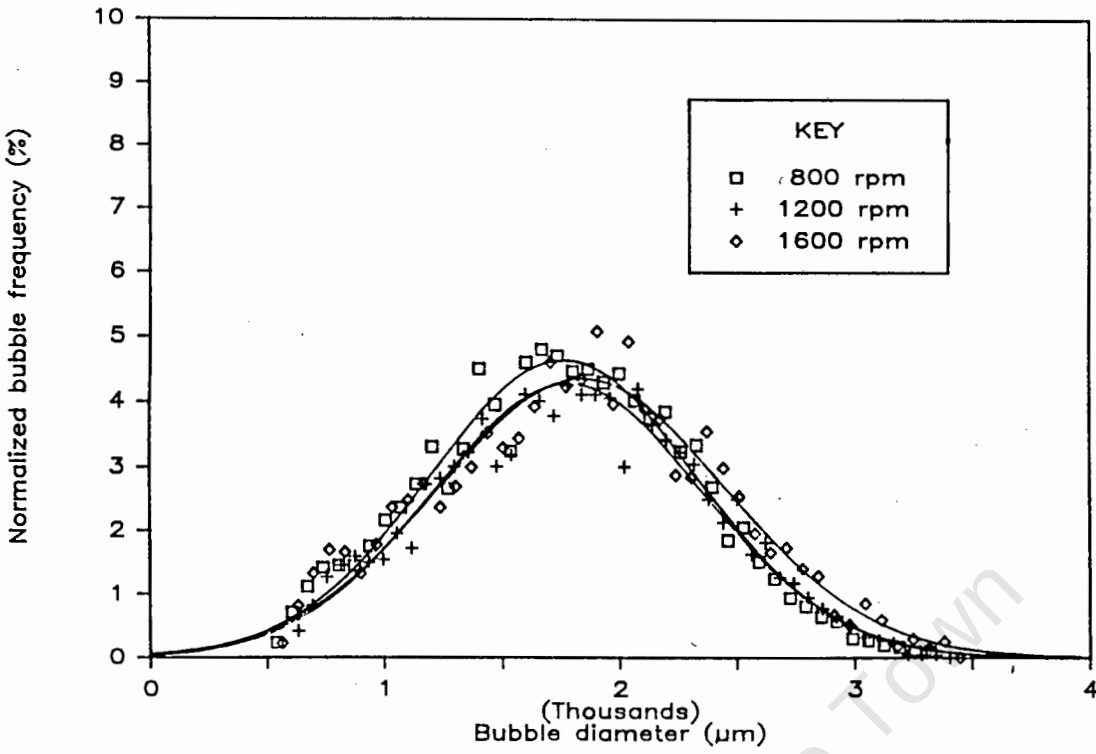


Figure 4.13 : Bubble size distributions induced in the batch flotation cell in the presence of dodecane. Dosage was $200 \mu\text{l}$. No MIBC. The oil was dispersed in 1 litre of water at 800, 1200 and 1600 rpm prior to filling the cell, reverting to a 1200 rpm impeller speed and beginning aeration. Aeration rate was $4 \text{ l} \cdot \text{min}^{-1}$.

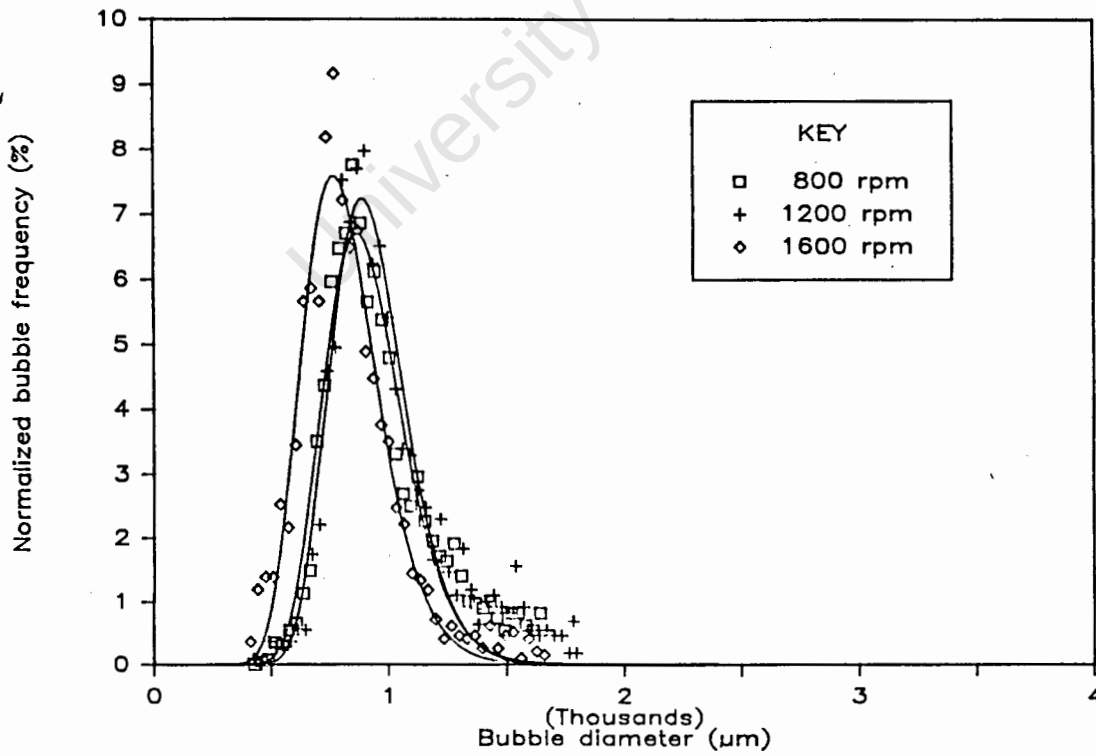


Figure 4.14 : Bubble size distributions induced in the batch flotation cell in the presence of hexyl benzene. Dosage was $200 \mu\text{l}$. No MIBC. The oil was dispersed in 1 litre of water at 800, 1200 and 1600 rpm prior to filling the cell, reverting to a 1200 rpm impeller speed and beginning aeration. Aeration rate was $4 \text{ l} \cdot \text{min}^{-1}$.

In the testwork discussed so far the reagents have been dispersed under very vigorous conditions¹. Testwork under less vigorous dispersion conditions was also conducted. In these experiments 400 μ l of the oils were added to 3 litres of water in the cell (i.e. to a full cell). A comparison of Figure 4.12 with Figure 4.11 shows that bubble distributions were hardly affected, even though the oils were comparatively poorly dispersed in relation to mixing conditions in 1 litre of water (refer back to Chapter 2). Oil droplet size is therefore not a crucial factor in determining the impact of oils on air bubble formation. Rather it is the behaviour of the oil at the air-water interface and in particular its spreading ability at this interface which is of prime importance.

4.7.2.5 The effect of agitation intensity

A comparison of Figures 4.10 and 4.11 shows that changing the agitation intensity, by altering the volume of water within the cell in which the oils were dispersed at 1200 rpm, produced no significant change in the bubble size distributions. The effect of agitation intensity was tested further by mixing 200 μ l of some oils in one litre of water at impeller speeds of 800, 1200 and 1600 rpm prior to filling the cell. The 1200 rpm impeller speed was resumed immediately prior to aeration. In this way the degree of oil dispersion was altered significantly while the effect of the mechanical action of the impeller on bubble dispersion was kept constant.

Dodecane and hexyl benzene were selected as representatives of the aliphatic and aromatic oils respectively. Figures 4.13 and 4.14 show that increased oil dispersion had little effect on the bubble distribution produced during aeration for either oil. Thermodynamics (spreading) clearly controls the process. Normal and log-normal distribution functions were used to model the data for dodecane and hexyl benzene respectively.

¹ In each experiment 200 μ l of oil was mixed in 1 l of water in the cell for 2 min, before adding 2 more litres of water and mixing for another minute before commencing aeration.

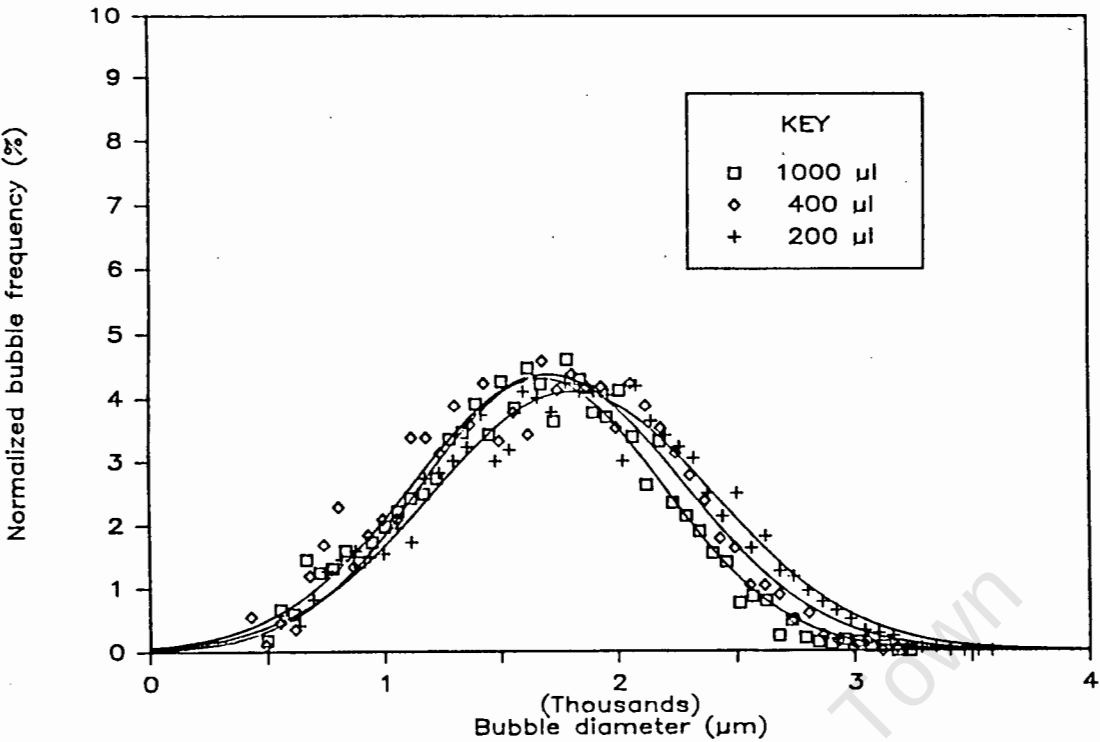


Figure 4.15 : Bubble size distributions induced in the batch flotation cell in the presence of dodecane. Dosages were 200,400 and 1000 μl . No MIBC. The oil was dispersed in 1 litre of water prior to filling the cell and beginning aeration. Aeration rate was $4 \text{ l}\cdot\text{min}^{-1}$ and impeller speed 1200 rpm.

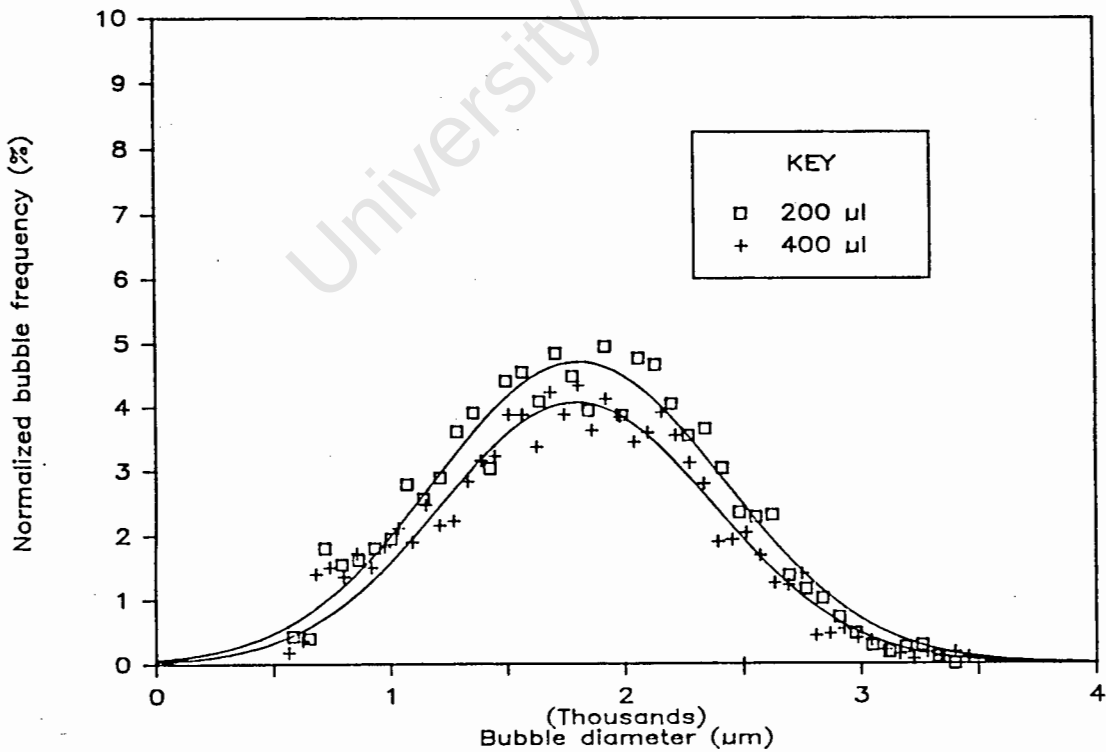


Figure 4.16 : Bubble size distributions induced in the batch flotation cell in the presence of the dodecane. Dosages were 200 and 400 μl . No MIBC. The oil was dispersed in a full cell (3 litres of water) prior to beginning aeration. Aeration rate was $4 \text{ l}\cdot\text{min}^{-1}$ and impeller speed 1200 rpm.

4.7.2.6 The effect of reagent dosage

The effect of dosage has already been considered in a general way in Section 4.7.2.3, where two sets of experiments were done in which the dosage was changed from 200 to 400 μl . However in these instances both the mixing volume and the oil dosage were changed simultaneously. The effect of a change in dosage at constant mixing conditions was therefore investigated. Two of the oils which had the least effect on bubble size were selected for testing in the belief that they would be most susceptible to dosage changes. Since these oils were evidently only weakly active at the air-water interface, increasing their dosage might promote whatever surface-active qualities they might possess. The oils were dodecane and the Pegasol 3745 210-220°C boiling range cut.

Figure 4.15 shows that raising the dodecane dosage from 200 to 1000 μl , while initially mixing the oil vigorously in one litre of water, produced no significant change in bubble size. Figure 4.16 shows that when the dodecane is mixed in a full cell, doubling the dosage from 200 to 400 μl also produced no significant change. This is further evidence that the behaviour of the oil at the interface rather than its concentration (assuming this is adequate) or droplet size dictates the effect it will have on bubble size.

More of a change was evident with the Pegasol cut. Figure 4.17 shows that the bubble size decreased when doubling the dosage from 200 to 400 μl though the change was not marked. The increased dosage evidently boosted whatever weak surface activity the oil or associated impurities possessed.

It is reasonable to assume, in general, that within the oil dosage range commonly used in flotation and certainly in that used in the batch flotation testwork in this thesis, dosage itself is likely to produce little change in the bubble size distributions. This conclusion is also in agreement with the thermodynamic (spreading) understanding of the process.

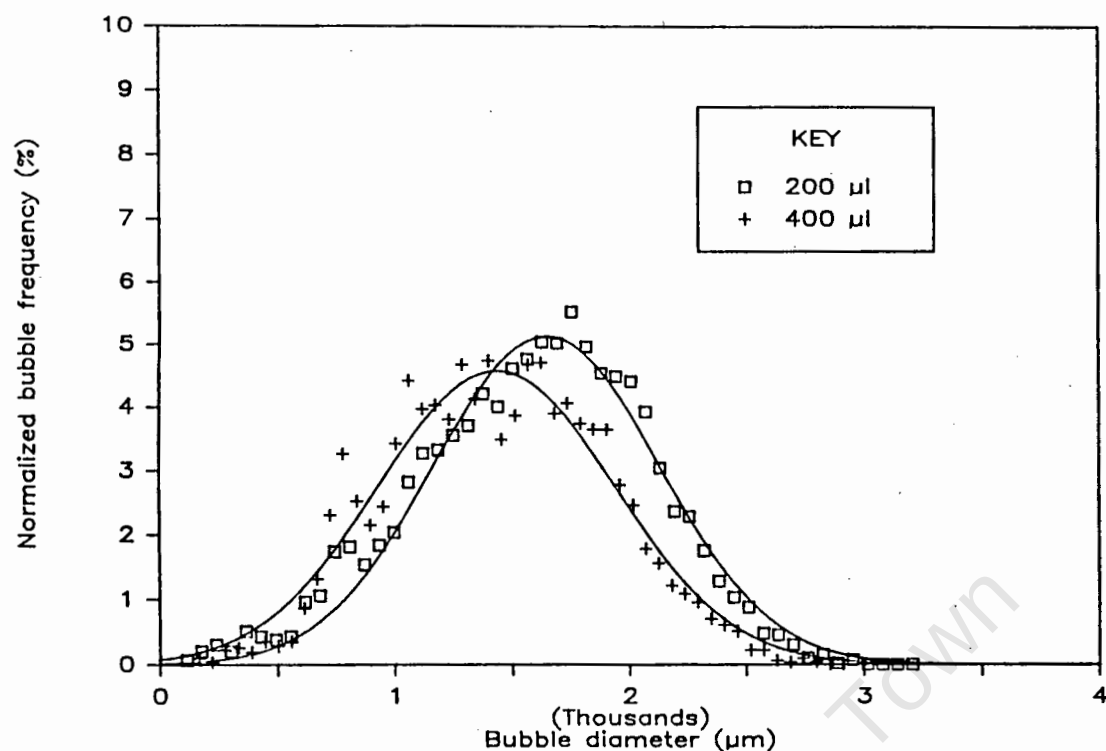


Figure 4.17 : Bubble size distributions induced in the batch flotation cell in the presence of the Pegasol 3745 210-220°C cut. Dosages were 200 and 400 µl. No MIBC. The oil was dispersed in 1 litre of water prior to filling the cell and beginning aeration. Aeration rate was 4 l.min⁻¹ and impeller speed 1200 rpm.

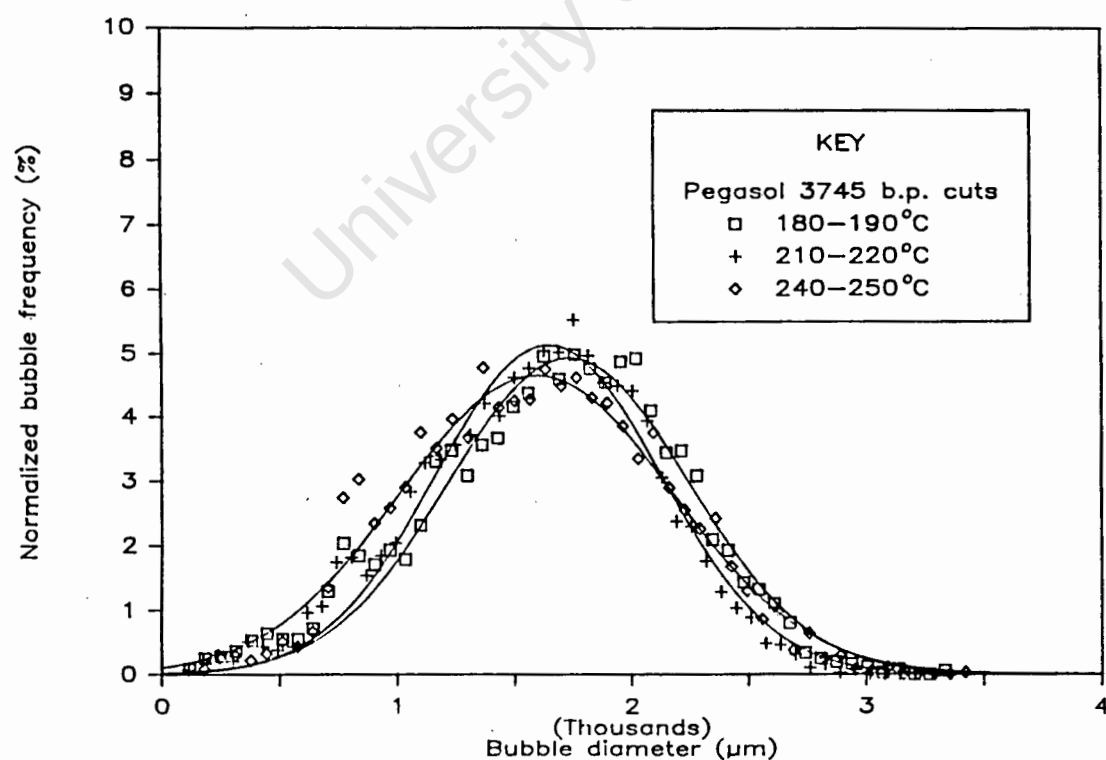


Figure 4.18 : Bubble size distributions induced in the batch flotation cell in the presence of the Pegasol 3745 180-190, 210-220 and 240-250°C cuts (independently). Dosage was 200 µl. No MIBC. The oils were dispersed in 1 litre of water prior to filling the cell and beginning aeration. Aeration rate was 4 l.min⁻¹ and impeller speed 1200 rpm.

4.7.2.7 Pegasol 3745 boiling range cuts

The effect of oil boiling range and viscosity on bubble size induced by oils of homologous chemical composition was investigated by using three Pegasol 3745 boiling range cuts (180-190, 210-220 and 240-250°C). 200 μl of each cut was dispersed in one litre of water for 2 minutes prior to filling the cell and commencing aeration. Figure 4.18 depicts the results and shows clearly that the cuts all induced similar bubble distributions. This result was not unexpected since the Pegasol 3745 cuts were known to produce droplets of similar size (Section 2.6.1.1.c). In other words their spreading ability, and consequently their influence on bubble size, is dictated by their interfacial properties, which are similar, and not by physical bulk properties such as viscosity.

4.7.2.8 Oil-MIBC joint action

So far only bubble distributions produced in the presence of either the oils or the MIBC have been considered. Obviously in an actual flotation situation both the reagents would be present. Since oil-frother joint action is known to be of importance to frothing (Section 4.2.5) it is vital to know how their joint presence influences bubble size.

Dodecane was selected to represent the aliphatics and hexyl benzene the aromatics for this testwork. This choice precluded the influence of unknown and unquantifiable surfactant impurities. In addition, a Pegasol 3745 cut of similar boiling range to these oils (210-220°C) was used. In each case 200 μl of the oil was vigorously dispersed in one litre of water. The MIBC was either added 10 s after the oil (to one litre of water) or to the full cell 1 minute prior to aeration. These procedures are termed "early" and "late" addition in the discussion which follows. In both cases 18 μl (6 $\mu\text{l.l}^{-1}$ of water) of MIBC was used. The MIBC was not added mixed in the oil since this procedure would diminish its frothing ability as discussed in Section 4.2.3.1 above.

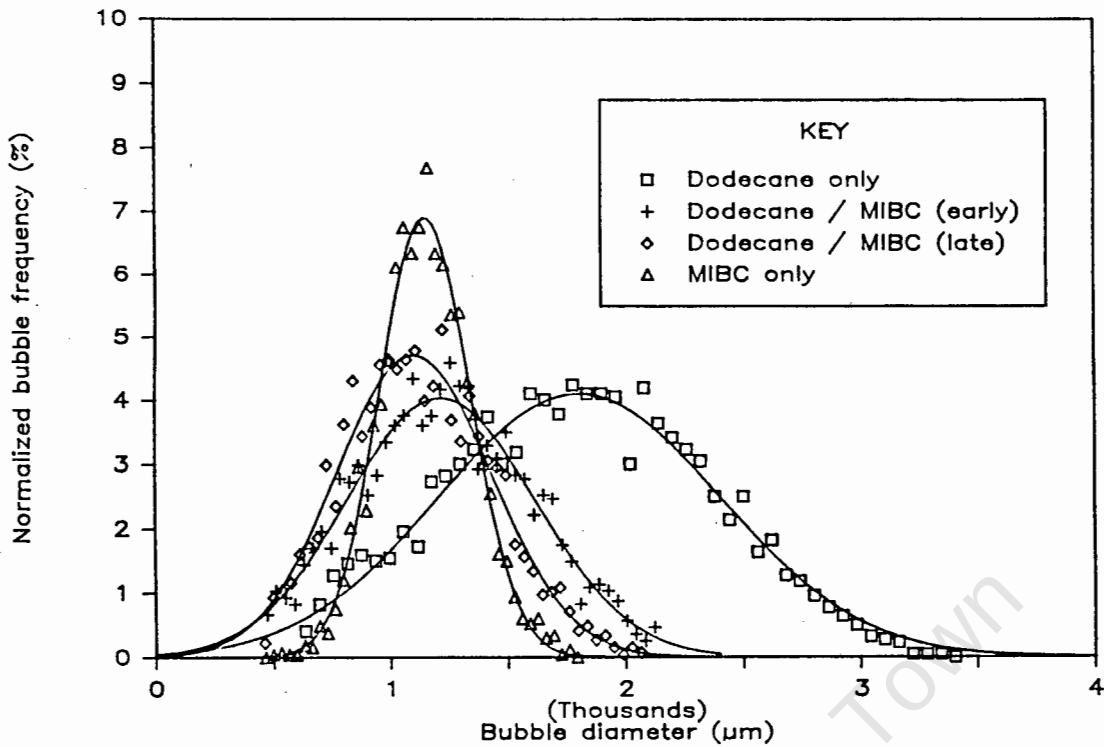


Figure 4.19 : Bubble size distributions induced in the batch flotation cell in the presence of dodecane. 200 μ l of the oil was dispersed in 1 litre of water prior to filling the cell and beginning aeration. 18 μ l of MIBC was added either 10 s after the oil (early addition) or to the full cell 1 minute prior to aeration (late addition). Aeration rate was 4 l.min⁻¹ and impeller speed 1200 rpm.

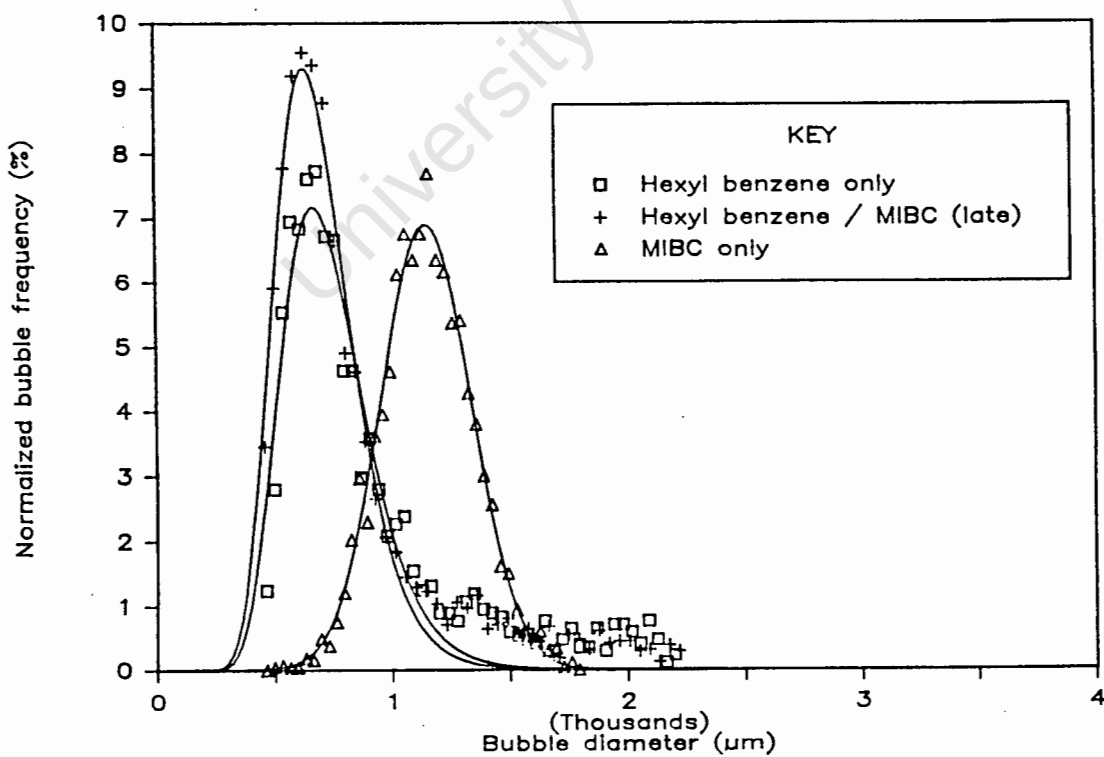


Figure 4.20 : Bubble size distributions induced in the batch flotation cell in the presence of hexyl benzene. 200 μ l of the oil was dispersed in 1 litre of water prior to filling the cell and beginning aeration. 18 μ l of MIBC was added either 10 s after the oil (early addition) or to the full cell 1 minute prior to aeration (late addition). Aeration rate was 4 l.min⁻¹ and impeller speed 1200 rpm.

a) Dodecane-MIBC joint action

Figure 4.19 shows the bubble distributions induced by the MIBC alone, by dodecane alone and by the two reagents in combination. In combination the mean bubble size was much the same as that found with the MIBC alone: 1.2 ± 0.4 mm (early addition) and 1.1 ± 0.3 mm (late addition) versus 1.2 ± 0.2 mm for MIBC alone. The reagents jointly produced a distribution that was more spread, than with MIBC alone, though not as broad as that induced by the dodecane alone.

The timing of MIBC addition had a small effect on bubble sizes. The bubble distribution following early MIBC addition had a larger mean and spread than that observed following late addition (1.2 ± 0.4 mm and 1.1 ± 0.3 mm respectively). This is most probably due to the transfer of MIBC to the oil phase in which it is preferentially soluble; this transfer then reducing its frothing abilities. Late MIBC addition was the procedure adopted later in the batch flotation testwork (Chapter 5).

When used in conjunction with dodecane, the MIBC very largely dictated the bubble size, though the presence of the oil detracted from the ability of the frother to induce a narrow bubble size range. As mentioned earlier, this is believed to be a result of oil-oil coalescence which in turn aids bubble coalescence. Though oils may induce smaller bubbles they cannot stabilize the interface to the same extent as true surfactants can, presumably because they lack strong polarity. Oiled-bubble electrical double layers are therefore comparatively poorly developed implying that inter-bubble repulsion is reduced.

b) Hexyl benzene-MIBC joint action

Figure 4.20 shows the bubble size distributions of MIBC, hexyl benzene and the two in combination. Apparently bubble size distribution was dictated exclusively by the collector oil and not by the frother at these dosages (which are typical of actual flotation dosages). The presence of MIBC merely increased the number of bubbles of the order of the mean size presumably by reducing the number of large bubbles slightly. MIBC had only a small effect on reducing the

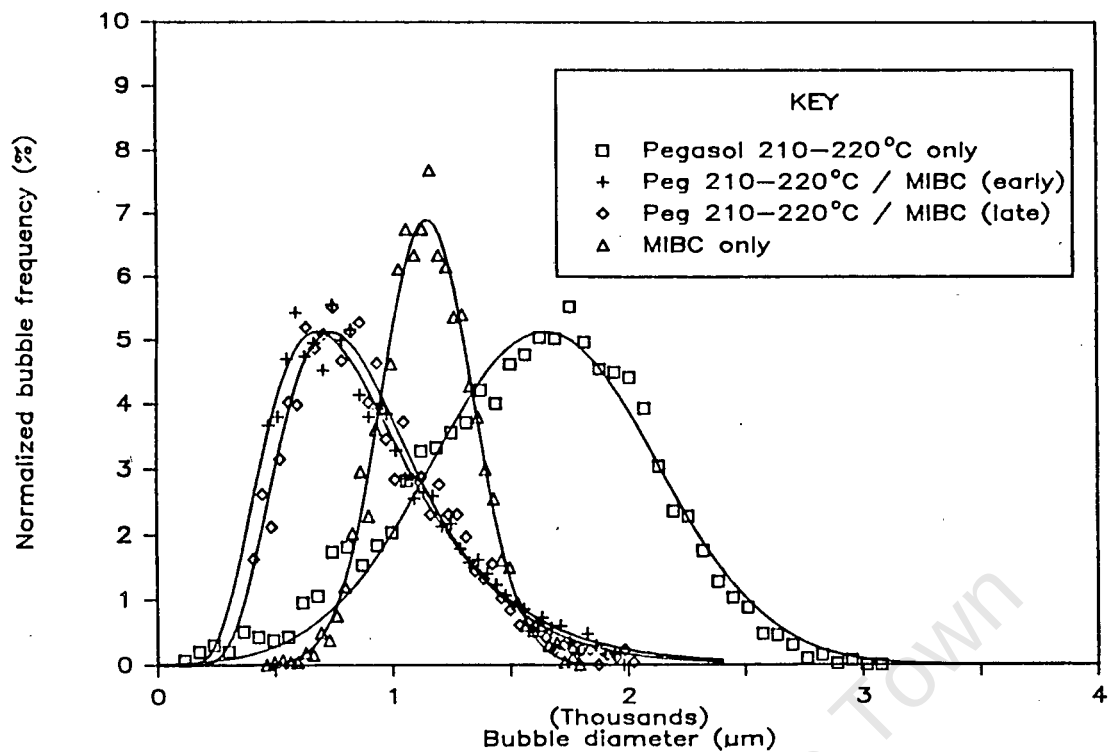


Figure 4.21 : Bubble size distributions induced in the batch flotation cell in the presence of the Pegasol 3745 210-220°C cut. 200 μ l of the oil was dispersed in 1 litre of water prior to filling the cell and beginning aeration. 18 μ l of MIBC was added either 10 s after the oil (early addition) or to the full cell 1 minute prior to aeration (late addition). Aeration rate was 4 l.min⁻¹ and impeller speed 1200 rpm.

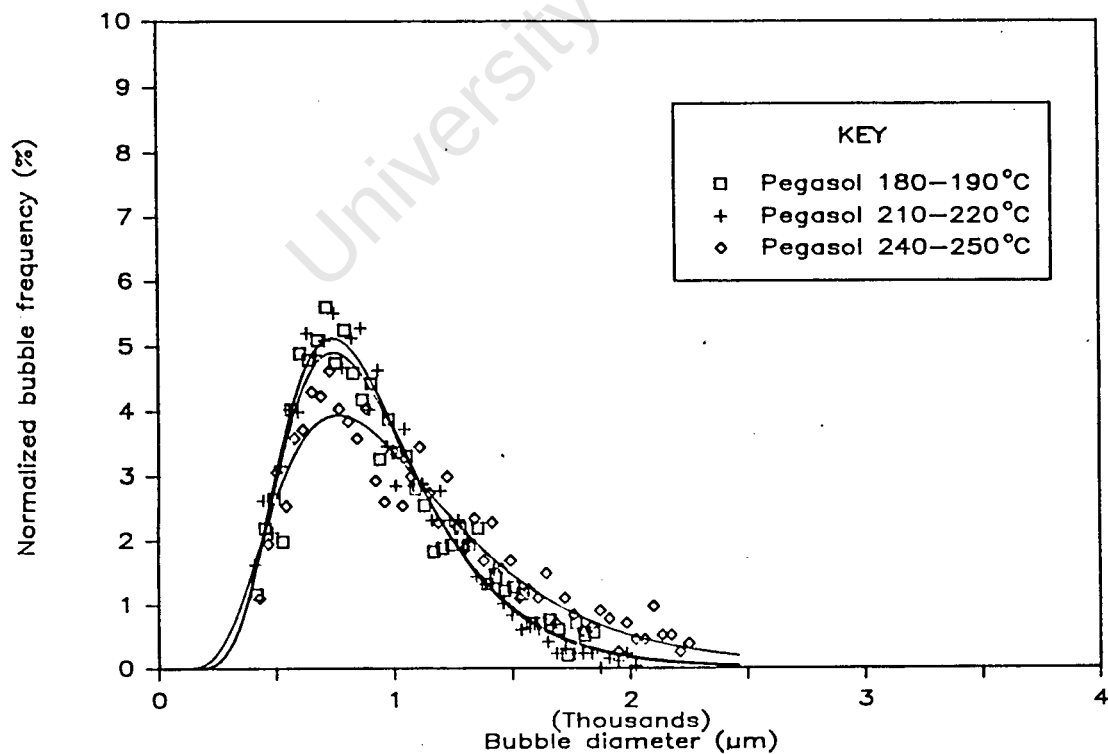


Figure 4.22 : Bubble size distributions induced in the batch flotation cell in the presence of three Pegasol 3745 cuts (180-190, 210-220 and 240-250°C); used independently. 200 μ l of the oils were dispersed in 1 litre of water prior to filling the cell and beginning aeration. 18 μ l of MIBC was added to the full cell 1 minute prior to aeration (late addition). Aeration rate was 4 l.min⁻¹ and impeller speed 1200 rpm.

number of fairly large bubbles associated with the use of hexyl benzene on its own. Nevertheless, a slight decrease in number affects total volume to a greater extent and will therefore noticeably increase the numbers of smaller bubbles.

The number of large bubbles, similar in size to those encountered with the aliphatic oils, though far scarcer, was initially attributed to the volumetric air flowrate being too high to produce consistently fine bubbles. However tests showed that the large bubbles still existed at aeration rates as low as 1 litre per minute. The existence of large bubbles was also thought to be due to the dynamic conditions inherent in the flotation cell. There may have been insufficient oil available or insufficient time for its spreading at the interface during the formation of some bubbles, as suggested earlier. However because these large bubbles persisted in the presence of MIBC it was concluded that the coalescence of oil films at the bubble surface encouraged the coalescence of the bubbles. Oils which spread readily at an air-water interface, and hence alter bubble size appreciably, are known to coalesce readily (Rehfeld, 1974).

c) Pegasol 3745 210-220°C-MIBC joint action

Figure 4.21 shows the bubble size distributions induced by MIBC, the Pegasol 3745 210-220°C boiling range cut, and the two in combination. It reveals a startling symbiotic relationship between MIBC and this oil. In the presence of both reagents the mean size of the bubbles produced was altered dramatically; from 1.6 mm for the oil alone and 1.2 mm for MIBC alone to less than 0.8 mm for the two reagents in combination. The mean bubble size was significantly smaller than that found when either reagent was used in isolation. The broadening of the MIBC distribution caused by the presence of the oil and the existence of significant numbers of small as well as comparatively large bubbles forced a shift to log-normal behaviour, because of the physical constraint of a positive bubble size.

The outcome of the joint frother-Pegasol oil action on bubble size was so pronounced in relation to that found with dodecane and hexyl benzene that experiments were repeated several times. However results always showed this behaviour. The effect of the joint MIBC-oil

action was then tested with some other Pegasol 3745 cuts, which were expected to behave similarly because of their homologous chemical constitution. 18 μ l of MIBC was added 1 minute prior to aeration (late addition) in each case.

Figure 4.22 shows that the joint action of the frother and the oil reduced bubble size considerably in all instances and that the distributions were indeed similar in all cases. Mean bubble diameters were all about 0.8 mm (see Table 4.2). The highest boiling range cut induced a somewhat broader distribution with a tendency to produce a number of relatively large bubbles which was not as apparent with the other cuts tested.

The joint action of the two reagents clearly changed interfacial behaviour from that produced in the sole presence of either reagent. This implies that different chemical or physical structures developed in the interfacial film. It is improbable that these are MIBC and alkyl or aryl molecular complexes or groupings since these were not in evidence with the pure aliphatic and aromatic oils respectively. Furthermore, the linear nature of the pure oils would be expected to allow closer packing of MIBC molecules at the interface (Glembotskii et al, 1970) than branched molecules typical of commercial oils like Pegasol 3745 would. The observed behaviour can only be attributed to some other source. This is probably an oil impurity with surface-active properties which are strongly enhanced by the presence of MIBC. Apparently the surface-active properties of this impurity are largely restricted to the air-water interface since the presence of MIBC did not improve dispersion of the Pegasol 3745 oil (Chapter 2).

The conclusion that pure alkyl or aryl hydrocarbon molecules and MIBC did not interact significantly, but that an oil-phase surfactant did, is in agreement with the penetration theory of Leja and Schulman (1954). They stated that such complexes are only formed following the *simultaneous* interaction of hydrophilic surfactant head groups and hydrophobic hydrocarbon chains on adjacent surfactants.

The deduction that surfactant impurities are responsible for this striking behaviour is unfortunate in that the type and action of such impurities are virtually impossible to quantify. Furthermore the

existence of such impurities and their probable inconsistencies in type and concentration from oil batch to batch (and certainly from one commercial oil to another) will make the prediction and later evaluation of plant performance with such oils difficult.

As far as this thesis is concerned, the Pegasol 3745 oil would be expected to behave differently from dodecane/other aliphatic oily reagents (Shellsol K) in the flotation testwork.

4.7.3 The effect of oil adsorption onto coal on the influence of the oil on bubble size

Adsorption of the oils by coal particles with its concomitant reduction in the concentration of free oil within the pulp water could be expected to result in differences between bubble sizes in the water-only and pulp situations. This would depend on how much oil is needed to affect the creation of bubbles. If the oil spreads very thinly at the air-water interface only a relatively small concentration of the oil would be necessary to influence bubble size.

Oil adsorption by coal is likely to have a limited impact on bubble creation in pulps where the equilibrium adsorption level is reasonably low. Though oils like benzene and other aromatic homologues adhere and spread fairly readily on coal (and are hence largely adsorbed) they will also spread well at an air-water interface. It might not be necessary that such oil is free in the pulp water. An oiled coal particle contacting the air stream could provide sufficient oil to the interface to influence bubble formation. Air bubbles may thus remove collector from the coal particles since the air-water interface is preferentially wet. Hence although oil may be adsorbed by the coal to the extent that little remains in the aqueous phase, it is postulated that the oil can be readily transferred to the air-water interface and so still influence bubble size strongly.

4.8 CHAPTER SUMMARY

The size of bubbles produced within a pulp at any fixed aeration rate will have a pronounced effect on flotation performance because of its influence on factors such as flotation rate and froth form and stability.

The influence of the collector oils themselves on bubble creation is often overlooked and the frother is tacitly assumed to control this. Testwork has shown that several oils influence bubble creation considerably and may even surpass the frother (MIBC) in this role at dosages conventionally used in flotation.

The aromatic oils, both pure and industrially derived, fall into this category - their presence ensures the formation of very fine air bubbles. Since the oils used were all extremely insoluble it is apparent that they can only affect interface chemistry by spreading sufficiently thinly at the interface; thereby adopting a quasi surface-active role. The fact that pure hexyl benzene reduced bubble size considerably indicates that its spreading ability at the air-water interface rather than the action of associated surfactant impurities is responsible for bubble size reduction. The air-water interface is effectively replaced by oil-water and oil-air interfaces of lower cumulative interfacial tension (energy).

The aliphatic oils, dodecane (pure) and Shellsol K (commercial), were found to have little influence on bubble size. Pegasol 3745, which consists of about 20 % aromatics, affected bubble size to a greater extent than the aliphatic oils but the effect was minor in comparison to the influence of aromatic oils. The Pegasol 3745 oil is evidently incapable of spontaneous spreading.

Because interfacial spreading phenomena dictate bubble size, oil dispersion and oil dosage have little effect on sizes. The oils, unlike true surfactants, do not produce narrow bubble size distributions since they are unable to induce the same degree of electrical double layer development in the aqueous phase adjoining the bubble surface as surfactants can. In fact the oils reduce this. Inter-bubble repulsion during collision is therefore poorer and coalescence increases. The

coalescence of oil films at the bubble surface will also enhance bubble coagulation and coalescence.

The most interesting and important observations concerned the effect of the joint oil-MIBC action on bubble formation, at dosages commonly used in flotation. With aliphatic oils the MIBC dictated the mean bubble size though the presence of the oils broadened the distribution presumably by enhancing bubble coalescence. The aromatic oils on the other hand dictated bubble size with the MIBC playing no significant role. Its presence was unable to reduce the number of large bubbles associated with the use of the aromatic oils, again indicating that the oil films coat the bubble surface thereby encouraging bubble coalescence.

With the Pegasol 3745 oil the joint action of the two reagents produced bubbles which were on average significantly smaller than those induced in the presence of either the oil or the MIBC in isolation. This was an unexpected effect and a very significant finding. The oil is therefore expected to induce apparently anomolous behaviour in its flotation performance. The effect was attributed to the "complexing" of MIBC and some surface-active constituent of the oil. This conclusion unfortunately highlights the difficulties which surfactant impurities in commercial oil stocks could cause in predicting and regulating flotation performance.

4.9 CONCLUSIONS

1. Aliphatic oils have little or no influence on the size of bubbles created in the pulp. At the same agitation and aeration conditions, aromatic oils reduce bubble sizes considerably. They are thus expected to be better flotation reagents than aliphatic oils since bubble size is of considerable importance to bubble-solid particle contacting efficiency, to the rate of flotation and to the structure and stability of the overlying froth phase.

2. The preceding conclusion is true of these two generic oil types if they are free of surface-active constituents. Commercial oils which contain surfactant impurities may reduce bubble size considerably when acting in combination with the frother (over and above the impact on bubble size of either reagent in isolation). This was found to be the case with the Pegasol 3745 oil and MIBC frother. For this to occur, commercial oils must possess some aromatic content, i.e. some polarity, since powerful surfactants (strongly polar and ionic) are essentially insoluble in "pure" aliphatic oils.
3. The degree of dispersion of the oil attained in conventional flotation, as well as the dosage of the oil normally used, have little effect on the impact of the oil on bubble size as this is governed by thermodynamic (spreading) criteria.
4. The bubble size (diameter) distributions (based on frequency) were well modelled by the normal distribution, either in its arithmetic or in its in geometric (logarithmic) form.

CHAPTER 5

FLOTATION TESTWORK

5.1 INTRODUCTION

The objective of conducting batch flotation testwork with the various hydrocarbon oils (as collectors) was to investigate the extent to which the observed flotation behaviour could be predicted or explained by the action of the oils in the sub-processes previously studied. These oils were known from previous flotation testwork (Franzidis, 1986 and 1987) to induce markedly different performance with any one coal. The flotation testwork was thus not aimed specifically at determining the best collector for the coal used in the experimental program or the best ways in which to float this coal; although, where such information was forthcoming from the results, it is nonetheless discussed.

This chapter begins with a literature review on the subject of bubble-oiled particle contacting, with special emphasis on the role of the oil in promoting adhesion and the postulated mechanisms by which this is achieved. Section 5.3 describes details of the experimental program carried out. Section 5.4 discusses the results of flotation experiments on an individual basis. The observed behaviour of the oils in the sub-processes (preceding chapters) and the underlying theory are used to interpret the results. Section 5.5 is a global discussion of the results, irrespective of oil type, dosage or conditioning procedure. The aims of these collective comparisons are, firstly, to draw conclusions on the relationship between variables such as concentrate grade and froth structure (water recovery), actual grade and theoretically possible grade (from liberation studies), etc.; and, secondly, to place the discussion of individual flotation results in perspective.

5.2 THEORY AND LITERATURE REVIEW

5.2.1 Introduction

The outcome of a flotation process is dependent on the cumulative effect of the behaviour of its sub-processes, which in turn are governed by both chemical and physical (mechanistic) actions. The earliest flotation research work concentrated on flotation chemistry (adsorption, contact angles, etc.) and largely ignored physical mechanisms such as particle-bubble collision. Trying to emulate the overall process by exclusive consideration of one or the other has however proved fruitless (Schulze, 1984, p.18).

While recognising the need to consider mechanistic actions, this literature review concentrates on the action induced by hydrocarbon oils on the coal flotation process. Mechanistic considerations (and particularly their theory) are not considered in any detail. Excellent texts in this regard are available (e.g. Schulze, 1984).

It is widely accepted that the overall probability of flotation is dependent on the probability of oiled particle-bubble contact, the probability of attachment and the probability of detachment, including detachment during froth cleaning (Equation 5.1). Acceptance of this approach has allowed the development of physically based kinetic models for flotation (Schulze, 1984):

$$P_f = P_c \times P_a \times (1 - P_d) \quad [5.1]$$

P_c , the probability of collision, is dependent on the relative particle and bubble sizes and densities, their respective trajectories and kinetic energies and other hydrodynamic influences such as liquid viscosity. The oils thus play no *direct* role in this step though they do have some influence via their role in determining bubble sizes and frequency, and particle and bubble surface tensions and charges.

P_a and P_d , the probabilities of attachment and detachment respectively, have not been well researched (Al Taweel, 1986) particularly in the context of insoluble collectors. The factors controlling these probabilities are complex and depend, inter alia, on

largely unquantifiable factors such as coal surface properties, oil properties, cell turbulence, bubble and particle sizes and the influence of surfactants.

The sections which follow review the current understanding of bubble-particle contact and adhesion, and the influence of various parameters (such as the coal surface, the presence of collectors and frothers and their mode of addition) on these processes.

5.2.2 The bubble-particle contact process

In an analagous manner to oil droplet-solid particle collision, the collision of an oiled particle and an air bubble can be divided into three stages :

1. Approach of bubble and solid particle leading to capture of the particle.
2. Destabilization and rupture of the aqueous film between the oiled particle and the bubble.
3. Initiation and expansion of the contact area leading to the formation of a (stable) aggregate.

The first two stages are not intrinsically part of bubble-particle attachment and hence in a direct sense are beyond the influence of the oils, though kinetic inefficiencies in these stages will affect the flotation process (Fuerstenau et al, 1983). The oils may have an indirect influence in Step 1 in that they may influence bubble size. They also have an indirect influence on Step 2 in that the presence of a hydrocarbon chain in the aqueous phase will disrupt the inter-molecular structure of water around it and thus decrease the aqueous phase viscosity in this region (Dibbs et al, 1974). Much of the theory on film thinning (Step 2) and contact and wetting (Step 3) is discussed in Section 3.2 with regard to oil droplet-particle adsorption but is generally applicable to air bubble-oiled particle contact as well. Points of difference will be expanded on in this chapter.

Leja and He (1984) pointed out that for successful attachment of air to solid, the solid must not only be sufficiently hydrophobic (i.e.

the adhesion must be thermodynamically favourable) but that a kinetic criterion must also be satisfied : the energy barrier inherent in film thinning must be overcome. The origin of this energy barrier is discussed in Section 2.2.5.1.

The first (thermodynamic) criterion is that :

$$\Delta G^s = \gamma_{wv} (\cos\theta - 1) < 0 \quad [5.2]$$

This criterion is normally achieved by the use of collectors; oils in the case of coal. The more negative ΔG^s is, the greater the probability of flotation. However, Laskowski (1974) and Fuerstenau et al (1983) concurred that Equation 5.2 describes the energy difference between final and initial states but does not consider the energies of intermediate states, for instance in bubble-particle approach. Further confirmation of the inattention given to intermediate states is offered by Špetl and Dedek (1966) who pointed out that contact angles, which are often used to evaluate the capacity of a bubble to adhere to a solid, give no indication of the process involved, since the contact angle merely represents the final phase of the contact process.

The bubble and the solid particle have markedly different densities and very often disparate sizes. Solid particles are normally considerably smaller than bubbles in froth flotation; though in treating nominally -0.5 mm r.o.m. coal fines, a fair proportion of large solid particles will exist. Whether the particle collides with the air bubble or not depends on the balance of viscous, inertial and gravitational effects and the form of the streamlines around the bubble and the particle itself (if this is large). The hydrodynamics of bubble-particle collisions have been discussed in several papers, e.g. Flint and Howarth (1971), Anfruns and Kitchener (1976), Ralston (1983) and in specialist texts, e.g. Schulze (1984).

Generally either Stokes or potential flow is assumed to represent the fluid flow around the rising bubble. However the actual flow behaviour is dependent on bubble size, and the use of a single stream function to model the process over a range of bubble sizes leads to inaccuracies according to Jiang and Holtham (1986). These researchers developed a model which uses different stream functions (depending on

the bubble Reynolds number) and they believed that this adaption considerably improves earlier models.

Hydrodynamic theories generally assume a single target sphere (bubble) and a single particle in an infinite pool of liquid (e.g. Anfruns and Kitchener, 1976; Jiang and Holtham, 1986). Some 17 years ago, Flint and Howarth (1971) reported that there were no theories to account for the hydrodynamic changes when a swarm of bubbles is present, as in flotation machines. This still appears to be largely the case (Schulze, 1984). Ahmed and Jameson (1985) stated that "there is a complete lack of experimental data on the collision process in stirred turbulent conditions, with all variables under control". Most research has been, or is, undertaken under highly idealized conditions. Flint and Howarth (1971) believed that the straightening of streamlines by the proximity of neighbouring bubbles increases collision efficiencies so that these may be several times higher than those predicted by single sphere theories.

As with oil droplet-particle collision dynamics (Chapter 3, Section 3.2.4), quantitative trajectory theories will not be discussed further, since (a) observations of flotation concentrate production will ratify that collisions can occur frequently and successfully, (b) the models appear to have limited application in real (multi-particle and multi-bubble) systems and, most importantly, (c) the oily collectors have no *direct* influence on the hydrodynamics of collision. A summary of experimental observations in this regard is however of interest.

Historically, two postulates existed to explain the attachment of particles to air bubbles :

1. That bubbles coursing up through the pulp encounter solid particles and that these collisions lead to mutual attachment.
2. That bubbles grow at gas nuclei present at the solid surface and that mechanically created bubbles play only a small role in the flotation process.

Smith et al (1957) found that very few solids, in sub-aeration type flotation cells, actually attached themselves to the bubble surface in the pulp, though the fluid surrounding the bubble often contained appreciable quantities of solids. (The vortex created behind a rising

yields, as predicted by the float-sink function, are represented by the smooth curve.

As may be seen, the flotation results for the milled unwashed coal were well displaced from their best possible levels. Even when mass yields were low the grades were no nearer to their potential levels. In fact the actual and best possible ash contents only approached one another as the concentrate mass approached that of the feed (as they must do when just about everything floats - which obviously defeats the beneficiation process).

The reasons for the displacement of the actual results from those theoretically possible could be several, including :

1. Inadequate reagent selectivity.
2. Excessive quantities of middling material (in terms of desirable ash content) which are dominated by hydrophobic carbonaceous material. This controls the flotation washability.
3. Rapid rates of flotation and concentrate removal which encourage entrainment and allow insufficient time for froth drainage. This will reduce grades in relation to the flotation washability.
4. Froth phase characteristics, including the ability of the froth to support large particles, and its mixing and drainage dynamics.

In the light of the adsorption (Section 3.5) and flotation testwork (Section 5.4.7), the first possibility was excluded, i.e. collector selectivity was considered adequate in distinguishing between coal and gangue surfaces.¹⁵ But although the selectivity of all the oily collectors was found to be good, particles of a certain ash content, which would be regarded as middlings, have an inordinately large carbonaceous surface area in relation to that of the ash-forming gangue minerals. These particles would be collected and would account for some displacement from the best possible separation function. This would explain the poor grade found even at low yields. Additional displacement from the density washability relation would result from inappropriate flotation control and poor froth phase characteristics.

¹⁵ Figure 5.40 also indicates that the macro-scale separation (selectivity) was much the same for all the oil types.

1. Large particles ($+150\ \mu\text{m}$) deformed the bubble on contact, but as the bubble regained its sphericity (most energetically favourable shape) the particle was invariably repelled.

Špetl and Dedek (1966) observed the approach of air bubbles and coal particles in a flotation cell using high speed cinematography and found that bouncing and loss of contact is dependent on the kinetic energy of the bubble on contact.

2. Medium sized particles ($-150\ +60\ \mu\text{m}$) collided and slid along the bubble surface to adhere at its lower pole. The time of sliding could be regarded as the available contact time.
3. Small particles ($-60\ \mu\text{m}$) were deflected by fluid streamlines unless they passed very close to the bubble surface.

As the particle size decreases so the influence of inertial forces decreases and that of interfacial forces increases. Leja and He (1984) believed that when inertial forces are too small to ensure contact, small particles rely on the interaction of their surface forces and those of the bubble and must therefore pass very closely. Electrostatic and/or Van der Waals forces may then induce the particle to "precipitate" on the bubble surface; though by the same token electrostatic interactions may result in particle repulsion.

Trahar (1981) observed that the flotation recoveries of coarse and fine particles of several minerals were considerably poorer than the recoveries of intermediate sizes. These observations were based on both plant and laboratory flotation data. The results presented conform to the understanding of the collision mechanisms for particles of various sizes discussed above. While the same trend was evident with the several minerals tested, Trahar (1981) pointed out that it is not possible to define the size ranges specifically since flotation response varies with both the type of mineral and the flotation conditions employed. It is more convenient to refer to fine, intermediate and coarse particles.

Deraguin and Dukhin (1961) proposed that a third capture zone exists between the long range hydrodynamic zone and the very short range molecular force zone and termed this the diffusio-phoretic zone. In this zone they proposed the disturbance of charges in the electrical double

layer caused by the approach of bubble and particle and the disturbance of bubble surface adsorption equilibrium by surface distortion leads to adsorbate concentration gradients. Diffusion to or from the bulk aqueous phase thus occurs and this affects particle-bubble capture. However in the approach of particles of reasonable size (i.e. not ultrafines), which are of practical importance, diffusio-phoretic forces apparently play only a minor role in particle-bubble attachment (Schulze, 1984, p.78).

Al Taweel et al (1986) found that flotation of small particles is controlled mainly by collision probabilities whereas that of larger particles is more strongly influenced by the strength of bubble-particle attachment. The flotation of a relatively coarse coal feed, as in this work (-500 μm r.o.m. material), would therefore be expected to be strongly influenced by the type of oil used as the collector, and by the type of surfactants present.

Ahmed and Jameson (1985) have shown experimentally that flotation rate is strongly dependent on bubble size, though obviously particle size, particle density and agitation conditions are also of importance. An increase of up to two orders of magnitude was found when bubble size was reduced from 655 μm to 75 μm (depending on agitation conditions). With coal feeds of constant size distribution, a reduction in bubble size would therefore be expected to enhance the flotation rate significantly. The theoretical model of Jiang and Holtham (1986) predicted a significant increase in collision efficiency for -50 μm solid particles and bubbles smaller than 360 μm in diameter; and a bubble size below 260 μm was predicted to offer the best collision efficiency for ultrafine particles.

5.2.3 The bubble-particle attachment process

After bubble-particle contact, adhesion must be sustained if the particle is to be floated. For successful attachment, the force of attachment must equal or exceed forces contributing to the destruction of the bubble-particle aggregate. It has been suggested (Tyurnikova and Naumov, 1981, p.141) that these forces can be related as follows :

$$F_1 = F_2 + F_3 + F_4 \quad [5.3]$$

where :

$$F_1 = \text{force of adhesion} = \pi d \gamma_{wa} \sin \theta$$

F_2 = Break off force due to gravity acting on the particle

F_3 = Break off force due to capillary pressure within the gas bubble

F_4 = Additional tear-off forces associated with the inertia of the particle and the drag force acting on the particle in turbulent zones of the pulp.

F_4 causes deformation (elongation) of the bubble surface resulting in an increase in γ_{wa} and θ in the vicinity of the elongation. F_1 therefore increases and it becomes increasingly difficult to detach the particle. (F_3 is not affected since surface tension over most of the bubble remains unaffected).

The mathematical expressions for the rupture forces (after Bogdanov) are given by Mackenzie and Matheson (1963). They used the relations to investigate the effect of coal particle size (s.g. = 1.35), relative particle-bubble velocity and the angle of incidence upon collision (rising bubbles and falling solids) and then calculated the contact angle necessary to maintain adhesion (F_1). Rupture was thus shown to be inevitable with large particles (1000 μm) subject to high velocities (over 30 cm.s^{-1}) and low angles of incidence (20° or less from the vertical). Head-on collisions of large particles and bubbles led to bouncing apart. In other instances typical coal-air contact angles¹ would be sufficient to maintain adhesion. Mühle et al (1982) considered the same set of forces acting on the aggregate and determined the maximum floatable particle size for given contact angles, turbulence, surface tension and particle and fluid densities. For example, for a particle with a density of 7.5 g.cm^{-3} and assuming an

¹ These are of the order of 120° (measured in the aqueous phase)

air-water interfacial tension of 50 mN.m^{-1} , Mühle calculated that particle-bubble aggregates subjected to an eddy acceleration (induced by the impeller) equivalent to one gravity unit (9.8 m.s^{-2}), would require contact angles of 10° and of 90° respectively for particles of a radius of 70 and $500 \mu\text{m}$. These same contact angles would sustain aggregates incorporating particles of about 35 and $300 \mu\text{m}$ respectively, if the eddy acceleration was equivalent to 10 gravity units.

As mentioned earlier, the adherence of air to the solid surface is governed thermodynamically by the possibility of lowering the surface energy. This is achieved by replacing a portion of the solid-liquid and liquid-air interfaces with a lower energy solid-air interface of equal area, i.e. that area of the adsorbed bubble which displaces the aqueous phase from the solid surface. Air nuclei adsorbed on the solid, as a result of exposure to the atmosphere or to air during conditioning, will increase the surface energy of the solid (as all adsorbed species do, Equation 3.9) so that bubble adherence will be enhanced since the accompanying decrease in free energy will be comparatively large. Pre-aeration during conditioning should consequently improve flotation performance. This is discussed in Section 5.4.1.1.a.

With regard to surface geometrical considerations, Špetl and Dedek (1966) found bubbles to adhere preferentially to surface asperities. The reasons could be that asperities puncture the thin aqueous film separating the solid particle and the bubble, stabilize the contact angle or reduce local surface charge; or a combination of these effects.

5.2.3.1 Induction and contact times

The relationship between particle and bubble contact time and the induction time (time between first encounter and aqueous film rupture) is known to be important in determining the success of attachment, and is therefore directly related to the probability of adhesion, P_a , in Equation 5.1. The induction time must be less than the contact time. Frothers are widely acknowledged to reduce induction times and their role in particle-bubble attachment is considered in more detail in Section 5.2.3.5. Geidel (1985) found that induction times obey an exponential distribution ($+100$ to $150 \mu\text{m}$ particles were studied) and believed this to be responsible for the success of

flotation kinetic models based on the gamma-distribution, of which the exponential distribution is a special case.

Ralston (1983) reviewed experimental times of bubble-particle contact, determined by using high speed cinematography, and reported that contact occurs in 10^{-2} s or less, a finding supported by Mackenzie and Matheson (1963). However Leja and He (1984) believed that the optical resolution of such techniques implies that measurement accuracy is limited to about 10^{-3} s and real contact time could be orders of magnitude smaller.

5.2.3.2 Adhesion theory

It is suggested that the particle, oil and bubble aggregate can be formed in several ways :

1. The bubble contacts the coal surface directly by adsorbing at a site unoccupied by oil.
2. The bubble adheres to the hydrocarbon phase which in turn adheres to the coal surface.
3. Bubble impact displaces the hydrocarbon from beneath the bubble to the edge of the contact area, i.e. the wetted perimeter. Klassen et al (1958) reported that photographic studies using oils containing dyes showed that the oil forms a rim along the bubble-particle-water wetted perimeter and believed that this rim stabilizes the adherence of large particles to bubbles.
4. Bubble impact displaces some oil to the contact perimeter but a thin layer of orientated hydrocarbon oil molecules remains between the air and solid phases in a manner analagous to surfactant adsorption.

The derivation of Young's equation (Section 3.2.6.1) assumes a planar, smooth solid surface onto which the oil droplet adsorbs. This assumption is reasonable as most droplets, in terms of number, are of the order of a few microns in size (see Chapter 2) which is much smaller than most of the coal particles in the pulp. Finch and Smith (1979) pointed out that the derivation has also been found to be valid

where the air bubble is comparatively larger than the solid particle, so that its surface is essentially flat over the area of contact.

However, air bubbles are not always that much bigger than many of the nominally -0.5 mm r.o.m. coal particles in the pulp, so the assumption of a reasonably planar surface for either the bubble or the solid is often unreasonable and the curvature of the surfaces will complicate the resolving of the interfacial tensions. The heterogeneity of the coal surface, from both physical and chemical points of view, also introduces largely unquantifiable complications. Surfactant (e.g. frother) adsorption at various interfaces within the system is certain to be evident and will also complicate an evaluation of the contact process.

If, for the moment, these complications are ignored, there still remain several complications arising from the existence of an independent liquid phase (the oil), i.e. the system is effectively a 4-phase system.

There is very little theory existing to interpret the behaviour of 4-phase systems. Despite the difficulties mentioned above, the extent to which the theory has currently been developed will be discussed.

Janczuk (1986) studied the adsorption of air bubbles onto a planar graphite surface which had been wetted with n-alkanes (from hexane to hexadecane). In developing his theory, a constant film thickness was generally assumed, as shown in Figure 5.1, although a variation was also considered in which the film thickness below the bubble increased. The hydrocarbon oil exists as a continuous film on the solid, the net result being a modification of the surface tension of the solid, in a quasi-surfactant manner, the difference being that the hydrocarbon film is many (perhaps hundreds of) statistical monolayers thick. The relevant interface is regarded as that between the hydrocarbon film and the water though the solid influences the interfacial tension of this interface (by influencing the orientation of the adjacent hydrocarbon molecular layers).

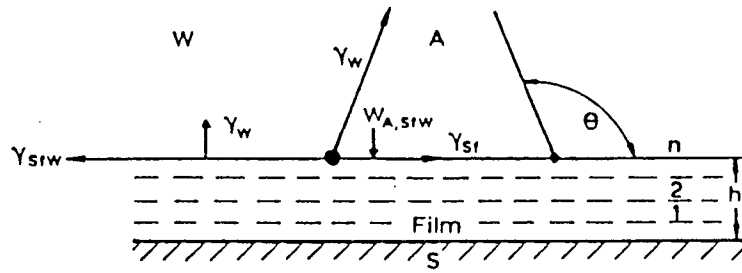


Figure 5.1 : Schematic representation of the equilibrium state in the system solid-n-alkane film-air bubble-water for a thin film. A, air; S, solid; W, water. (After Janczuk, 1986).

The oil was assumed to have a zero spreading coefficient at the air-water interface to avoid unmanageable complications to the theory. However in reality it is evident that a thin film or minute lenses would in fact exist on the bubble (and modify its surface properties) since repeated bubble contact was the means used to reduce the oil film on the solid.

The solid was assumed to control the structure of the *thin* hydrocarbon film. This orientation of statistical monolayers of the oil adjacent to the solid surface reduces the effective solid surface tension, i.e.

$$\gamma_{sfa} = \gamma_{sa} - \pi \quad [5.4]$$

where γ_{sfa} is the surface tension of the solid with a thin hydrocarbon film on its surface. The water itself is assumed to have no effect on the hydrocarbon film structure at the solid-hydrocarbon film-water interface (sfw).

π can be regarded as the pressure within the stable hydrocarbon film between the solid and the air bubble in an analogous manner to the disjoining pressure (Section 3.2.5). Janczuk (1986) equated this pressure to either the work of spreading, or the work of immersional or of adhesional wetting - depending on his experimental approach - and used these relationships to predict contact angles. Young's equation incorporating a suitably modified solid surface tension was used for this purpose.

$$\gamma_{sfa} - \gamma_{sfw} = \gamma_{wa} \cos \theta_e \quad [5.5]$$

or, substituting Equation 5.4,

$$(\gamma_{sa} - \pi) - \gamma_{sfw} = \gamma_{wa} \cos \theta_e \quad [5.6]$$

The terms γ_{sa} and γ_{sfw} were evaluated assuming a completely hydrophobic solid and an entirely non-polar hydrocarbon liquid, i.e. their interactions were assumed to be dictated entirely by dispersion forces², so that the theory of Fowkes³ could be used to estimate these values (see Janczuk, 1986). Equation 5.6 was used to predict contact angles.

Actual contact angles were initially measured in the presence of an excess hydrocarbon film. Following these measurements the thickness of the hydrocarbon film was regulated by repeated contact with fresh air bubbles, each one removing a proportion of the oil until a stable film remained. The contact angle was again measured. In some instances (excess hydrocarbon film) the correlation between actual and predicted contact angles was excellent. The correlation was reasonable for films of reduced thickness for the aliphatic hydrocarbons in the series decane to hexadecane; but not with lower boiling point homologues.

In this particular experimental situation (a flat surface and a continuous surface hydrocarbon film) Young's equation proved an adequate model.

However, in actual coal flotation this author believes that this scenario is unlikely, for several reasons :

1. The coal surface cannot be regarded as completely hydrophobic (as discussed in Section 3.2.8), nor are all oily collectors entirely non-polar. In addition to pure dispersion forces there will be a degree of polar interactions which will vary with the coal and oil used. Interfacial and surface tensions will change and cannot be readily *calculated* as explained in Section 3.2.6.1. In addition a

² Dipole-dipole interactions

³ A semi-empirical theory used to predict interfacial tension between phases exhibiting little or no polar interactions.

hydrocarbon film is very likely to exist or form on the bubble surface upon contact with the solid (as discussed below).

2. None of the oils studied in this thesis (and by extension other high boiling point oils normally used as coal collectors) spread spontaneously on a coal surface (see Section 3.2.8). The oils will exist as discrete droplets, though some adjacent ones may coalesce to produce larger droplets - provided the presence of surfactants does not preclude this by stabilizing the oil-water interface; or that inertial forces do not disrupt the newly created larger droplets. Klassen et al (1958) believed that coalescence is the only mechanism which can induce a film on the solid surface, though applied mechanical force and inter-particle contact do promote spreading.
3. Since the oils exist as discrete droplets they often cannot be regarded as thin films as, in terms of molecular thickness (statistical monolayers), they are very thick and it is thought that the surface energy of the solid may have little influence on a large portion of the oil-water interface.
4. There is a strong possibility of an oil film or lens existing on the bubble. Bubble contact with an oiled particle can also induce some spreading at the air-water interface, depending on the type of oil used. This mechanism could allow a thin film of hydrocarbon oil to form between the bubble and the solid surface. The extent to which this occurs would be dependent on the oil type, since several oils, notably high boiling point saturated alkanes, do not spread spontaneously at the air-water interface; while others do.

Aronson et al (1973) specifically studied four phase systems. They studied the stability of a four phase contact line (solid-oil-water-vapour). The solid was assumed to be homogeneous, flat and rigid as is normally the case in such studies, while the oil droplet and a thin non-continuous water film were spread on the solid surface. Vapour formed the fourth phase, overlying the oil and water and just contacting the solid surface at the 4-phase line of contact between solid, water, oil and vapour (Figure 5.2a). This system is geometrically more realistic in terms of flotation than that studied by Janczuk (1986) but is not quite analagous to that in coal flotation

since the extents of the water and vapour phases are reversed. In flotation the aqueous phase forms the bulk overlying phase and the vapour (air) a bubble which is attached to the solid surface. The development of the theory is nevertheless similar.

Aronson et al (1973) investigated the stability of the 4-phase contact line in terms of the fluid contact angles and interfacial tensions by considering the system in a state infinitesimally removed from the 4-phase contact state and evaluating the tendency for interfacial movement following this displacement. The general finding was that conditions for a stable 4-phase line of contact were limited and that in practice the system tends to separate into 3-phase contact lines. Figure 5.2a represents the 4-phase system exhibiting a 4-phase contact line. Figure 5.2b shows (infinitesimal) movement towards the oil-solid-vapour and water-solid-vapour 3-phase contact lines and Figure 5.2c the tendency to form solid-oil-water and oil-water-vapour contact lines.

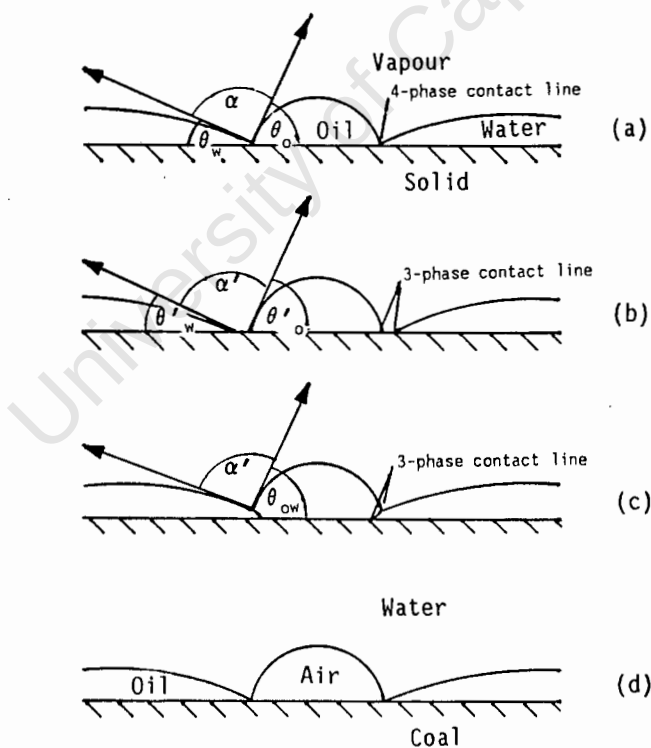


Figure 5.2 : 4-phase system configurations ((a), (b), (c) after Aronson et al, 1973)

It may be argued that in a flotation system where the extent of water and air (vapour) are reversed, Figure 5.2d would be a more reasonable representation of the 4-phase contact line. The geometry of

Figure 5.2d assumes that the oil does not spread over the coal or the air to even the extent of a microlayer, and that the air bubble is in contact with the coal. These are not necessarily realistic assumptions. In addition the geometrical axisymmetry of the system is also not necessarily realistic but is assumed for simplicity, as are the assumptions of a rigid, planar and homogeneous solid, though the latter two are patently untrue of a naturally arising coal surface.

Subsequently Aronson et al (1976) made specific studies of the static profiles of several solid-oil-water-vapour configurations involving an oil droplet attached to the solid and partially submerged by a water film. This system is again different to that found in the 4-phase coal flotation system with respect to the extent of some phases and in respect of the geometry of the system; though similar thermodynamic considerations will apply.

The possible variations in the shape of the various 3-phase contact lines (contact angles and the curvature of the fluid menisci) made their study of the behaviour of the 4-phase system very complicated from a geometrical point of view. The system configurations could only be determined by numerical iteration for a system with set boundary conditions and selected interfacial angles. The solutions for a set of interfacial angles yielded a series of interfacial profiles. Since the study of these profiles is not directly relevant to the flotation case, they are not considered further. The accompanying thermodynamic considerations, however, are useful for determining the type of 4-phase behaviour which can be expected in flotation and are discussed below.

The conditions for the stable formation of a 4-phase geometrical configuration similar to that shown in Figure 5.2d (4-phase contact line) are:

$$\gamma_{oa}^2 > \gamma_{wa}^2 + \gamma_{ow}^2 - 2\gamma_{wa}\gamma_{ow} \cos(180 - \alpha) \quad [5.7]$$

where $\alpha = 180 - \theta_o - \theta_a$.

Inequality 5.7 was derived, by this author, by following a similar argument to that of Aronson et al (1973) who derived an inequality of similar form: the interfaces considered in Inequality 5.7 are not precisely those considered by Aronson et al

(1973), but have been altered to conform to those most likely to be found in coal flotation.

The behaviour of the 4-phase flotation system may now be considered, using typical values for the interfacial and surface tensions. These are listed in Table 1.4.

Typical values of the air-coal-water contact angle, θ_a (measured in the air) are 55 to 60° (Horsley and Smith, 1951). Typical values for the oil-coal-water contact angle, θ_o (measured in the oil) are between 60 and 150° (Brown et al, 1958). Substituting these values, and those typical of the interfacial tensions (Table 1.4) in Inequality 5.7 showed that this inequality does not hold for any combination of these typical values. In other words a stable 4-phase contact line will not exist in coal flotation. 3-phase contact lines, oil-coal-water, oil-coal-air and air-oil-water, will prevail.

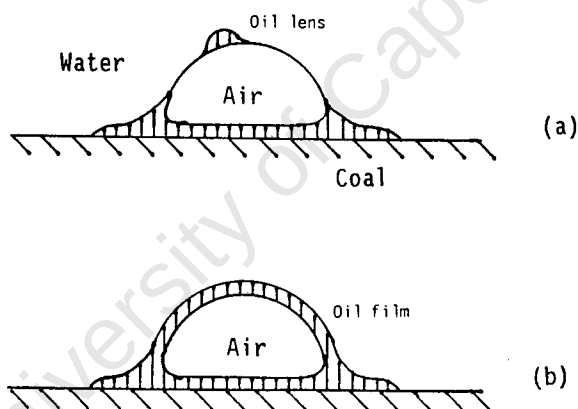


Figure 5.3 : Schematic representation of likely phase configurations in a coal flotation system

Probable configurations, envisaged by this author, are shown schematically in Figure 5.3a and b for conditions of oil spreading and non-spreading respectively. In view of the known air-avidity of oils, and the observations of Klassen et al (1958) that oils form a rim at the bubble-solid contact perimeter, a "collar" of oil on the air-solid contact perimeter is depicted. The thickness of the layer of oil at the air-water interface is exaggerated for clarity. The thickness of oil arising between the coal and the air bubble may be substantial as assumed in the work of Janczuk (1986) and is discussed in more detail below.

Earlier, reference was made to the possibility of the air bubbles adsorbing onto oil which in turn adsorbs onto the coal surface, i.e. there is no direct bond between the coal surface and the air. Finch and Smith (1979), in their review of emulsion flotation theory, implied that this mechanism is probably typical of such 4-phase systems. The air-oil adsorption is regarded as one of simple fluid-fluid coalescence, along the lines suggested by Torza and Mason (1969) who studied the coalescence of two immiscible liquid drops suspended in a third immiscible liquid. The oil represents a low energy surface which is readily dewetted thereby allowing air-oil adhesion.

The spreading coefficient as defined during the derivation of Inequality 2.6 is, for three unspecified fluid phases,

$$F_{si} = \gamma_{jk} - (\gamma_{ij} + \gamma_{ik}) \quad [5.8]$$

F_{si} must be positive for spontaneous spreading. If it is negative a contact angle or else no attachment occurs. Torza and Mason (1969) showed from Equation 5.8 that three equilibrium conditions are possible for the three fluid phases; engulfing, partial engulfing and no adhesion.

In terms of coal flotation, where the fluid phases are water, oil and air, possible changes in phase behaviour where water already surrounds the other two phases are therefore :

$$\gamma_{wa} > \gamma_{ow} + \gamma_{oa} \quad (\text{air engulfed by oil}) \quad [5.9]$$

$$\gamma_{ow} > \gamma_{oa} + \gamma_{wa} \quad (\text{oil engulfed by air}) \quad [5.10]$$

$$\gamma_{oa} > \gamma_{wa} + \gamma_{ow} \quad (\text{no oil-air contact, i.e. water is not displaced}) \quad [5.11]$$

$$\gamma_{wa} < \gamma_{ow} + \gamma_{oa} \quad (\text{air-oil contact angle formed}) \quad [5.12]$$

From the values given in Table 1.4 it is evident that Inequalities 5.10 and 5.11 will not hold and that an air-oil interface or spreading of oil at the air-water interface will *always* occur when bubbles and oil come into contact. The particular behaviour exhibited

will be dependent on the oil-water interfacial tension and thus on the type and purity of the oil.

The adhesion of an oiled particle to an (unoiled) bubble is therefore somewhat different to the adhesion of a bubble to a solid surface which has collector adsorbed on a free-molecular basis. In the latter instance Leja and Schulman (1954) have proposed that the interactions of the two sets of surfactants, the frother at the air-water interface and the collector at the solid-water interface, control the adhesion. The two surfactant layers inter-penetrate and the resulting frother-collector molecular interactions reduce interfacial tensions and stabilize the adhesion. Similar surfactant interactions may well occur at the oil-air interface formed but classical fluid-fluid coalescence (between oil and air) will permit adhesion even in the absence of surfactants. If the bubble is itself oiled, then coalescence of the oil layers on the oiled bubble and on the oiled particle will also occur. The influence of the oil in this respect is considered in more detail in Section 5.2.3.4 below.

Summary

In summary it appears that a 4-phase line of contact is unlikely to occur in a 4-phase coal flotation system (and is definitely unstable) and that the oils will form a small "collar" along the bubble-solid-water wetted perimeter. If they are aromatic or not highly refined they will spread over the air-water interface. It is very probable that an oil layer exists between the solid and the air bubble (oiled or unoiled), the adhesion of the bubble to the oil droplet being one of classical fluid-fluid coalescence.

In considering a model for 4-phase systems the coal must be assumed to be rigid, flat and homogeneous, the latter assumptions and particularly the last being entirely unrealistic. Furthermore the actual behaviour of the oils will be strongly influenced by the type and concentration of surfactant and the degree to which these adsorb at the available interfaces. These difficulties, further complications introduced by the dynamic, non-equilibrium environment typical of flotation cells as well as the difficulties in accounting for actual

interfacial profiles (system geometry) amount, in the opinion of this author, to a virtually intractable modelling problem.

There seems little prospect of developing a comprehensive model for this system at present. In the light of the need to make serious simplifying assumptions in order to model the adhesion process it seems that the well-established Young's equation, in which the geometry of the oil phase is ignored but the influence of the oil film or lens on air-water and coal-air interfacial tensions is included, is currently as good a model as any.

5.2.3.3 The influence of the coal surface

In coal flotation the ratio of hydrophobic to hydrophilic coal surface sites is governed by the relative proportions of non-polar hydrocarbon massive and of polar surface groups. These latter are non-ionizable carbonyl and aliphatic alcohol groups and ionizable carboxylic and aromatic alcohol (phenolic) groups; as well as polar and ionized mineral groups.

A degree of surface hydrophobicity is essential to satisfying the thermodynamic criterion represented by Equation 5.2, since there is otherwise no inducement for the thinning and rupture of the aqueous film between bubble and oiled particle. On the other hand the ionizable groups produce electrical charges which can hinder the adhesion process (and hence flotation) even in a thermodynamically favourable system. Coal surface oxidation is therefore clearly harmful to flotation.

Taylor et al (1981) suggested that many of the flotation problems associated with the alteration of coal surface properties (increased hydrophilicity) as a result of weathering could be avoided by treating freshly mined material, i.e. by avoiding extensive coal stockpiling prior to treatment. Although heavily oxidized coals can be rendered floatable by using promoters (Section 3.2.7.1) these reagents are also likely to improve the floatability of typical gangue minerals, thereby diminishing the chances of effective beneficiation.

A means of evaluating coal wettability, and by association coal surface characteristics, is given by Hornsby and Leja (1984). The

the air bubbles thereby preventing or delaying the formation of a stable film. Increased reagent dosages are inevitably required.

The influence of the type of oil and its purity (with regard to surface-active constituents) on bubble-oil coalescence has been discussed in Section 5.2.3.2 above. The strength of the bubble-particle aggregate and the role played by the oil in this regard is now considered.

As in oil droplet-particle adsorption, the turbulent conditions within a flotation cell make it imperative that the air-oiled particle contact angle increases rapidly after contact if the particle-collector-bubble aggregate is to be stable. If the collector is unable to provide this increase then rupture invariably occurs.

The difference between the static contact angle and the maximum possible angle gives an idea of the flexibility of the aggregate system. Flexibility has been found to increase with a decrease in particle size. Trahar (1981) has shown that the minimum degree of hydrophobicity needed for flotation decreases with the size of the particle. Small particles thus permit a fair degree of latitude in the collector strength needed for maintaining the bubble-particle aggregate. Some oils may therefore be unsuitable for coarse coal flotation while being able to float fine particles adequately.

Glembotskii et al (1970) reported that the strength of particle-bubble attachment depends on the thickness of the hydrocarbon film and that the accumulation of oil along the wetted perimeter increases the bond strength. Janczuk (1983) studied the stabilizing effect of n-alkanes (the homologous series from hexane to hexadecane) on quartz-air adhesion. He found that the force needed to detach air bubbles is influenced by the thickness of the hydrocarbon film and the length of the hydrocarbon CH_2 -chain. The force increases with the latter and displays a definite maximum with the former. The shorter the hydrocarbon chain length the more readily the oil spreads over or diffuses into the air bubble thus reducing the film thickness on the solid. If this solid surface film is thinned too far by the process, the strength of attachment decreases. Long chain hydrocarbons are more resistant to spreading and diffusion and therefore stabilize the bond.

In a flotation system the bubble may become oiled prior to contact with solids. Laskowski and Miller (1984) indicated that the attachment of an oiled bubble and an oiled particle will be facilitated by the coalescence of their respective oil films or lenses and that this mechanism would be absent for oil-free bubbles. They quoted attachment times up to 20 times faster (5 ms) with oiled bubbles as opposed to un-oiled ones.

Smitham and Firth (1982) stated that the mechanism by which the oil increases the strength of bubble-oiled particle adhesion is still not clear. The ease with which the oil and air phases coalesce (as discussed above) in relation to the attachment of the bubble to a solid surface, as well as the ability of some oils to engulf the bubble, provide a suitable qualitative explanation.

5.2.3.5 The role of frothers

The performance of the froth flotation process is characterized by two indices : 1. the recovery and 2. the grade of the concentrate. The frother affects both indices in that it influences the formation and stabilization of the froth and particle-bubble attachment.

As has been mentioned before, frothers used in practice are usually non-ionic surfactants since this property limits their collecting ability and reduces their sensitivity to pH and water quality. Non-ionic surfactants can have widely varying hydrophile-lipophile balance (H.L.B.) values (Section 2.2.4), i.e. their surface-active tendencies can vary in both type and intensity. For this reason frothers can be expected to have varying influences on the flotation process as a whole, since their adsorption is not restricted to the air-water interface. Some frothers (those with H.L.B. values above 7) will assist oil dispersion.

The influence of non-ionic surfactants on oil spreading and adhesion will be limited since they possess negative polarity which will restrict their interaction with unwashed coal surfaces. Their effect with very hydrophobic coal will be to reverse their adsorption orientation and hence to increase the hydrophilicity of the coal

surface as the coal surface (negative) charge increases. Surfactants with positive polarity or charge are expected to be beneficial to oil adhesion and spreading.

The type of frother and consequently its interfacial behaviour determines the form and persistence of the froth with any one oil. This in turn influences the size of particle which may be retained in the froth. Comparatively weak frothers may be unable to support large particles in the froth; the froth will tend to collapse.

The influence of the type of frother on recovery of coal of various size fractions (+500, -500 +88 and -88 μm) has been studied by Klimpel and Hansen (1987). Kerosene was used as the collector at dosages of 0, 1 and 2 lb.ton^{-1} and frother at a dosage of 0.2 lb.ton^{-1} , based on solids mass.⁴ Commercial frothers were found to have an optimum operational particle size range. MIBC is more effective with fine rather than coarse coal particles.

Frothers are often believed to harm concentrate grades, but because typical frothers are non-ionic this effect should only be prevalent at excessively high dosages. Aston et al (1981) found that MIBC rendered Newcastle (Australian) coal somewhat more hydrophilic (at a $10^{-3} \text{ mol.l}^{-1}$ [$136 \mu\text{l.l}^{-1}$] dosage) in that it increased the proportion of coal remaining in the water phase of an aqueous/hexane system. This is a much higher (up to 10 times) dosage than normally used in flotation. They acknowledged that the effects of non-ionic surfactants in water-mineral-oil systems are very complex and not thoroughly understood at present.

Tyurnikova and Naumov (1981, p.98) believed that frothers improve the strength of air bubble-particle attachment because they reduce the bubble capillary tension and hence the force of attachment required (Equation 5.3). On the other hand, Finch and Smith (1975) found that a decrease in bubble surface tension, which accompanies progressive surfactant adsorption, and is therefore a time dependent phenomenon, generally hindered bubble-particle attachment, implying that newly created bubbles will adhere best. However once attachment

⁴ Frother dosage on the basis of mass per mass of coal is not the best manner in which to add frother, as discussed in Section 5.2.3.5.a, and can cause misleading comparisons between frothers since molecular concentrations will vary.

was achieved, further bubble aging had no apparent effect. Electrical double layer repulsion is probably the reason for the observed attachment-retarding action of surfactants.

The impact of an alteration of bubble surface tension is also manifested in other ways. For instance, Špetl and Dedek (1966) found amyl alcohol (a surfactant similar to MIBC) reduced bubble speed. Reduction in bubble speed is reported to have a favourable influence on adhesion, though this could also be attributed to the influence of the surfactant at the solid surface. A reduction in bubble speed would be evident in flotation systems since surfactants are always present. This is due to the surfactant immobilizing the interface and preventing internal gas circulation so that the fluid drag over the bubble is increased. Surfactants adsorbed at the bubble surface result in the bubbles behaving more like a solid particle. However there is constant movement of surfactant as the bubble rises, with the surfactants tending to congregate at the pole opposite to that encountering the liquid stream. Surface rigidity is therefore not symmetrical. This movement also induces dipolar behaviour as discussed in Section 4.2.2.2.

Leja and He (1984) considered a less widely appreciated beneficial action of the surfactant. They postulated that the presence of frothers at the air-water and solid-water interfaces (of the bubbles and particles respectively) is able to improve particle-bubble contact and adhesion by helping to overcome the electrostatic repulsive forces which will be encountered as the electrical double layers of each encounter one another. In coal flotation both the oiled coal and the bubbles are likely to be negatively charged. Upon encounter, redistribution of charges takes time; this time depends on fluid viscosity, ion mobility in the diffuse layer and the conductivity of the solid.

Leja and He (1984) postulated that the attachment process can be accelerated (i.e. induction times reduced) by non-ionic surfactants with their permanent dipoles (in MIBC this would be the OH-group). Their dipolar nature allows them to reorientate themselves when encountering another electrostatic field, so that electrostatic repulsion is summarily turned to electrostatic attraction as shown by Figure 5.4.

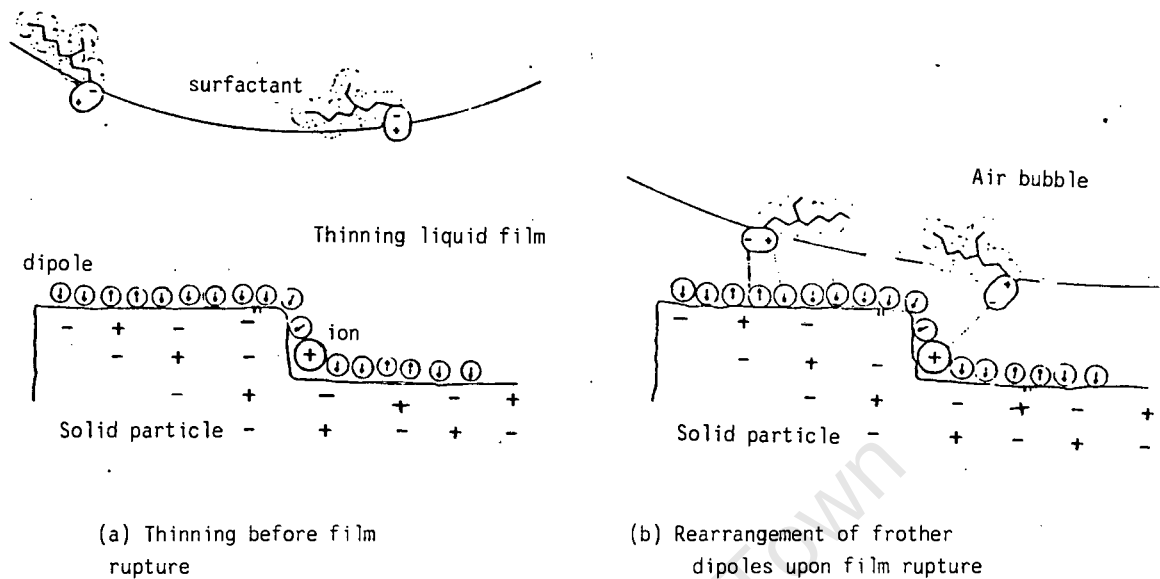


Figure 5.4 : Model of frother action involving realignment of dipoles. (Modified from Leja and He, 1984).

Two conditions are necessary though for promoting successful bubble-particle adherence :

1. The surfactant dipole re-orientation time must be shorter than the contact time. Re-orientation times from 10^{-10} to 10^{-12} s are quoted. Exact measurement for alcohol type frothers is hampered by the overwhelming excess of water molecules which possess a similar dipole moment. The density of the surfactant packed at the respective interfaces affects the overall re-orientation time so that in practice this evidently varies from 10^{-5} to 10^{-11} s. These times are considerably shorter than the dynamic contact time normally quoted in the literature, this being of the order of milliseconds.
2. The surfactant molecules must be sufficiently diffuse in the interfacial film to allow the reversal to occur. Close packing at the interface in a manner analogous to inter-molecular distances in liquids or even solids is therefore harmful. Close packing (because of strong adsorption) is resisted by molecular "bulk" which is in turn enhanced by side branching. Leja and He (1984) believed this is the reason why branched alcohols, which have less

intrinsic frothing power than their normal-isomers, are actually better frothers in flotation systems.

A final proviso is that the frother molecule must be capable of fostering Van der Waals bonds in addition to enhancing temporary electrostatic attraction as the latter effect will be countered by the re-orientation of water molecules, which are themselves strong dipoles. (Van der Waals bonds develop between the hydrocarbon portion of the frother and similar groups at the solid and oil surfaces).

a) Frother addition

Whether frother should be added in terms of solids mass or in terms of water volume has been debated in the literature, though it would appear self-evident that its vital activity at the water-air interface would make dosage according to its water concentration essential. This notion is substantiated by the work of Swanson et al (1984). They found the yield of coal to increase rapidly with increasing frother (MIBC and Teric 405) concentration until a definite plateau was reached. A frother concentration of around 10 g.t^{-1} of water ($12 \mu\text{l.l}^{-1}$ for MIBC) was the minimum for effective flotation. Eveson et al (1957) reported that optimum frother (MIBC) concentrations were 18 to $25 \mu\text{l.l}^{-1}$ for pulp solids contents between 4 and 12 % , and 25 to $30 \mu\text{l.l}^{-1}$ for solids contents of 12 to 20 %. The higher dosage was needed with the higher pulp densities in order to replace frother lost from the (batch) cell as concentrate was removed.

Jowett (1958) studied the influence of frother adsorption (onto coal) on coal recovery and found that in batch flotation many Australian bituminous coals remove the frother (20 % cresylic acid in ethanol) from the pulp rapidly. Cresylic acid is a phenol (aromatic alcohol) so MIBC (aliphatic alcohol) might be expected to be similarly adsorbed. Early frother addition would therefore be expected to harm flotation performance.

Eveson et al (1956) studied the adsorption of pure phenol from aqueous solution by coal and found the adsorption obeyed Freundlich's isotherm over the range of concentrations used (between 47 and $1417 \mu\text{l.l}^{-1}$) :

$$x/m = Kc^n \quad [5.13]$$

where : x = mass adsorbate (phenol) adsorbed
 m = mass adsorbent (coal)
 c = Equilibrium concentration of adsorbate
 K, n = constants

The equilibrium adsorption levels increased with increasing coal specific surface area, which itself tends to increase with decreasing rank.

Since coal recovery is dependent on frother concentration in solution and this can be severely reduced by adsorption onto coal or oil (or absorption by oil), frother dosages must often be increased to ensure adequate recovery. In terms of frother adsorption by the coal, prolonged conditioning is an aggravating factor; as is increased pulp density when frother dosages remain fixed. Jowett (1958) established that flotation recovery was unaffected by conditioning time or pulp density at high frother dosages but was markedly dependent on this at lower dosages (which are generally used in flotation). The presence of oil may also contribute to the loss of surfactants from air-water interfaces. In addition to adsorption at the oil-water interface, the partitioning of frothers like MIBC, which are preferentially soluble in oil (Section 2.2.4.3), may result in a net loss of oil from the aqueous phase, and hence the air-water interface, if conditioning with frother is prolonged.

Since conditioning is essential for oil dispersion and adsorption it appears practical to add the frother to the pulp as late as possible. The prior adsorption of oils is also known to reduce the adsorption of frother, presumably by reducing the number of coal surface adsorption sites.

5.2.4 The observed flotation activity of various hydrocarbon oils

Pooley (1967) reported that insoluble, neutral hydrocarbon liquids are the most efficient coal collectors. Petukhov (1979) recommended hydroxy compounds with long, water repellent radicals which should consist of at least seven carbon atoms for flotation of low rank coals.

The oxidation of hydrocarbon oils has been found to improve their flotation performance. Tyurnikova and Naumov (1981, p.144) quoted researchers as finding that the maximum efficiency of kerosene as a coal flotation agent occurs when its proportion of oxidized constituents is 12-14 %. However further oxidation leads to dramatic increases in the ash minerals recovered. This is obviously because the increased polar nature of the oil allows it to interact excessively with the hydrophilic (polar) solid surfaces.

Flotation activity is clearly dependent on oil molecular structure, inter-molecular bonding energies and so on. Tyurnikova and Naumov (1981) listed reagents in order of decreasing flotation activity as :

Unsaturated,
aromatic,
naphthenic (cycloparaffinic), and finally
non-cyclic saturates.

A typical commercial oil molecule could well be a composite structure of paraffinic, naphthenic and aromatic structures as shown by Figure 5.5.

Non-polar oils of petroleum origin can have different physico-chemical properties (viscosity, molecular weight, chemical structure) depending on the origin of the crude. Unsaturated hydrocarbons are unlikely to be present in commercial oils because their reactive nature makes them a rarity in crude oils (Kirk-Othmer Encyclopedia of Chemical Technology, 1978, Vol.17, p.124). Though a considerable quantity of olefins are produced during the refining process these are relatively low boiling point (often gaseous) compounds. Crude oil also possesses various oxygen, sulphur and nitrogen bearing organics as well as waxes. These substances are largely but not entirely removed during refining. Certain species of the former group (those in which the functional group is charged or polarized) will display surface-active character. Glembotskii et al (1970) reported that mineral oils rarely possess more than 30-40 % aromatics. Normal and iso- paraffinic and naphthenic (cyclo-paraffinic) compounds constitute a larger proportion, though this proportion tends to decrease with an increase in oil boiling range, i.e. molecular weight (Kirk-Othmer Encyclopedia of Chemical Technology, 1978, Vol.17, p.120).

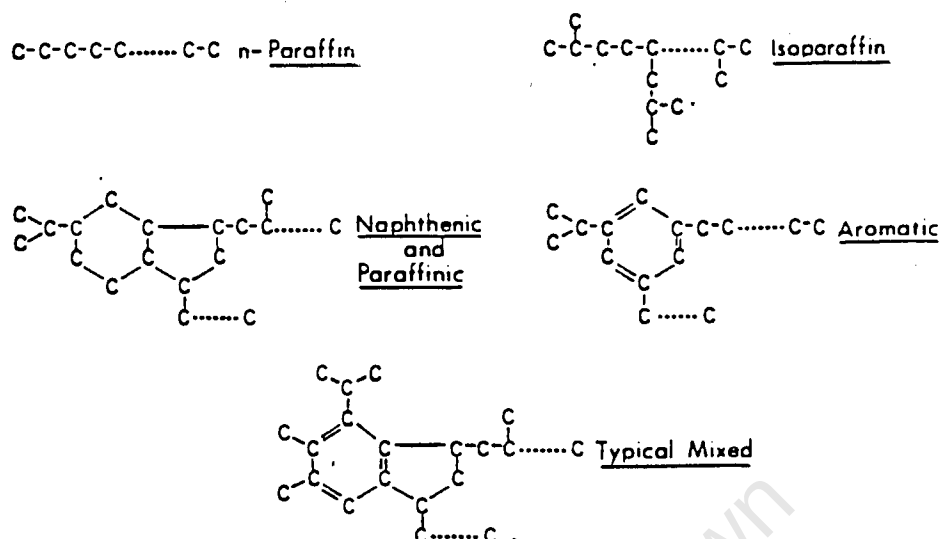


Figure 5.5 : Structural diagrams of typical hydrocarbon molecules found in petroleum oils. (After Smit and Bhasin, 1985).

Smit and Bhasin (1985) also found clear distinctions in the performance of oils with different molecular structures when floating molybdenite which, like coal, is naturally hydrophobic. In this case aromatics were poor collectors, though the performance hierarchy can be expected to differ from that of coal. Malyuk et al (1979) found aromatics out-performed naphthenes and iso-paraffins in the flotation of martite.

The flotation performance manifested with various oils is obviously influenced by the coal itself since the floatability of a coal is governed to a considerable extent by its inherent physico-chemical nature. Bituminous coals are generally acknowledged to be more floatable than those of lower or higher rank. With any one coal, flotation performance is strongly influenced by the choice of the collector-frother combination. The coal flotation activity of various oils is considered below. The joint action of oil and frother is discussed in Section 4.2.5.

Brown et al (1958) reached the rather unexpected conclusion that value as a flotation collector was connected with the poor spreading ability of the oil. Poor oils with respect to flotation performance were those with the smallest negative spreading coefficient, i.e. those that spread most easily on the coal. The best pure flotation reagents were

the worst spreaders though this was not always the case with the impure oils. Paraffin, decane and hexadecane and high boiling point petroleum fractions were found to be good collectors while benzene and p-xylene were not. This is apparently in conflict with the observations of other workers discussed above. Unfortunately, although the work of Brown et al (1958) was related to flotation performance, few actual flotation results were presented thereby making an assessment of their conclusions impossible.

Brown et al (1958) concluded that poor coal flotation reagents (oils) are not poor because of adsorption within the coal, as is often postulated, as values of the adhesion tension ($\gamma_{ow} \cos \theta_e$) indicated that spontaneous spreading into capillaries or pores does not often occur (see Section 3.2.8); though benzene did spread easily and could penetrate coal fissures more readily than the other oils used. They suggested that poor flotation performance is a result of oil spreading onto air bubbles and leaving a deficiency on the coal. The oils which do not spread at the air-water interface are therefore the best collectors.

Steedman and Krishnan (1987) reported that light, more refined oils such as kerosene and fuel oil exhibit a better selectivity for carbonaceous material than heavier oils (bunker oil, coal tars); the latter apparently possessing functional groups capable of interacting with the mineral matter surfaces.

Tyurnikova and Naumov (1981, p.134) found the highest flotation activity with hydrocarbon reagents with boiling points falling between 200 and 250°C. Typically, these reagents have 13 to 15 carbon atoms per molecule and a molecular mass of around 185. Glembotskii et al (1970) believed that the decrease in performance above 240°C is caused by the low dispersity of viscous oils and consequently the unlikelihood of sufficient conditioning time in flotation practice. The decreased performance of lower boiling point homologues has already been discussed (Section 5.2.3.4).

Whelan (1953) investigated some distillation fractions of commercial oils as well as some simple substituted phenols as collectors for coal. He took three oils and fractionated each of them into 12 narrow (20°C) boiling ranges. These fractions were then tested for their flotation power.

The oils had the following compositions:

Oil A: 13 % unsaturates, 54 % aromatics, 33 % paraffins.

Oil B: 29 % unsaturates, 60 % aromatics, 11 % paraffins.

Oil C: 100 % aromatic (pure phenol)

Unsaturates were classified as those soluble in 80 % sulphuric acid, aromatics as those soluble in 98 % H_2SO_4 (but not 80 %), and paraffins those insoluble at both concentrations.

Two coals were used in this testwork: an easy-to-float coal from Gresford colliery in Wales, and a more difficult-to-float coal from Beddlington in Northumberland. Ash contents were 24 and 26 % respectively. The oil dosages used were 0.30 and 0.73 kg.tonne⁻¹ for the Gresford coal and 1.10 and 1.85 kg.tonne⁻¹ for the Beddlington coal.

Little variation was found except that fractions boiling below 180°C or above 280°C were less effective than those in the middle of the range. Good yields of clean coal were obtained from both raw coals with the 180 to 240°C fractions obtained from the A and B oils. Oil A (high alkane content) fractions were slightly superior. Oil C gave excellent results with Gresford coal but not with Beddlington coal.

This is surprising in that the somewhat polar nature of phenol should allow it to interact with the polar groups inherent on the surface of more difficult-to-float coal (via a hydrogen bonding mechanism in particular). Presumably some other shortcoming of this oil was responsible. At equivalent yields oil B gave the best results with respect to ash content and oil C the worst. The latter behaviour is expected because of the ability of phenol to interact with polar gangue mineral groups. Whelan (1953) concluded that the effects are complex and that mixtures of collectors are often more effective than their individual components.

Glembotskii et al (1970) and Malyuk et al (1970) suggested that viscosity is an important appraisal criterion for hydrocarbon collectors since the properties of non-polar oils are interrelated with their viscosity. These authors believed that viscosity can influence the collector droplet size and so ultimately the flotation performance. However, the review of the literature on oil dispersion (Section 2.2)

indicated that the viscosity of the oil⁵ has little influence on the size of the oil droplet in a dispersion. Figure 2.12 shows the similar droplet size distributions of three Pegasol 3745 boiling (and hence viscosity) ranges. Smit and Bhasin (1985) stated that oils of particular character (paraffinic, naphthenic or aromatic) each have a distinctive temperature-density-viscosity relationship. The oil-water interfacial tension and the presence of surfactants (with which the former is associated) control droplet dispersion characteristics.

To eliminate droplet size as a variable, Malyuk et al (1970) emulsified all the oils tested at the same kinematic viscosity (82 cS) by altering the temperature and then conducted flotation under ambient conditions. In floating *martite*, they found that the effect of the oils on flotation performance increased dramatically between about 3 and 400 cS. This could not be attributed to different droplet sizes since these were the same. This finding supports the notion that it is the chemical characteristics of the oil (to which viscosity is related) and not the size of the droplet *per se* which is responsible for the induced flotation performance.

At viscosities greater than 400 cS the effect of a viscosity increase on flotation performance levelled off. Glembotskii et al (1970) suggested that the increase in viscosity, which is largely a result of increased Van der Waals bonding within the oil, increases the strength of bubble-particle contact. Viscous oils can therefore be expected to be more effective than lower viscosity oils in flotation of coarser particles.

In contrast to Malyuk et al (1970), Mishra and Holmes (1981) found little change in recovery or in concentrate ash levels of coal floated with commercial oils increasing in absolute viscosity from 3 to 627 cP: no attempt was made to regulate droplet size. This finding supports the belief that viscosity is itself an insufficient criterion for predicting flotation performance. A -1 mm feed coal was used with a size distribution similar to that of coal used in this thesis (see Table 5.1). The distribution is given below :

⁵ The viscosity of the continuous-phase is of importance (Equation 2.12). In coal flotation the continuous phase is water.

-1000 +500 μm	21.0 %
-500 +250	21.5 %
-250 +150	17.2 %
-150 +75	17.1 %
- 75 +63	1.7 %
- 63 +53	7.0 %
- 53	14.1 %

Malyuk et al (1970) also found (when floating martite) that the flotation performance was greater with aromatics than with the naphthenes and iso-paraffins of the same viscosity. They also found that sulphur containing oils were more effective than others and suggested that the higher aromatic content associated with such oils may be responsible. [Perhaps though trace constituents of the oil such as alkyl aryl sulphonates (detergents) were responsible for this]. A further finding was that the flotation effect of oils of the same class increased with viscosity.

Despite the apparent advantages of the correct oil selection, Klimpel and Hansen (1987) believe that gains in performance achieved with oils of varying composition are often overruled by economic considerations and other factors such as the efficiency of dispersion and the choice and dosage of the frother. Indeed the sub-processes studied have highlighted the importance of interfacial phenomena and surface activity. The determining influence of surfactants, which includes the type and dosage of frother, is patently evident. Nevertheless the generic type of oil (paraffinic, aromatic or naphthenic) is clearly important to flotation performance.

5.2.5 Summary

The overall probability of particle-bubble attachment depends on the probabilities of collision, attachment and detachment. Direct collision is acknowledged to be the most important means of generating solid-bubble contact, though precipitation of microbubbles (in part by cavitation) on the solids can improve flotation performance in combination with the direct contact mechanism. The thermodynamic criterion necessary for attachment, i.e. a lowering of free energy of the new interface formed is normally achieved by using collectors.

Assuming particle-bubble attachment is thermodynamically favourable it is still necessary that the physical (mechanistic) encounter be such that sufficient energy is available to pass through high energy intermediate steps such as aqueous film thinning. The success of contact is thus also dependent on particle size and particle kinetic energy. Large and/or high energy particles often "bounce" off bubbles while ultra-fine particles lack the inertia to collide with the bubble and can only be captured by interaction of the respective surface forces. This necessitates that particle and bubble pass very closely.

Successful attachment requires that induction times are less than contact times which are widely quoted as being of the order of milliseconds. The tenacity of the established bond is then dependent on the forces of attachment outweighing forces contributing to its destruction, i.e. gravitational and inertial forces and forces resulting from the disparate internal and external bubble pressures. The strengthening of attachment is a major function of the collector though the mechanisms by which oils achieve this with coal are not fully understood and have not been adequately theoretically modelled.

In coal flotation, solid particles and air bubbles are not necessarily of vastly disparate sizes so that the contact surface cannot always be regarded as planar. This complicates the resolution of interfacial tensions. Modelling difficulties are compounded by largely unquantifiable elements such as coal surface properties, oil properties and surfactant distribution. Since oil droplets do not spread spontaneously on coal and hence cannot be expected to form a thin or continuous film, an extra (fourth) phase must be accounted for in any model. The oil is also likely to exist on the bubble surface either as a film or as a lens. Young's equation can only be used to model the adhesion process after some simplifying and often unrealistic assumptions are made. However, in the absence of any other model and on account of the difficulties in developing such a model, it must suffice.

The mechanism by which the bubble attaches to the oiled coal particle has not been definitely established. Direct contact with the coal surface appears unusual and it is most likely that a thin film and possibly even a fairly substantial oil layer exists between the bubble and the actual solid surface. The adhesion is then largely one of classical fluid-fluid coalescence (between the oil and the air bubble).

An air-oil interface or spreading of oil at the air-water interface will *always* occur when bubbles and air come into contact. The particular behaviour exhibited (spreading or non-spreading) will be dependent on the oil-water interfacial tension and thus on the type and purity of the oil. During bubble-particle contact the fluid-fluid coalescence of oil films or lenses existing on the initially independent particle and bubble can also facilitate attachment. Actual bonding behaviour in terms of oil redistribution is partly dependent on the oil type used since some oils, notably high boiling point saturated alkanes (paraffins), do not spread spontaneously, even at the air-water interface.

With respect to adhesion strength an optimum oil film thickness (between solid and air bubble) will exist. Too thin a film will produce a weak bond while too thick a film is itself open to disruption by pulp turbulence. In addition to its presence between the bubble and the particle, the oil has also been observed to congregate along the wetted perimeter, forming a "fringe" or "collar" which strengthens attachment.

Hydrocarbon oils are effective coal collectors only when they are retained as droplets, i.e. as an independent oil phase. Oils with boiling ranges between 200 and 250°C are widely acknowledged to be the most effective coal collectors. The decrease in performance above 240°C is believed to be caused by the low dispersity of viscous oils and consequently the unlikelihood of sufficient conditioning time in flotation practice. At the other end of the scale, lower boiling point homologues are believed to be less effective as coal collectors as they are more volatile and water-soluble. By vapourizing into the air bubbles, these oils prevent or delay the formation of a stable film.

It has been suggested that an increase in viscosity, which is largely a result of increased Van der Waals bonding within the oil, increases the strength of bubble-particle contact. Viscous oils can therefore be expected to be more effective than lower viscosity oils in flotation of coarser particles. Viscosity is thus believed to be an important appraisal criterion for coal collectors. In so far as it relates to the chemical nature of the oils in terms of Van der Waals bonding, polar interactions, fluid-fluid coalescence rates, etc., this is understandably so. It has also been proposed that oils which spread poorly are likely to be good collectors.

In terms of the chemical constitution of the oil, the order of coal flotation activity is aromatic, naphthenic and iso-paraffinic. The origin of the crude from which commercial oils are produced is therefore important. In addition to the induced dipole-induced dipole interactions (London-Van der Waals), the polar interactions which are possible with aromatic oils are probably responsible for their improved flotation performance. These interactions could also explain why partially oxidized hydrocarbon oils (with their polar functional groups) have been found to be successful coal collectors; particularly if the coal is oxidized. However, within these groups, small gains in collector performance may be heavily outweighed by economic considerations and other factors such as the efficiency of dispersion and the choice and dosage of frother.

Apart from the obvious benefits of reducing bubble size and promoting a stable froth, frothers also enhance bubble-particle attachment by (a) reducing bubble capillary tension, which is one of the forces contributing to detachment, (b) reducing bubble speed in the pulp, and (c) assisting in temporarily overcoming electrostatic repulsion during the particle-bubble approach (both are likely to be negatively charged).

The frother should be added on the basis of the pulp water volume and not according to the mass of solids. If MIBC is used, dosage level of $12 \mu\text{l.l}^{-1}$ water is suggested as a minimum. As MIBC is preferentially soluble in oil, MIBC addition to the pulp should be independent of the oil and should take place as late as possible to ensure that a good proportion of MIBC molecules congregate at the air-water interface and so retain their frothing ability.

5.3 EXPERIMENTAL PARTICULARS

5.3.1 Flotation reagents

5.3.1.1 Collectors

Hydrocarbon oils were selected as collectors. The reasons for choosing particular oils are outlined in Section 1.3.2 above. The oils

used chiefly were dodecane, hexyl benzene, Shellsol AB and Pegasol 3745. Details of these oils are given in Table 1.3.

5.3.1.2 Frother

Methyl iso-butyl carbinol (MIBC) [4-methyl 2-pentanol] was used as a frother in most of the experiments. DIBK (5-nonanone) was used in a short series of tests.

5.3.2 Coal

Withbank Number 2 seam coal from the Greenside Colliery washing plant was used in all the testwork. Three distinct samples were used : washed coal, i.e. low ash coal (l.a.c.) containing nominally 7 % ash, run-of-mine (unwashed) coal and thickener underflow. More details of these coal samples may be found in Section 1.3.1.

Initial tests were performed with the sample of washed coal.⁶ It soon became apparent that no substantial differences in flotation performance existed irrespective of the oil used.

The work was continued with the unwashed coal. Significant differences in flotation performance were observed. Most work was therefore conducted with this coal. The use of the unwashed coal in the flotation experiments allowed direct comparison of the results with those of the adsorption studies, which were also mostly conducted with this coal sample.

Thickener underflow coal was used on a limited scale. The thickener underflow coal is the stream at which beneficiation by flotation would in reality be aimed. However little work was done with it since physical treatments (such as cycloning) and chemical treatments (in thickening) could have misdirected interpretation of flotation results in terms of the sub-processes studied.

⁶ Two samples of this coal were obtained from the colliery at different times, but all the coal used in the flotation testwork was from the later batch. Most of the adsorption work using the washed coal was also done with this sample. A few adsorption tests (Figures 3.29 and 3.34) were done with the sample acquired earlier.

5.3.2.1 Coal preparation

The as-received samples of washed and unwashed coal were rod-milled to produce material suitable for both adsorption studies and flotation. For both coals, one kilogram batches of coal (at a time) were milled in a 257 mm diameter stainless steel mill with fourteen 25 mm (diam.) by 290 mm stainless steel rods. The mill was operated at 80 rpm for the time required to produce the desired size distribution (from a predetermined milling curve for each coal sample).

The washed coal was prepared by rod-milling -6mm coal (dry). The +500 μm material was removed and the -600 +500 μm used for adsorption testwork. The -500 μm material was used in flotation. Its size distribution is given in Table 5.1. The -150 μm sub-fraction of this fraction was used in earlier flotation work while the entire -500 μm fraction was used in later work.

The unwashed coal was prepared by rod-milling -12 mm +6 mm "peas" (dry). The +500 μm material was removed and the -600 +500 μm used for adsorption testwork. The -500 μm material was used in flotation. The entire -500 μm fraction was used for the flotation work.

Five such one kilogram batches were milled consecutively, the products screened (the +500 μm fraction removed) and the -500 μm fractions blended. This provided a reserve which ensured that feed coal for several subsets of flotation experiments was homogeneous.

The dried thickener underflow coal was not subjected to any size reduction before flotation. Its size analysis (as received and used in flotation) is given in Table 5.1 below.

Table 5.1 : Cumulative size distributions of the milled washed and unwashed coal and the thickener underflow samples used in the flotation testwork.

Size (wet)	Cumulative mass percent passing		
	Washed coal	Unwashed coal	T/underflow
75 μm	33.0 %	30.6 %	60.7 %
106	35.3	37.9	65.6
150	43.8	46.6	74.0
180	50.5	52.8	77.7
250	61.9	64.4	83.2
300	71.2	72.6	85.7
425	89.4	89.7	90.6
500	100.0	100.0	93.3

5.3.2.2 Coal storage

All coal was stored dry under nitrogen until needed for flotation. This was in order to minimise the possibility of surface oxidation.

5.3.3 Experimental equipment and procedures

5.3.3.1 Flotation cell

A three-litre Leeds-type sub-aeration laboratory batch flotation cell, equipped with a pulp level controller and electronic impeller speed regulator was used for all testwork.

5.3.3.2 Flotation parameters

Several parameters remained fixed throughout the flotation testwork. Values of these parameters were selected on the basis of the batch flotation results of Fickling (1986) who investigated the effect of operational parameters on the flotation performance of four South African coals. Unless specified otherwise the parameter levels chosen were :

Impeller speed : 1200 rpm
Aeration rate : 4 l.min^{-1}
Froth height : 1.5 cm
Particle size : $-500 \mu\text{m}$
Pulp solids : 5 % (m/m) nominally
(150 g of feed was used but a small amount was lost through the level control device when aeration began, i.e. when pulp level increased).

Filtered tap water was used in all instances. No attempt was made to regulate pulp temperature (although this was monitored), ionic strength or pH. However experiments within each subset were conducted successively (on the same day) and therefore under very similar conditions.

5.3.3.3 Flotation technique

The manner in which coal was added to the cell and contacted with the reagents varied according to the conditioning procedure selected (see below). However, the procedure for removing concentrates from the cell, using a fixed froth height manual scraping technique, was always the same. This procedure is described in detail in Appendix 5.1.

Six concentrates were removed consecutively to provide flotation macro-kinetic data (recovery vs. time). After completion of this procedure a final (seventh) concentrate was removed from the pulp surface as some coal which had obviously floated was evading the fixed froth height scraper. This material at times constituted a significant proportion of the total concentrate and would have distorted the results if it had been flushed into the tailings. (A similar situation would not arise in a continuous flotation cell into which fresh feed was constantly being introduced). The seventh concentrate is represented in all results as the final concentrate removed after 380 seconds. This is not a true (significant) time and was chosen merely to allow for the graphical representation of the concentrate.

Concentrates were filtered, oven dried at 80°C, weighed and two samples of each were ashed. Cumulative coal recovery was calculated.

5.3.3.4 Conditioning procedures

It became apparent (during preliminary flotation testwork) that the way in which the oils were dispersed (intensity of agitation and presence or absence of frother) and the manner in which they were either subsequently or simultaneously contacted with the solid particles was of major importance to flotation performance, particularly with the unwashed, coarse ($-500\text{ }\mu\text{m}$) coal feed.

For this reason four conditioning procedures were investigated. Two of these involved dispersing the oils in a limited amount of water prior to coal slurry addition, and the other two involved dispersing the oils in the coal pulp itself. Other permutations, such as prior oil dispersion in a cell filled to capacity with water only, were not considered. (In this case, it was believed that dispersion would be poorer and the approach would be impractical to implement on an industrial scale). The effect of the timing of frother (MIBC) addition was also investigated (see Section 5.4.5).

The procedures used are designated by their acronyms and are defined as follows :

1. llpm - low level prior mixing of the oil (coal and frother absent initially).
2. llpm/f - low level prior mixing of the oil with the frother (coal absent initially).
3. hpdc - high pulp density conditioning, i.e. oil added to a coal pulp in a partially filled cell (without frother initially).
4. lpdc - low pulp density conditioning, i.e. oil added to a coal pulp in a full cell (without frother initially).

Low pulp density conditioning (lpdc) is the usual way of contacting the reagents with the coal pulp in laboratory batch flotation experiments.

The coal was always prewetted (with water) before contact with the oil. In the cases where the oils were predispersed (11pm and 11pm/f) the coal was added as a dense slurry. In instances where the flotation cell was not filled to capacity immediately (i.e. 11pm, 11pm/f and hpdc) the amount of water introduced by way of slurry and wash water was controlled to ensure cell volumes were the same in all cases, so that mixing dynamics were similar.

The sequential order of reagent and coal addition according to each conditioning procedure is indicated below (the impeller is running throughout the sequence).

11pm :-

0 s : Collector added to 1 l of water in cell.
10 s :
1 min :
2 min : Coal slurry added (includes 100 ml of
slurry water and 150 ml wash water).
5 min : Cell filled.
6 min 53 s : MIBC added.
7 min 53 s : Air turned on.

11pm/f :-

```

0 s      : Collector added to 1 l of water in cell.
10 s     : MIBC added.
1 min    :
2 min    : Coal slurry added (includes 100 ml
          slurry water and 150 ml wash water).
5 min    : Cell filled.
6 min 53 s :
7 min 53 s : Air turned on.

```

hpdc :-

0 s : Dry coal added to 1.1 l of water in cell.
 10 s :
 1 min :
 2 min : Collector added (and 150 ml of water).
 5 min : Cell filled.
 6 min 53 s : MIBC added.
 7 min 53 s : Air turned on.

lpdc :-

0 s : Dry coal added to 1.1 l water in cell.
 10 s :
 1 min : Cell filled.
 2 min : Collector added (below pulp surface).
 5 min :
 6 min 53 s : MIBC added.
 7 min 53 s : Air turned on.

5.3.3.5 Flotation repeatability

Prior to commencing the flotation program, four experiments were carried out under identical conditions using the Greenside thickener underflow coal to confirm the repeatability of the operator's experimental technique. 400 μ l of dodecane and 18 μ l of MIBC was used. Low pulp density conditioning (lpdc) was used.

Figure 5.6 shows that repeatability was good. The total concentrate ash varied between 10.2 and 10.5 %. However the deviation obtained in this series of tests cannot be applied automatically to all the results of the testwork program. Occasionally the reagent dosage levels and conditioning procedures led to poor and somewhat erratic results which were not the result of experimental error. These instances are mentioned and an indication of repeatability is given.

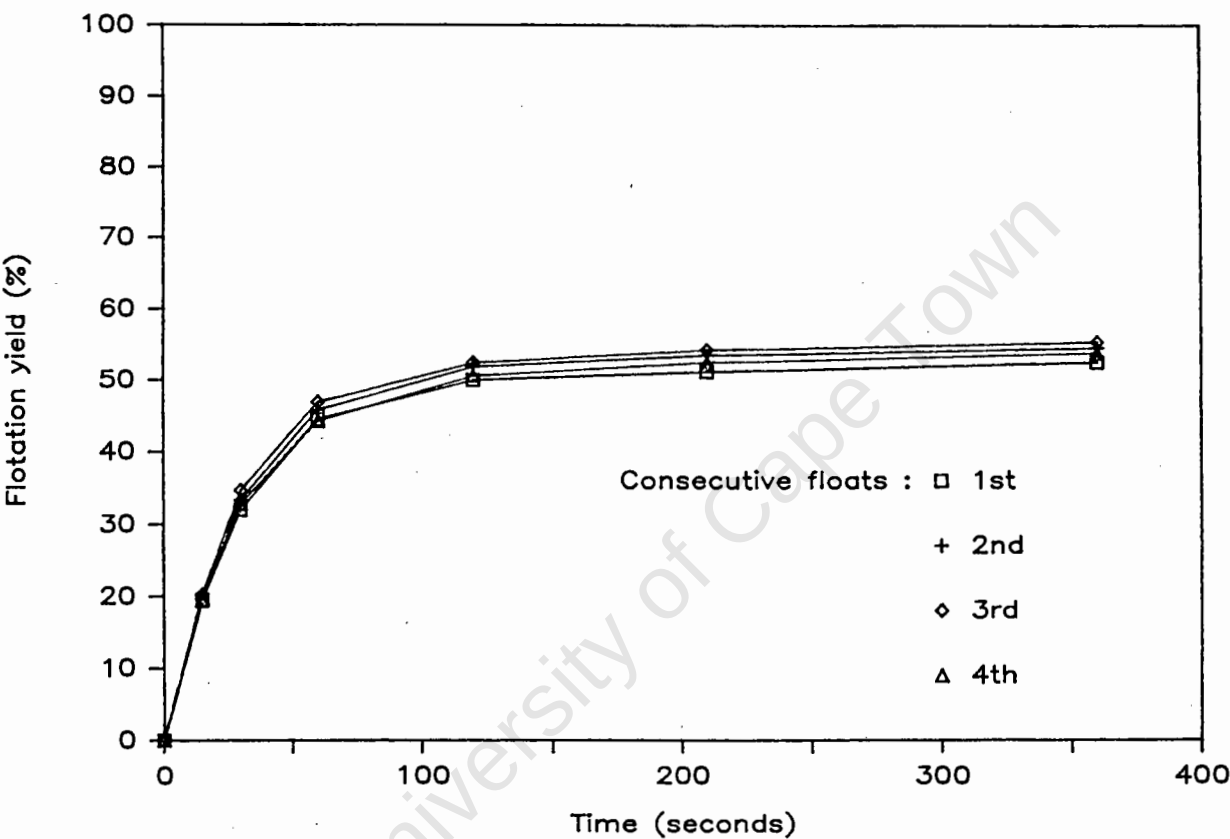


Figure 5.6 : Flotation technique repeatability. Greenside No.2 seam thickener underflow coal.

5.3.3.6 Analyses procedures

- a) Coal samples were ashed in accordance with a standard procedure (SABS Standard Method no. 926).
- b) To enable comparison of flotation results with the maximum theoretical yield obtainable at a particular ash content, float-sink tests were conducted in accordance with the centrifugal procedure developed by Harris (1987) and described by Franzidis and Harris (1986).

5.4 RESULTS AND DISCUSSION : INDIVIDUAL FLOTATION RESULTS

Since the behaviour of the different oils is the primary focus of this work the results are arranged below in sub-sections according to oil type rather than according to dosage, etc. Each sub-section is then divided further into sections which concern the influence of conditioning procedure, oil dosage, MIBC dosage, and oil properties on flotation performance. Some tests inevitably encompass one or more of the above variables so cross referencing is unavoidable.

A general discussion and comparison of the flotation performance induced by the oils follows in Section 5.4.4; and of the influence of the mode of MIBC addition in Section 5.4.5. The flotation results obtained with the Greenside *washed* and *thickener underflow* samples are dealt with in Section 5.4.6. Finally, the results of the testwork concerning the selectivity of an oil in a flotation situation are presented (Section 5.4.7).

Unless specified otherwise, all the results discussed below pertain to the -500 μm fraction of the milled Greenside unwashed coal.

Raw data spreadsheets are included in Data Appendix 5 (available on request). A summary of the results is included in tabular form in Appendix 5.5.

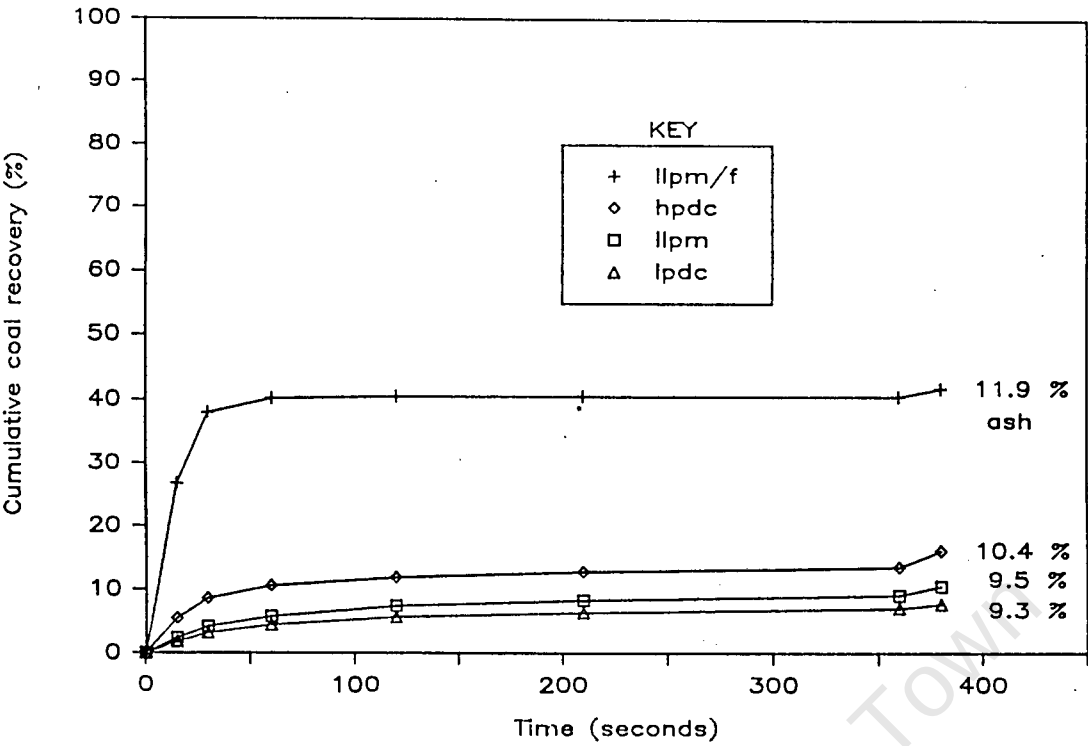


Figure 5.7 : Flotation performance after various conditioning procedures. 200 μ l of dodecane and 18 μ l of MIBC per float. Milled Greenside No.2 seam unwashed coal ($\sim$ 500 μ m).

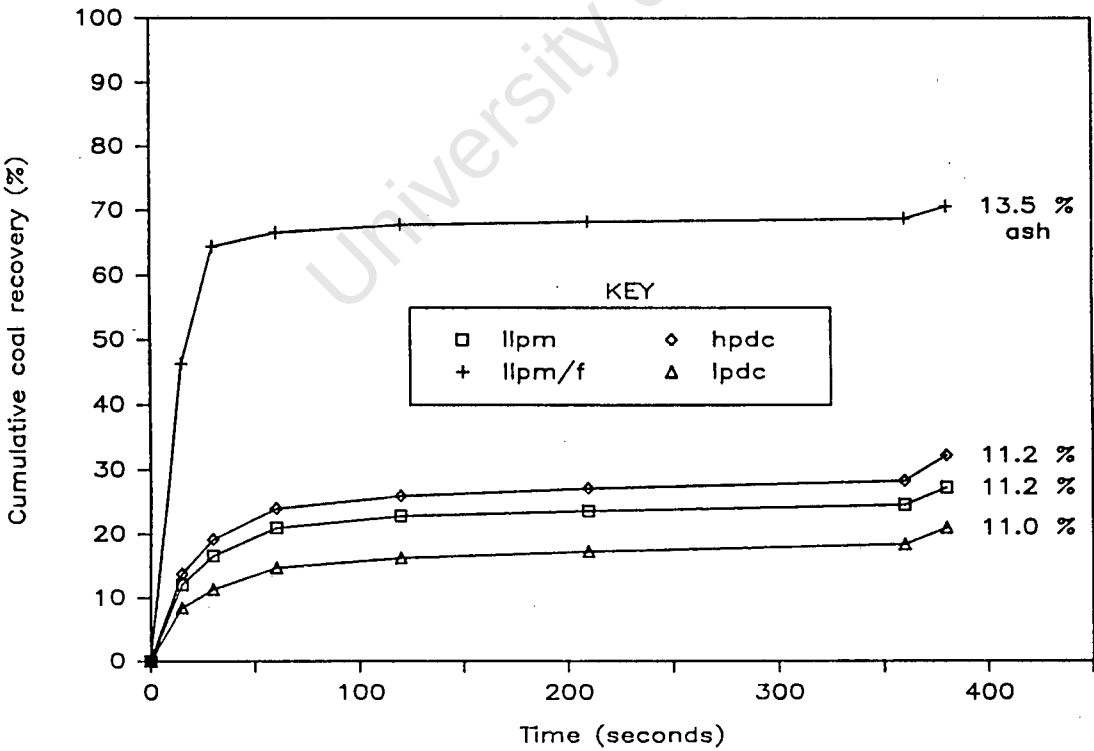


Figure 5.8 : Flotation performance after various conditioning procedures. 400 μ l of dodecane and 18 μ l of MIBC per float. Milled Greenside No.2 seam unwashed coal ($\sim$ 500 μ m).

5.4.1 Aliphatic oils

5.4.1.1 n-Dodecane

a) The effect of conditioning procedure

i) Recovery

Figure 5.7 shows that llpm/f conditioning improved flotation performance markedly at a 200 μl dosage (per 3 litre float) of dodecane in conjunction with 18 μl of MIBC. Coal recovery jumped to 40 % compared to 10 % or less with the other conditioning methods. Amongst the other conditioning procedures, hpdc induced better performance than llpm and lpdc. The latter was the least effective conditioning procedure used, though it is the approach usually adopted in laboratory batch flotation tests.

The llpm/f phenomenon found with dodecane is interesting since the early addition of MIBC would be expected to reduce flotation performance considerably, as discussed in a review of the literature in Section 5.2.3.5.a above. Experimental observation of the impact of the mode of MIBC addition is discussed further in Section 5.4.5 below.

The increased performance at llpm/f conditioning cannot be attributed to better collector dispersion as a result of the presence of MIBC. In fact dispersion was found to be poorer (Figure 2.9) when MIBC was present than when the oil was dispersed alone but in a similar manner, i.e. llpm.⁷

Better recoveries at llpm/f also could not be attributed to enhanced adsorption and spreading of the dodecane onto the coal surface as a result of the presence of MIBC, as adsorption was unaffected by its presence (as shown in Figure 3.24).

Finally, results presented in Chapter 4 show that the presence of MIBC reduces the bubble size significantly, but this phenomenon is common to all the conditioning procedures. In fact llpm/f should be a

⁷ In addition significantly better coal recoveries were produced with some of the other reagents at conditions where droplet sizes were known to be larger. Degree of dispersion (droplet size) is therefore not the factor dominating this flotation performance.

poorer way of adding frother in that more of the frother is likely to be adsorbed by the coal and the oil than would be the case if it were added shortly before aeration commenced, as was the case with the other conditioning methods.

The reason for the increased flotation performance at 11pm/f was apparently related to the influence of MIBC on the production of fine bubbles from the air induced by the impeller under these vigorous agitation conditions, or by cavitation behind the impeller blades. Fine bubble formation was much less marked under 11pm and hpdc conditions (frother absent) and absent at the lpdc condition (full cell). Two mechanisms advantageous to flotation performance are postulated which involve the presence of these fine bubbles:

1. These very small bubbles compete with oil droplets for the adsorption of MIBC thereby reducing the harmful effect of the dissolution of MIBC in oil (on its frothing ability).
2. These bubbles also contact the coal slurry as it is added to the cell (before the cell air supply is turned on). While they may be too small to float the comparatively large coal particles, they act as "catalysts" or promoters for the adsorption of large air bubbles introduced into the pulp when aeration begins, in this way promoting flotation performance. Sutherland (1948, p.396) reported that air/gas precipitation is useful in enhancing flotation, a fact also implicitly recognized for hydrophobic solids (and coal in particular) by Aston et al (1981) and by Tyurnikova and Naumov (1981). Smith et al (1957) reported that prolonged pre-aeration of pulps whilst conditioning has been found to be beneficial to flotation with many minerals. Very intense mixing with associated cavitation (behind the impeller blades) can also precipitate gas on the solid surface causing a similar effect.

ii) Grade

Even at very poor recoveries (Figure 5.7) concentrate grades were 9 to 10 % ash. Despite significantly higher recoveries at 11pm/f, ash levels increased only slightly (to 11.9 %) and not significantly in terms of the liberation characteristics of the coal. Global

flotation results (Section 5.5.3) show that the higher ash content obtained in a concentrate is very often directly related to increased recovery, i.e. that the ash content trend parallels the relation representing the degree of liberation.

b) The effect of dosage level

i) Recovery

Increasing the dodecane dosage from 200 to 400 μl per float (1000 to 2000 g.t^{-1} coal) produced the same trends in flotation performance with the various conditioning procedures. Comparison of Figure 5.7 with 5.8 shows that the higher dodecane dosage markedly improved coal recovery under all conditions. Furthermore the very poor results obtained at 11pm with a 200 μl dosage of dodecane (Figure 5.7) were found to improve progressively as the dodecane dosage was increased as shown by Figure 5.9.

The increased dodecane dosages did not affect grades beyond the increase which could be expected as a result of the greater mass of coal floated. In terms of grade, over-oiling does not appear to be detrimental with dodecane (or aliphatics). In other words the presence of excess oil did not result in adsorption or spreading onto gangue surfaces. The selectivity of aliphatic oils for hydrophobic carbonaceous material was clearly shown by the selectivity testwork presented in Section 3.5.

The improved recoveries at higher dodecane dosages (at the same MIBC dosage) would suggest :

1. that dodecane was poorly dispersed and hence not available to sufficient particles in the pulp (if dosages were low);
2. that higher concentrations of dodecane in the pulp water encouraged dodecane adsorption onto coal particles; or,
3. that the dodecane has some influence on the size of bubble created in the pulp and as a consequence on froth stability.

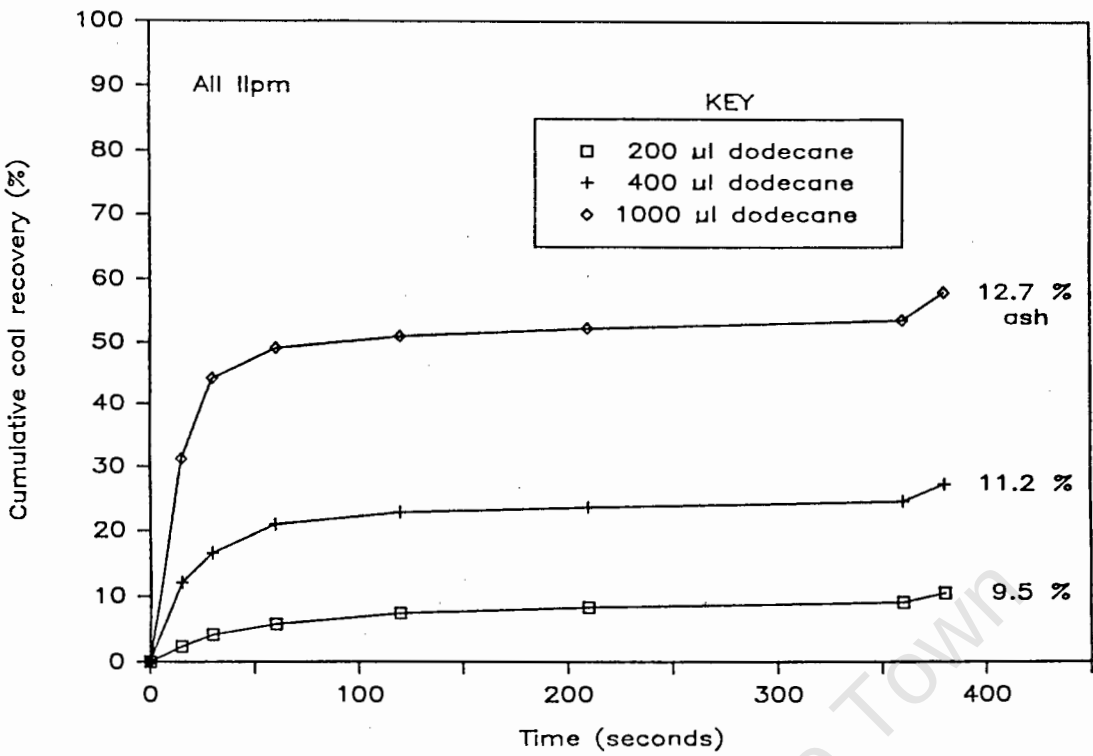


Figure 5.9 : Effect of dodecane dosage on flotation performance at 11pm. 18 µl MIBC per float. Milled Greenside No.2 seam unwashed coal (-500 µm).

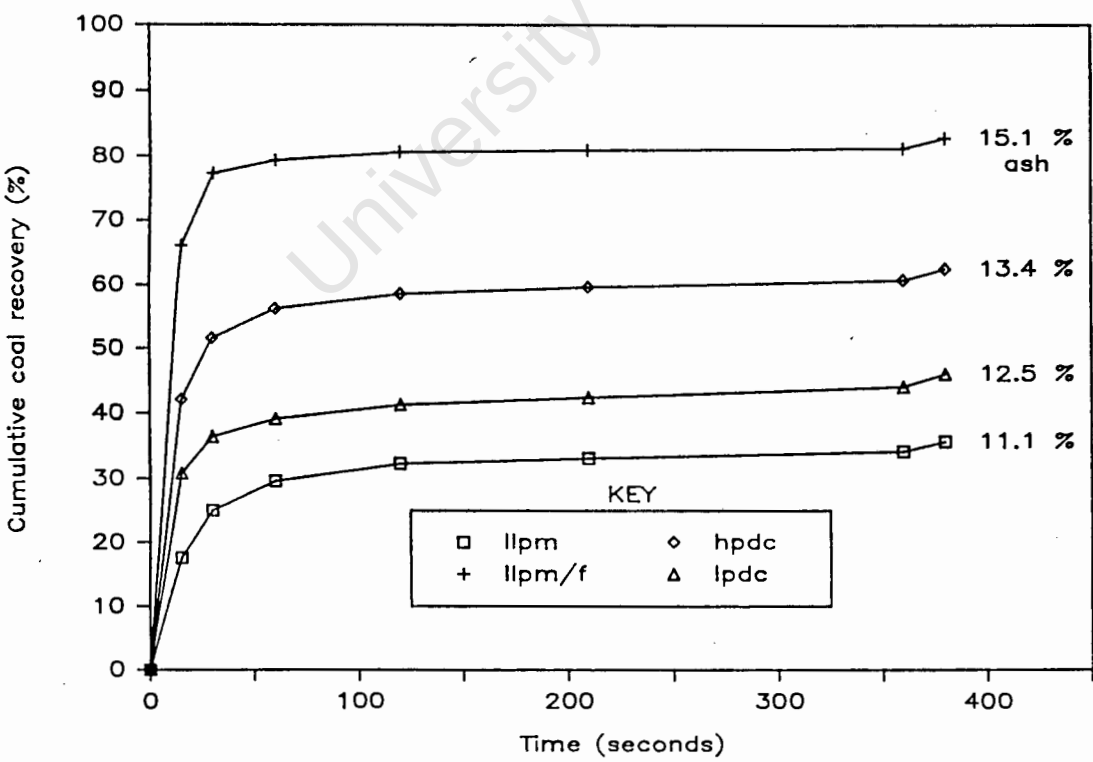


Figure 5.10 : The effect of various conditioning procedures on flotation performance using 200 µl of dodecane and 36 µl of MIBC per float. Milled Greenside No.2 seam unwashed coal (-500 µm).

4. that the manner in which dodecane disperses and its spreading characteristics at various interfaces has a small influence on froth phase stabilization which is enhanced by increasing its concentration.

Droplet size analyses showed that the first possibility could be discounted. Although dodecane does not disperse to the same degree as say, hexyl benzene, at least 10^4 droplets are present in each millilitre of pulp water even at the low dosage (refer to the droplet number distributions in Section 2.6.2).

The second possibility, that dodecane adsorption at the lower dosage was insufficient for effective flotation, and that adsorption would be greater at the higher dosages can also not be supported. Undoubtably the increased number of droplets and hence of particle-droplet collisions at higher dosages would increase the mass of dodecane adsorbed to some extent. However, the adsorption study indicated that at a dosage approximately equivalent to the $400 \mu\text{l}$ dosage used in flotation some dodecane remained unadsorbed, suggesting that most of the coal surface area that could have been covered had been. Obviously, when floating $-500 \mu\text{m}$ coal particles, the surface area available would be much greater than that of the equivalent mass of $500\text{-}600 \mu\text{m}$ coal used in the adsorption work: but it is thought that the dosage should still be adequate. The 10.6 % recovery (Figure 5.9) is too low to be attributed to inadequate dosage entirely. (This will be confirmed by results presented in the following section).

With regard to the last possibility, the influence of dodecane on bubble size is small. Bubble size is an important aspect in determining froth stability. With this oil large dosages of frother generally have to be used to produce the desired froth stability, especially with coarse coal feeds. The bubble sizing studies showed that increasing the dodecane dosage did reduce the bubble size to a small degree, from $1.8 \pm 0.6 \text{ mm}$ to $1.7 \pm 0.5 \text{ mm}$ (Figure 4.15) but this is insufficient to explain the large increase in recovery.

Thus none of the first three proposed reasons for improvement in recovery holds. The fourth possibility is related to the manner in which dodecane is distributed on coal and bubble surfaces. The dodecane droplets will exist at both the coal-air and air-water

interfaces as lenses, as spreading is not spontaneous at either interface. This behaviour might possibly stabilize the froth physically in an analagous manner to fine hydrophobic solids. Apart from visual observation of increased froth stability, this mechanism was not explored further since a study of the froth phase fell beyond the scope of this research.

It is nevertheless concluded that increasing the dodecane dosage enhanced the mechanical froth stabilizing characteristics of this oil and that this was mainly responsible for the increased coal recoveries. Table 5.2 shows that an increase in dodecane dosage (from 200 to 400 μl) improved the recovery of coarse material. This is indicative of improved froth strength and stability. The influence of an increase in MIBC dosage on the recovery of coarse size fractions is also shown. This is discussed in more depth in Section 5.4.1.1.c below. Unlike the aromatic collectors, dodecane did not produce an acceptably stable and structured froth at low reagent (oil and MIBC) dosages.

ii) Grade

Figure 5.8 shows that the grades obtained at 400 μl of dodecane per float followed similar trends to those achieved at a lower (200 μl) dodecane dosage. The three conditioning procedures which produced low recoveries, (llpm, lpdc and hpdc) had similar grades of about 11 %. The ash level increased to 13.5 % after llpm/f but the increase may be largely attributed to the increased recovery (70 %) as verified in Section 5.5.3.

Figure 5.9 shows that the grades worsened, i.e. the ash content increased, from 9.5 to 12.7 % as the dodecane dosage was raised from 200 to 1000 μl . Again this behaviour conformed to the relation between increased ash levels and increased concentrate yield.

c) The effect of MIBC dosage level

Froth stability, to which bubble size is a prime contributing factor, appears to be the vital factor in determining concentrate yields. Solid particles that ultimately appear in the flotation tailings are not rejected by chemical selectivity alone; *physical size*

of the solids is of some importance. Thus, in the results described above, the poor frothing/froth stabilizing characteristics of the dodecane meant that only the finer particles could be supported in the froth if MIBC dosage was low. Larger particles are nevertheless collected and transported to the pulp surface (as evident from results presented below). The ability of the froth to sustain these large particles is of great importance to improved yields since typical coal feeds are likely to possess a significant proportion of coarse material by mass.

That a 200 μl dodecane dosage was sufficient for collecting purposes, provided that adequate froth stability could be maintained, was confirmed by floats in which only the frother dosage was increased. Figure 5.10 shows the recoveries at a 200 μl dosage of dodecane when MIBC dosage was 36 μl per float. These results should be compared with those in Figure 5.7 where dodecane dosage was the same but the MIBC dosage was 18 μl per float. The same trends existed; 11pm/f still gave the best performance but at the increased frother dosage the froth was in all instances more stable and better able to support material floating to the pulp surface. This is clearly shown in Table 5.2 below. The size distribution of particles in the concentrate was practically identical to that in the feed.

Table 5.2 : Cumulative size distributions of the unwashed coal in the flotation feed and in the flotation concentrates. Dodecane as collector and MIBC as frother. 11pm/f conditioning.

Size (wet)	Cumulative mass percent passing			
	Feed	Conc.	Conc.	Conc.
		Dodecane/MIBC dosage (μl)		
		400/18	200/18	200/36
75	30.6	31.1	41.8	30.3
106	37.9	39.6	51.1	39.4
150	46.6	48.1	59.3	47.7
250	64.4	66.1	76.4	65.1
300	72.6	75.0	83.7	73.8
500	100.0	100.0	100.0	100.0

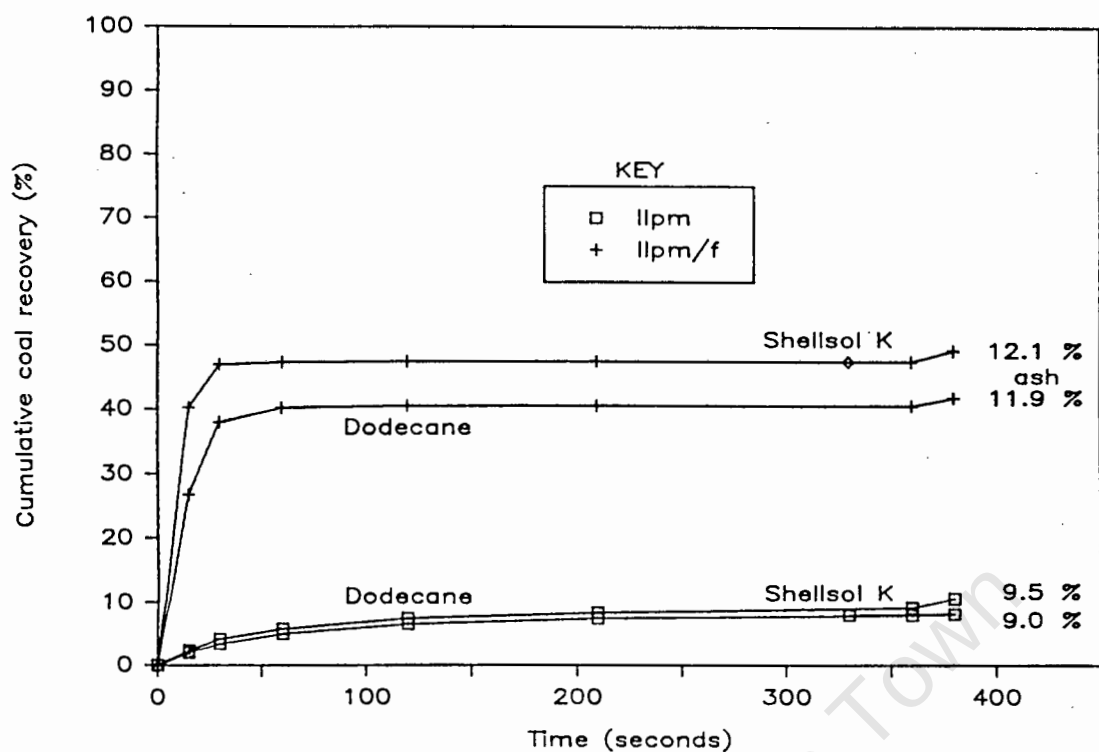


Figure 5.11 : Comparison of flotation performance achieved with dodecane and Shellisol K. 200 μ l dosages with 18 μ l of MIBC per float. Milled Greenside No.2 seam unwashed coal (-500 μ m).

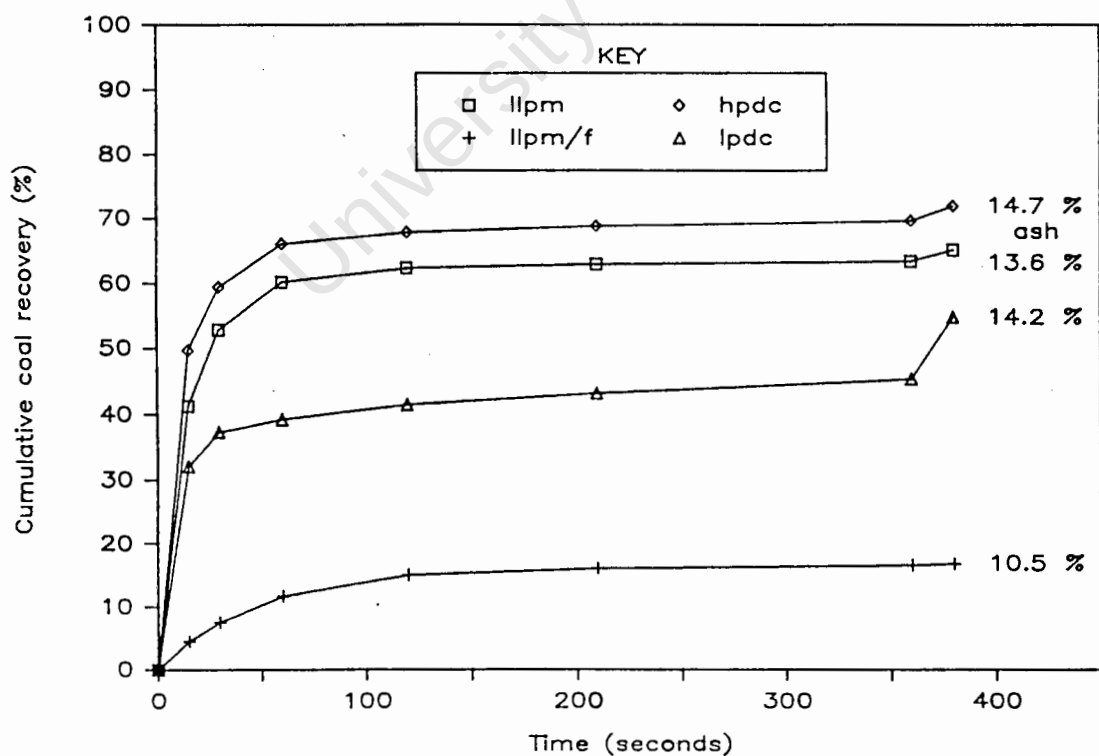


Figure 5.12 : The effect of various conditioning procedures on flotation performance using 200 μ l of hexyl benzene and 18 μ l of MIBC per float. Milled Greenside No.2 seam unwashed coal (-500 μ m).

The effect of increased MIBC dosages on the grade is difficult to gauge because of the dependence of the grade on the yield of concentrate. The coal is also poorly liberated which further compounds an evaluation. For these reasons the effect of conditioning procedure, collector dosage levels, etc. on concentrate grades will not be considered in a quantitative sense in further discussion of the individual flotation results. Qualitative observations are included in the discussions on recovery and are no longer considered in separate sub-sections.

In order to make meaningful comparisons of concentrate grades, the ash and recovery levels of each float must be "normalized". This is undertaken in Section 5.5, where the relationships between yield, grade and feed coal liberation are considered for the experimental program as a whole.

Nevertheless it is concluded that provided that the froth phase is appropriately regulated by selection of a suitable conditioning procedure and frother dosage, dodecane can be a very effective collector (in terms of yield) for this coal.

5.4.1.2 Shellsol K

Shellsol K is a predominantly (more than 99.5 %) aliphatic oil with a boiling range encompassing the boiling point of dodecane. In the flotation experiments it behaved very similarly to dodecane as a collector.

Figure 5.11 shows that at a 200 μ l dosage and with 18 μ l of MIBC, Shellsol K exhibited the same trends found with dodecane, namely that 11pm/f improved recoveries which were very poor otherwise. Grades and froths (in terms of water content and therefore bubble size) were also very similar.

It was seen in the investigation of the sub-processes that the dispersion and adsorption characteristics of Shellsol K as well as its effect on bubble formation were very similar to those of dodecane, so their equivalence in terms of flotation performance was not unexpected. In all probability flotation performance would be very similar to that of dodecane at other conditions so no further testwork

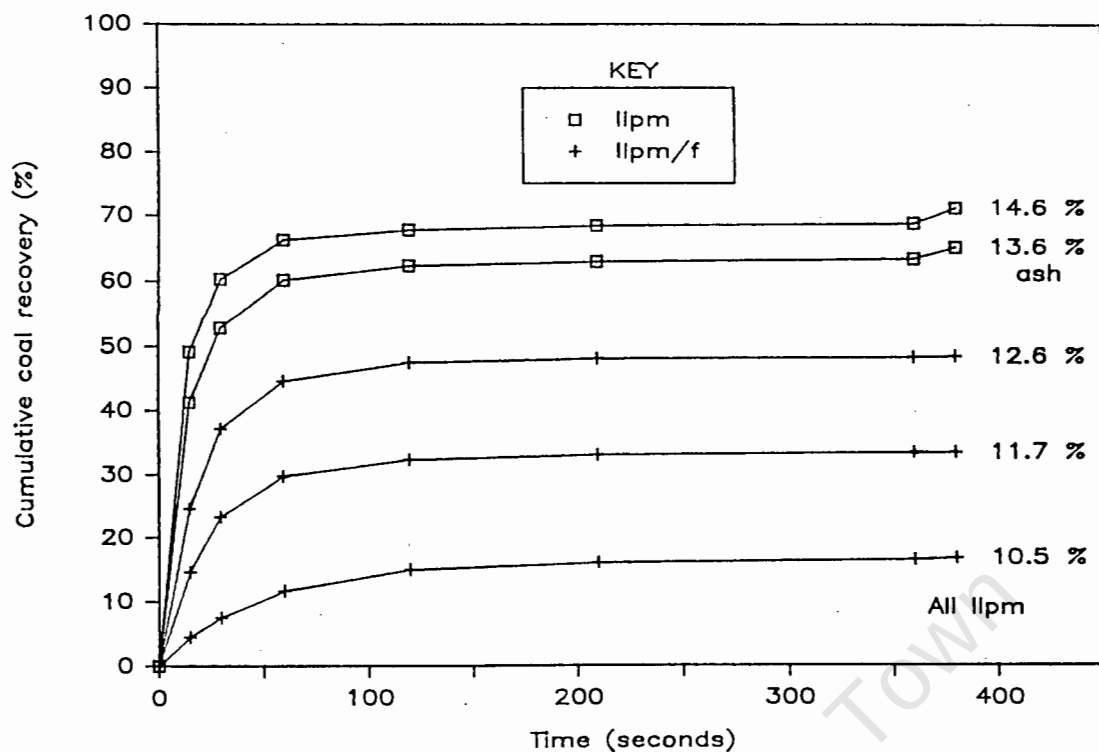


Figure 5.13 : Repeatability results. 200 μ l of hexyl benzene and 18 μ l MIBC per float. 11pm and 11pm/f conditioning procedures. Milled Greenside No.2 seam unwashed coal ($\sim 500 \mu$ m).

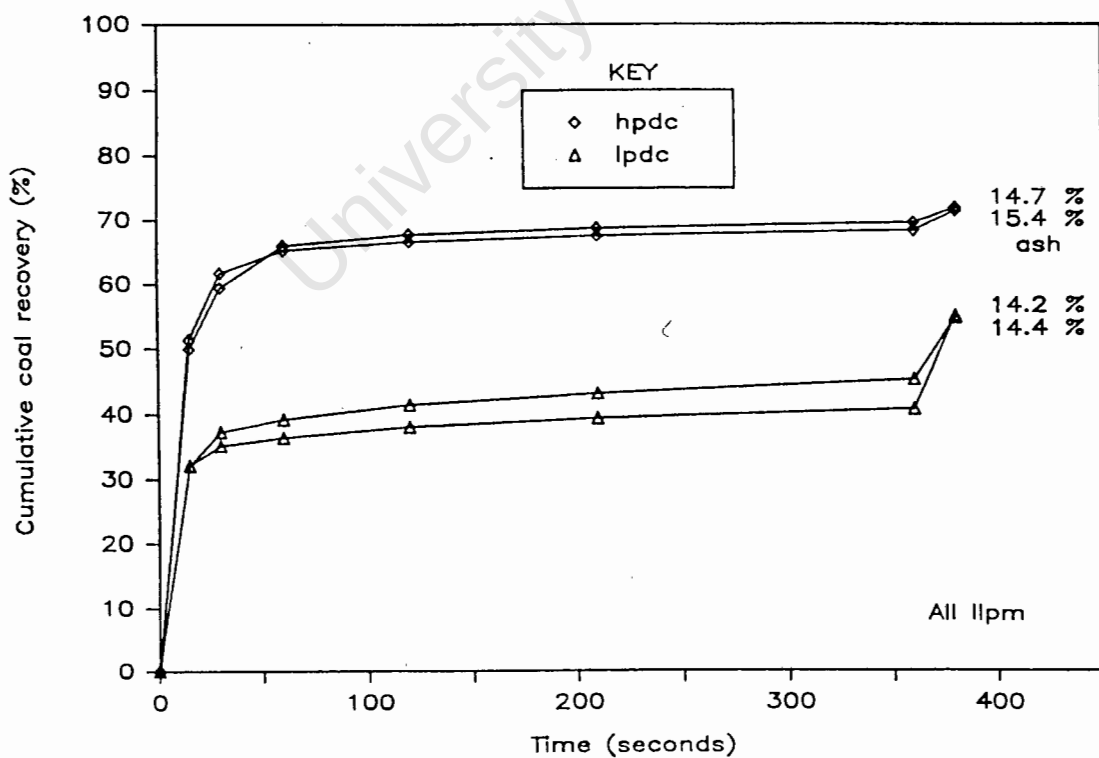


Figure 5.14 : Repeatability results. 200 μ l of hexyl benzene and 18 μ l MIBC per float. hpdc and lpdc conditioning procedures. Milled Greenside No.2 seam unwashed coal ($\sim 500 \mu$ m).

was undertaken. By extension, it is reasonable to suppose that other industrially produced aliphatic oils, of similar boiling ranges, would behave in similar ways.

5.4.2 Aromatic oils

5.4.2.1 n-Hexyl Benzene

a) The effect of conditioning procedure

Figure 5.12 shows the effect of the various conditioning procedures on the flotation performance of hexyl benzene. In contrast to the results obtained with dodecane, 1lpm/f with 200 μ l of hexyl benzene had no beneficial effect on flotation and gave the worst results. The poor performance of the hexyl benzene at 1lpm/f was not consistent, as may be seen by the results of repeatability work shown in Figure 5.13, but was definitely detrimental. This was more consistent with the belief that early frother addition encourages frother absorption by the collector oil thereby reducing its presence at the water-air interface and hence its frothing capabilities.

The fact that 1lpm/f improved the performance with dodecane in spite of this was attributed to the induction of minute bubbles which enhanced the otherwise poor frothing characteristics of dodecane. Though these bubbles would also be induced when hexyl benzene was used, it is a good frother (in the sense that it reduces bubble size) and is not dependent on this mechanism. Other weaknesses induced by the conditioning method will therefore be more evident.

Although 1lpm/f with hexyl benzene was detrimental to flotation this is relative and the method did at times produce better yields than with dodecane at similar dosages. It is evident from the repeatability results shown in Figure 5.13 that at this dosage and with this conditioning procedure the hexyl benzene float was unstable.

Figure 5.12 shows that much better flotation performance was achieved at conditions where the oil was better dispersed (hpdc and 1lpm) irrespective of whether the oil was pre-dispersed or not. Both these procedures produced better results than lpdc, in terms of both

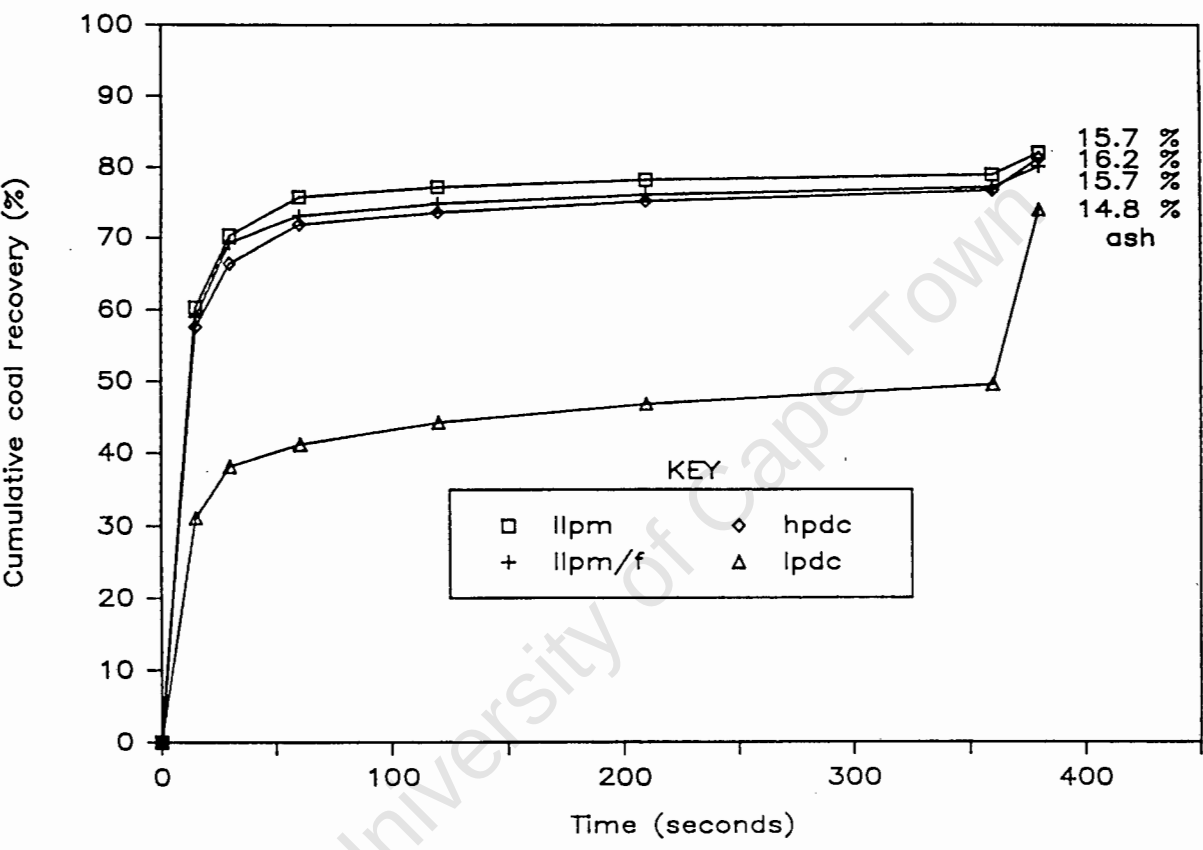


Figure 5.15 : The effect of various conditioning procedures on flotation performance using 400 μ l of hexyl benzene and 18 μ l of MIBC per float. Milled Greenside No.2 seam unwashed coal (-500μ m).

yield and grade; as expected. The lpdc test nevertheless showed a big increase in the 7th concentrate (which is material which had floated but which evaded the fixed height scraper). This suggests that the form of the froth was different. Besides 11pm/f, the other conditioning procedures showed acceptable (11pm) or good (hpdc, lpdc) repeatability even though repeat floats were conducted several months apart; as may be seen from Figures 5.13 and 5.14.

The distinctive feature of lpdc in relation to the other conditioning procedures is less vigorous dispersion of the oil as it is carried out in a full rather than a partially filled cell. Droplets are hence that much larger. Hexyl benzene is known to be a powerful coal agglomerator (Buys, 1987) and this trait could be responsible for the dry brittle froth prevalent at lpdc since the larger droplets could be expected to enhance agglomeration. The existence of agglomerates would result in individual bubbles being more heavily loaded so that the solids to water ratio within the froth would increase. In addition to pulp phase agglomeration an analagous process of air bubble and oil coalescence appeared to occur in the froth. The coalescence of bubble and oil led to a partial collapse of the froth. This effect seemed to be related to the existence of comparatively large oil lenses, as it was not evident when oil lenses were small, i.e. when the oil had been vigorously dispersed.

b) The effect of dosage level

Figure 5.15 indicates that the detrimental effect observed with 11pm/f conditioning was absent when the hexyl benzene dosage was raised to 400 μ l. This reinforced the belief that an inadequate frothing ability, induced by 11pm/f conditions at low hexyl benzene and MIBC dosages (because of MIBC adsorption), was responsible for the poorer recoveries. The increased dosage of hexyl benzene would imply that a greater proportion of MIBC should be absorbed and adsorbed and flotation results would be expected to be poorer. As this was not the case, it suggests that the collector oil can also act as a frother/froth stabilizer.

Figure 5.15 also clearly shows that, in addition to adequate oil dosages, the method of conditioning plays an important role in

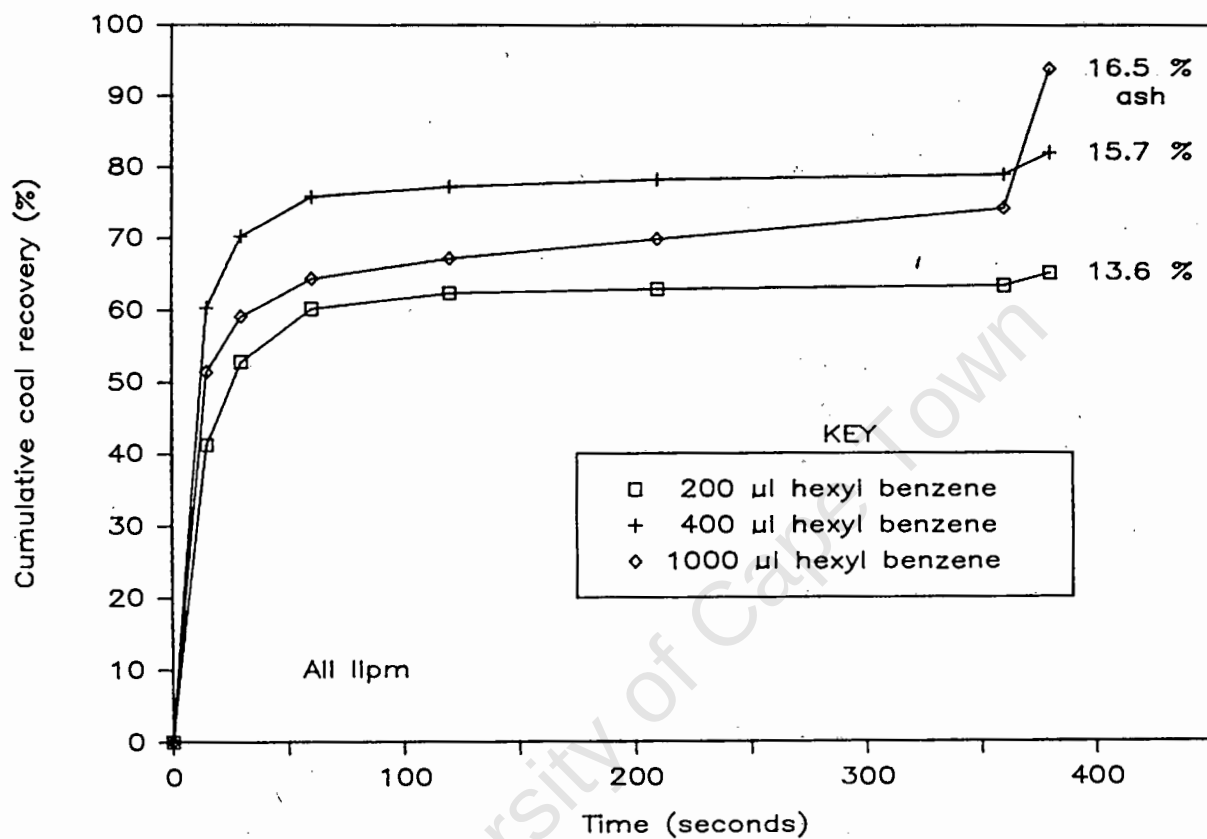


Figure 5.16 : The effect of hexyl benzene dosage on flotation performance at 11pm. 18 µl of MIBC per float. Milled Greenside No.2 seam unwashed coal (-500 µm).

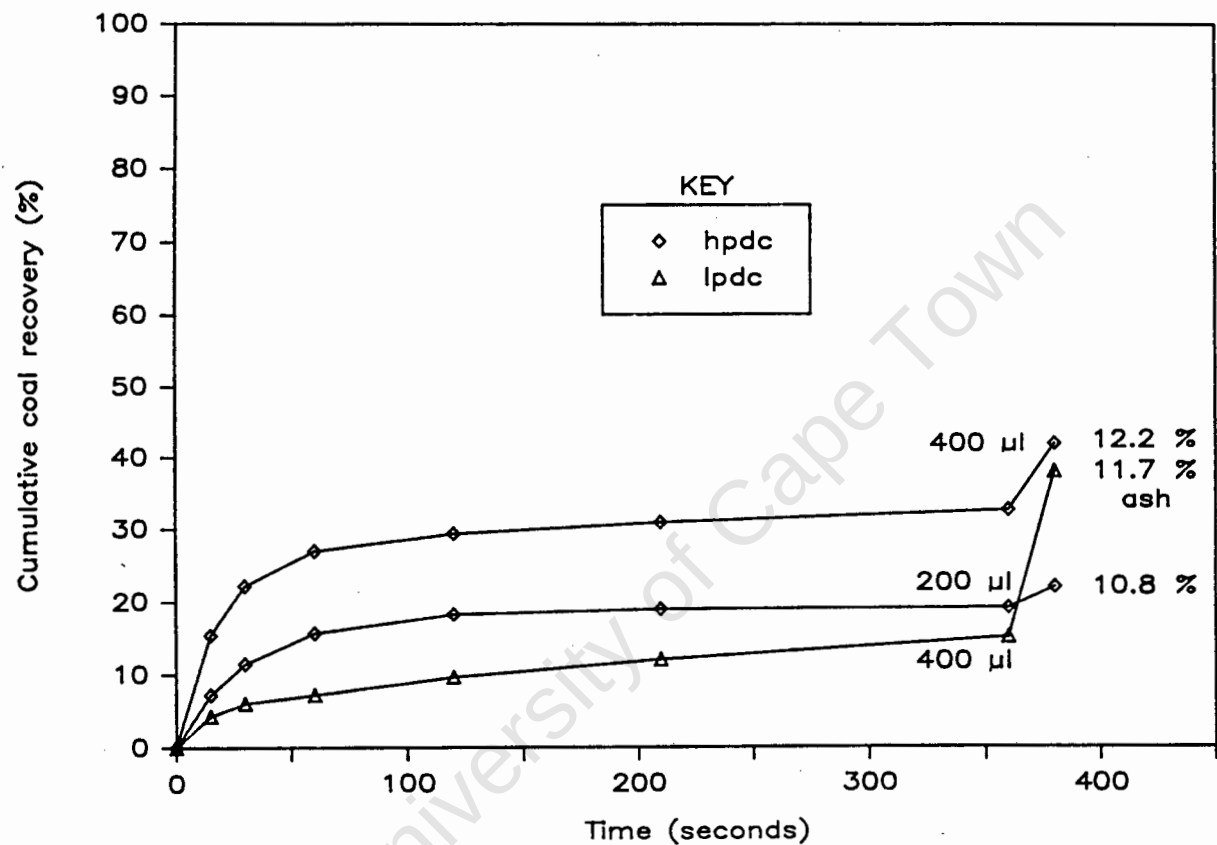


Figure 5.17 : Flotation performance with no MIBC (frother) present. 200 and 400 μ l of hexyl benzene. Milled Greenside No.2 seam unwashed coal ($-500\ \mu$ m).

was that less coal could be recovered by the fixed height scraper, though more coal was actually floated as shown by the size of the 7 th concentrate (which was scraped out by hand). A progressive decrease in the grades coincided with an increase in concentrate recovered. At the very high yields (90.5 %), achieved with 1000 μl dosage, grades were only a little better (16.5 %) than those of the feed coal (20.5 %) since most of the feed material was floated.

The large 7 th concentrate at the 1000 μl dosage was again explained by the propensity of hexyl benzene to act as a coal agglomerator. At conditions where the oil was not as vigorously dispersed, thereby producing larger droplets (lpdc), or where an excess of the oil was available (high dosages) this agglomeration tendency apparently harmed froth structure, producing a thick, brittle froth which effectively capped the pulp and prevented further concentrate recovery.

c) Intrinsic frothing ability

Results of the bubble sizing studies (Chapter 4) show that hexyl benzene has an intrinsic ability to perform as a frothing agent in that it decreases bubble size significantly. To explore this frothing potential in terms of an ability to maintain a froth, a number of floats were done with no MIBC (frother) present. Figure 5.17 shows the results.

Hexyl benzene at both a 200 and 400 μl dosage gave limited coal recoveries, in relation to those obtained in the presence of MIBC, but up to 40 % of the coal was floated in some instances. Woodburn and Flynn (1984) found that the critical kerosine addition necessary for froth stability, in the absence of a frother, was 35500 g.t^{-1} of coal. Below this dosage no froth was formed. They studied ultra-fine particles ($-45 \mu\text{m}$) of a low rank coal. Unfortunately no details were given about the characteristics of the kerosine used. Their findings suggest that it must have been largely aliphatic in character (i.e. with minimal frothing ability) since the critical dosage is more than an order magnitude higher than that used in this work (1000 and 2000 g.t^{-1}); and the ultra-fine particulate nature of the feed should itself have contributed to froth stability.

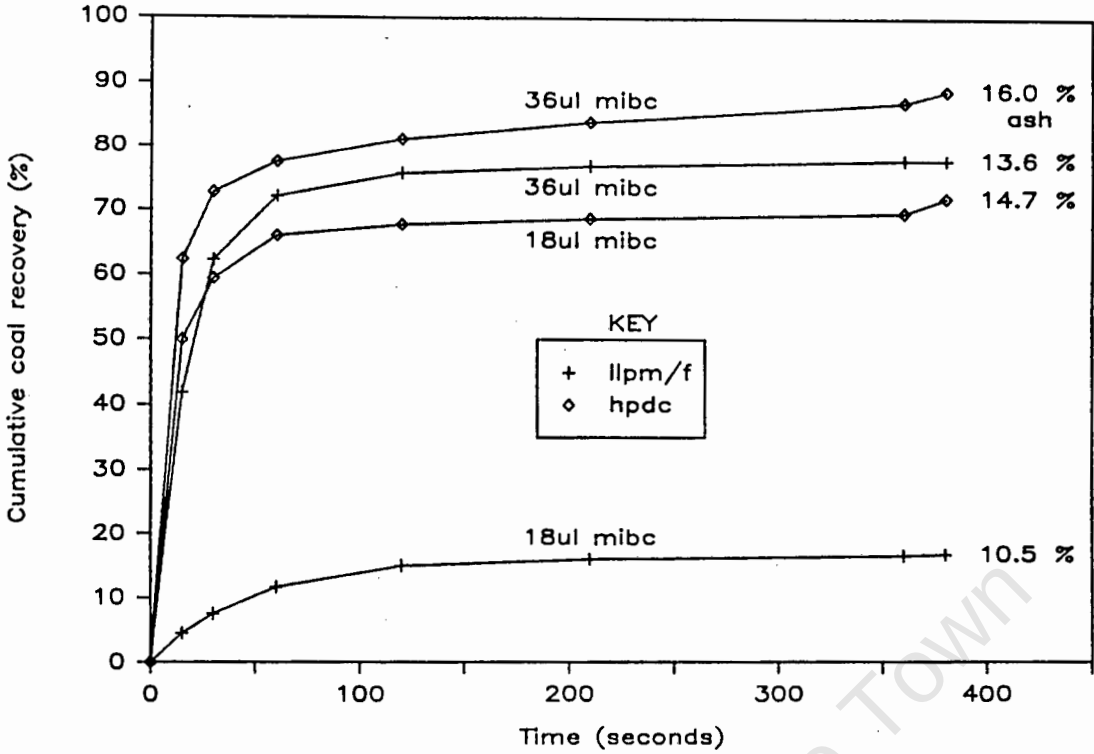


Figure 5.18 : The effect of MIBC (frother) dosage on flotation performance with 200 μ l of hexyl benzene. Milled Greenside No.2 seam unwashed coal ($\sim 500 \mu$ m).

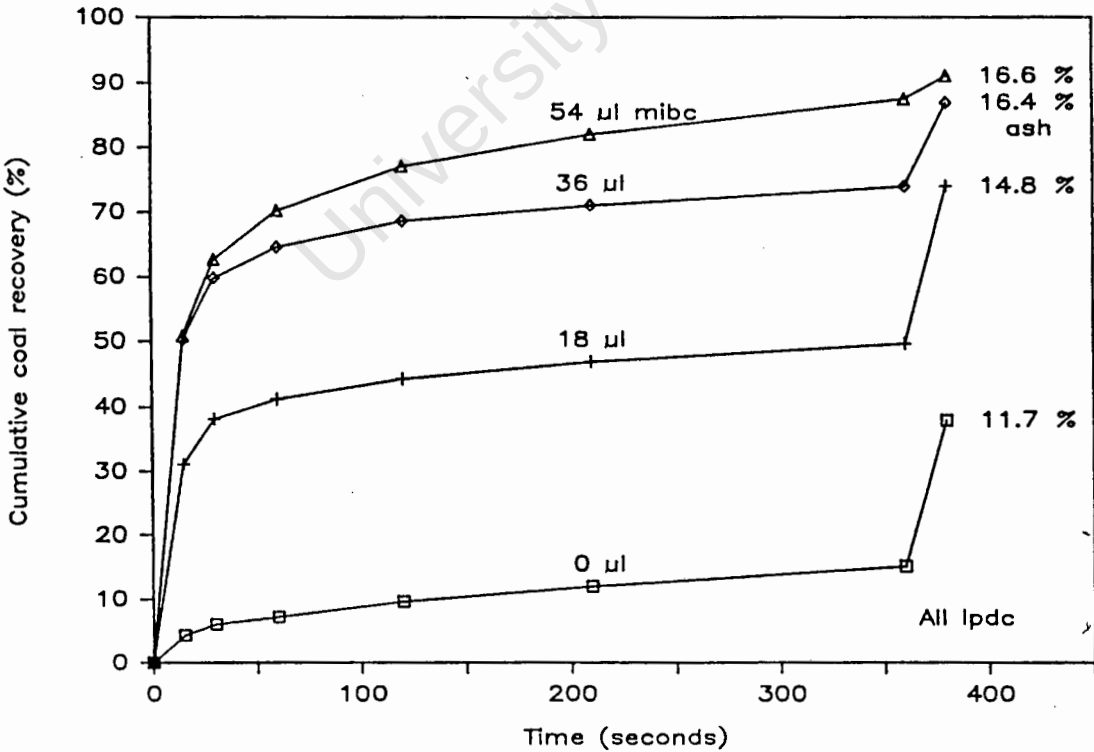


Figure 5.19 : The effect of MIBC (frother) dosage on flotation performance at 1pdc. 400 μ l of hexyl benzene. Milled Greenside No.2 seam unwashed coal ($\sim 500 \mu$ m).

Though a froth was maintained to some extent with the use of hexyl benzene alone, MIBC was obviously required to enhance this and so promote flotation. The agglomerating/coalescence tendency discussed above will prejudice the ability of hexyl benzene to maintain a froth, despite its ability to reduce bubble size. This emphasised the importance of oil-MIBC (collector-frother) joint action.

Since the influence of MIBC is not in promoting oil dispersion (as it tends to reduce this) nor in promoting adsorption its presence is evidently required for bubble-particle attachment and/or for froth stability. The former suggestion is improbable since MIBC is likely to hinder oiled particle-air adhesion by developing electrical double layers at the water-oil and air-water interfaces which repel one another. The latter suggestion therefore appears to be more reasonable. Oil-air and oil-oil adhesion can be regarded as one of classical fluid-fluid coalescence. This would be enhanced by the absence of surfactants. The presence of MIBC would consequently hinder oiled bubble-oiled bubble coalescence in the froth, and thus promote froth stability, via the same electrical double layer repulsion mechanism by which it reduces the rate of bubble-bubble coalescence.

Trends observed when MIBC was present, e.g. the "overcrowded", brittle froths obtained with the lpdc procedure (seen previously in Figure 5.15) were still evident. This indicates that the oil was indeed responsible for this behaviour; probably because of an agglomeration tendency.

d) The effect of MIBC dosage level

Figure 5.18 shows that increasing the MIBC concentration to 36 μl per float largely overcame the poor performance observed at 11pm/f at an 18 μl dosage. The higher frother concentration also increased the recovery using hpdc and would presumably tend to do so with other conditioning regimes. Interestingly, at the higher MIBC dosage, the grade was better after 11pm/f conditioning than after hpdc (at an MIBC dosage of 18 μl) even though recovery was larger. This was attributed to the decreased flotation rate at 11pm/f.

The flotation results discussed so far demonstrate the dual role oils like hexyl benzene play in both collecting coal and inducing an appropriately stable froth phase. If frother dosages are inadequate, sufficient hexyl benzene must be available for both collecting and frothing roles in order for flotation to be successful; and vice versa. Evidently a 200 μl dosage of hexyl benzene, at a low frother concentration (18 μl per float), was a critical level and inadequate for both collecting coal and supplementing the MIBC in froth formation/stabilization.

The effect of MIBC concentration on the "porridgy" froth resulting from the lpdc procedure was investigated. Figure 5.19 shows the results. As the MIBC concentration was increased so the coal recovery improved. This was not due to better chemical collection of the coal. 400 μl of hexyl benzene was used, which is twice the dosage known to produce excellent recovery (see Figure 5.18 for example) providing froth characteristics are appropriate. Rather it was the influence of MIBC on the froth which was responsible. Some frother is required to maintain the froth, but additional dosages improve the froth water content and hence the resilience and mobility of the froth and consequently the recoveries. The increased froth water-to-solids ratio is shown in Table 5.3 (the manually collected 7 th concentrate is excluded).

Table 5.3 : Effect of MIBC dosage on froth water content (lpdc with 400 μl hexyl benzene).

MIBC dosage	Water recovered in concentrate (a)	Mass of solids in concentrate (b)	Ratio (a/b)
0 μl	19.00 g	19.40 g	0.98
18	-	67.92	-
36	140.96	101.64	1.39
54	197.37	121.63	1.62

The increased water-to-solid ratio cannot be attributed entirely to a decrease in bubble size. Above a dosage of 36 μl the

effect of MIBC on further bubble size reduction is small. In addition mobile (wet) froths were attained at low MIBC additions ($18 \mu\text{l}$) providing the appropriate conditioning procedures were selected (see Figure 5.15). These latter results would suggest that reduced oil droplet size is responsible. However, since MIBC is known to hinder oil dispersion, the improved results at high MIBC dosages at lpdc were not due to smaller oil droplets. Moreover, MIBC cannot reduce agglomeration tendencies within the pulp since it is added some time after the oil and agglomeration would presumably have developed by then. The effect must then have been a froth phase one. Evidently the increased concentration of MIBC and the accompanying development of electrical double layer repulsion further stabilized the bubbles by preventing their coalescence with large oil lenses and thereby the partial collapse of the froth as discussed earlier.

It may be deduced that the inter-relation of MIBC with the oil is complex. If one partner is missing then flotation performance is poor. Depending on how the two are contacted with each other, and with the coal, and in what absolute and relative proportions they are added, so the flotation performance is altered to very significant degrees. Woodburn and Flynn (1984) also encountered the mutual dependence of the frother and collector oil when floating ultra-fine low rank coal ($-45 \mu\text{m}$). They used kerosine⁸ as collector and Montanol-361 (principal component: 2-ethyl-hexan-1-ol)⁹ as frother. In the absence of either reagent, the dosage of the other had to be increased dramatically in order to prevent yields dropping sharply. The joint action of collector oil and frother will become increasingly vital to flotation performance with progressively coarser coal feeds - like those used in this thesis: the $-500 \mu\text{m}$ feed used is believed to be more representative of the slurry discard streams at which beneficiation by flotation would be aimed in practice.

The high MIBC dosages used in this series of tests did not have an adverse effect on grades in relation to the yield of coal. But the liberation of this unwashed coal sample (see Section 5.5.2) is insufficient to assume that this would be so in general. However if the grades are unaffected, increasing MIBC dosage is a possible cure

⁸ Unfortunately no details about this oil were given.

⁹ A non-ionic alcohol frother similar to MIBC (4-methyl-2-pentanol).

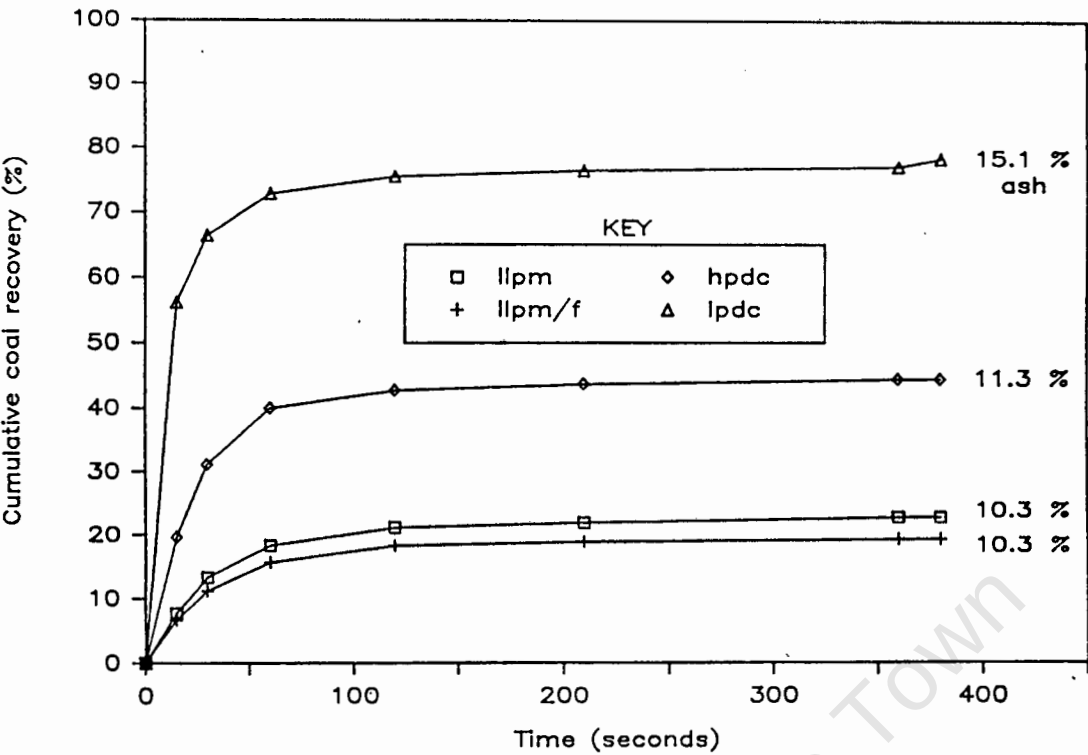


Figure 5.20 : The effect of various conditioning procedures on flotation performance using 200 μ l of Shellisol AB and 18 μ l of MIBC per float. Milled Greenside No.2 seam unwashed coal (-500 μ m).

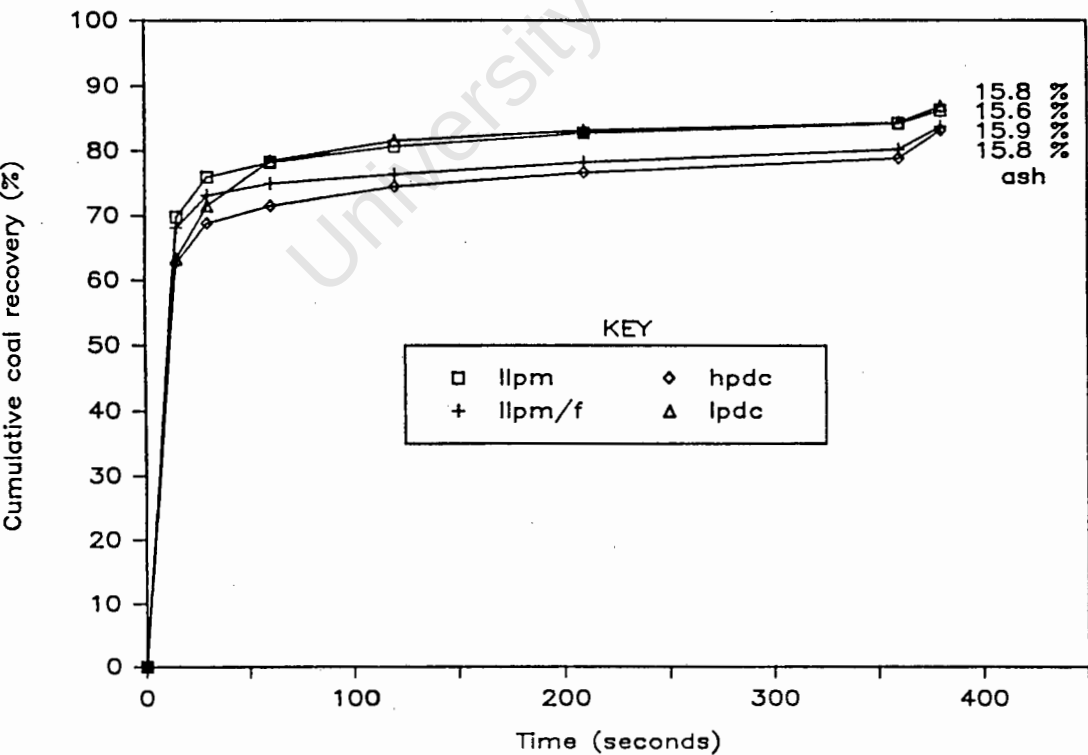


Figure 5.21 : The effect of various conditioning procedures on flotation performance using 400 μ l of Shellisol AB and 18 μ l of MIBC per float. Milled Greenside No.2 seam unwashed coal (-500 μ m).

for poor performance, lpdc being the usual manner of contacting reagents with the coal pulp.

5.4.2.2 Shellsol AB

a) The effect of conditioning procedure

A comparison of results shown in Figure 5.20 with those in Figure 5.12, indicates that at a 200 μl dosage (per float) of Shellsol AB and with 18 μl MIBC, trends were obtained that were unlike those with hexyl benzene under similar conditions except for the fact that 11pm/f conditioning appeared detrimental. 11pm conditioning also gave poor results and the best results were achieved with lpdc. The froth crowding effect apparent with hexyl benzene under lpdc conditions did not occur, so possibly some constituents of this commercially produced oil have surface-active properties which helped to offset coalescence tendencies within the froth phase, in a similar manner to that of increased MIBC dosages with the pure hexyl benzene oil. Shellsol AB is known to be a good coal agglomerator (Buys, 1987).

Froths in all instances were fluid as evidenced by the lack of unrecovered but floated coal (7th concentrate). Nevertheless the froth at lpdc conditions was drier than that produced under other conditioning regimes. Conditions of 11pm and 11pm/f produced froths with a significantly higher water to coal content ratio than the other conditioning procedures as shown in Table 5.4.

This could be due to changes in bubble size or in bubble loading. Bubble size was similar under a variety of mixing intensities with both aromatic and aliphatic oils, i.e. largely independent of the oil droplet size distribution (see Figures 4.13 and 4.14), which suggests that it would be similar irrespective of the conditioning method. Increased bubble loading as a consequence of the formation of coal particle aggregates at conditions more favourable to agglomeration (i.e. lpdc) and the accompanying partial collapse of the froth due to bubble-oil lens coalescence is therefore believed to be responsible.

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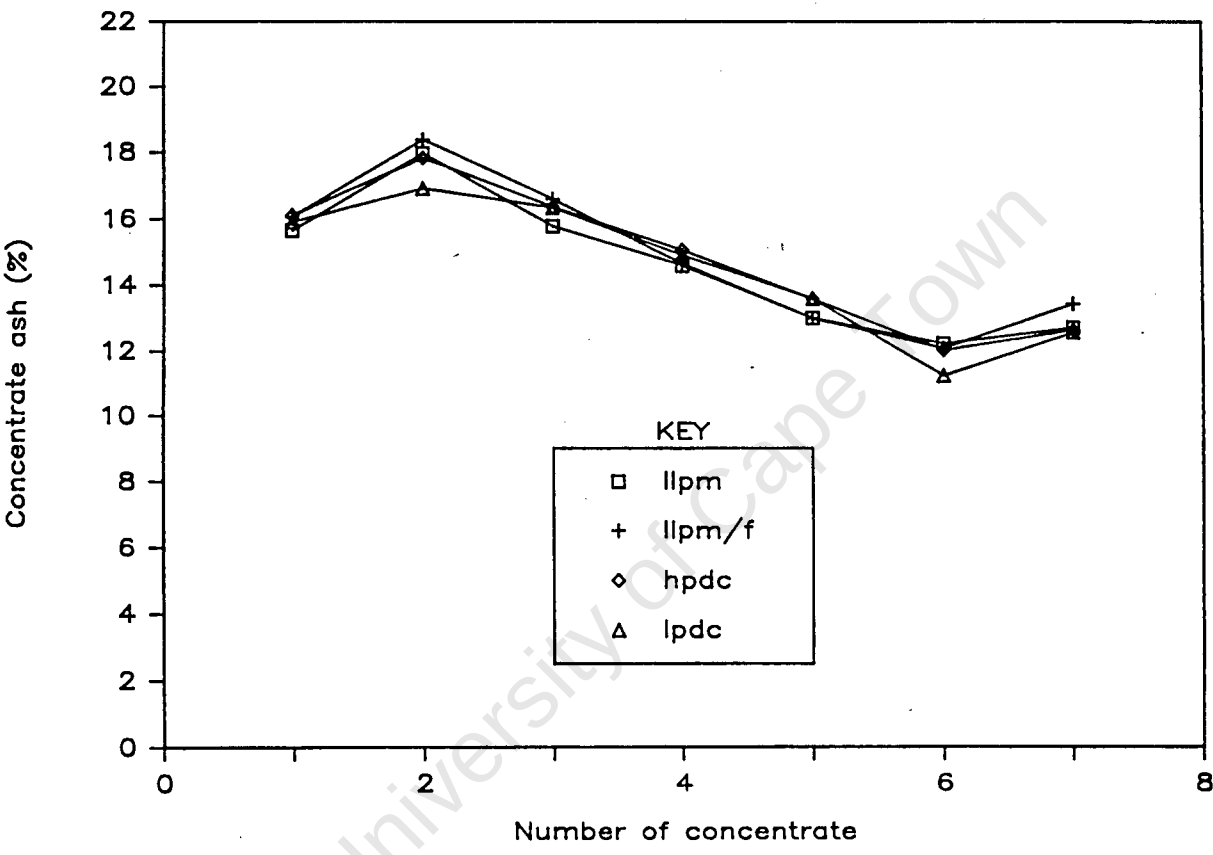


Figure 5.22 : Grades of successive concentrates obtained after various conditioning procedures. 400 μ l of Shellisol AB and 18 μ l of MIBC per float. Milled Greenside No.2 seam unwashed coal (-500 μ m).

Table 5.4 : The effect of conditioning procedure on water recovery

Conditioning procedure	Mass of water in concentrate (a)	Mass of coal in concentrate (b)	Ratio (a/b)
1lpm	63.27 g	29.18 g	2.17
1lpm/f	58.48	24.63	2.37
hpdc	84.83	57.81	1.47
lpdc	132.11	105.97	1.25

b) The effect of dosage level

The hierarchy of results shown in Figure 5.20 is difficult to interpret and is at variance with the results discussed in the sections above. For instance conditions producing less adequate oil dispersion (lpdc) unexpectedly gave the best flotation performance. However MIBC dosages were low (18 μ l per float) as were those of the oil (200 μ l per float). It is presumed that the flotation dynamics were in an unstable state as a result of the inadequacy of the two partners to perform both collecting and frothing roles satisfactorily; either because their dosages were too small or because the coal was deprived of reagent by some other means. By increasing the dosage of one or the other, it was believed that the expected and explainable performance hierarchy would be forthcoming. This was found to be the case. Figure 5.21 shows that at a 400 μ l dosage of Shellsol AB, conditioning procedures had little effect on recoveries, which were excellent. Concentrate ash levels contents were also unaffected and were all essentially identical.

However, the distribution of grades amongst the successive concentrates deserves some discussion. Figure 5.22 shows that the second concentrate ash was significantly higher than the first irrespective of conditioning procedure. Thereafter the grade of the concentrates improved. The grade of the seventh concentrate appears anomalous but this is because it is constituted from coal which floated throughout the test. The high ash content of the second

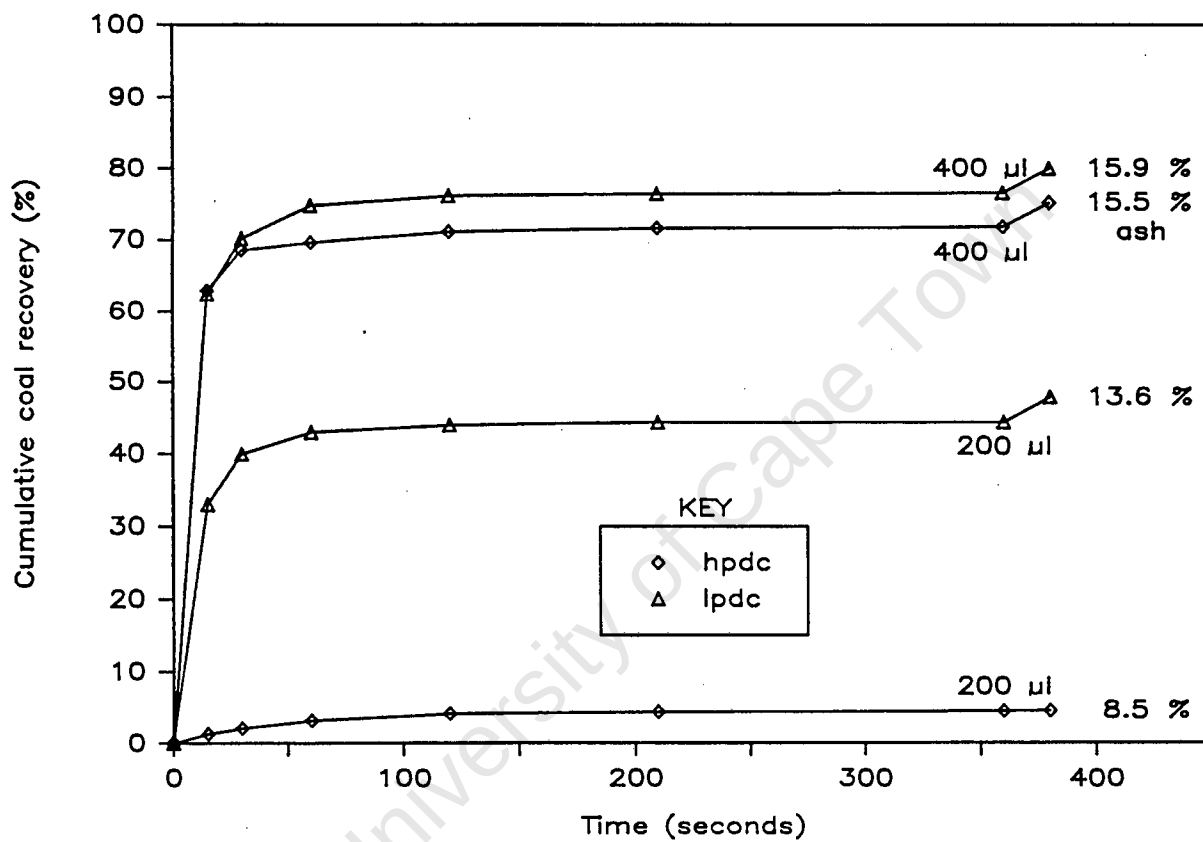


Figure 5.23 : Flotation performance with no MIBC (frother) present. 200 and 400 µl of Shellsol AB. Milled Greenside No.2 seam unwashed coal (-500 µm).

concentrate can be explained as follows. The initial rapidity of the flotation results in entrainment of gangue. However the cleaner coal is preferentially collected and floats earlier than less clean coal (middlings) to form the upper layers of the developing froth. These two effects balance the grade of the first concentrate. The less clean coal, together with whatever gangue may drain from the lower levels of the froth which constitutes the first concentrate, forms what becomes the second concentrate which consequently has a substantial relative ash content.

The high second concentrate ash content seemed to occur in all instances where flotation kinetics were very rapid, i.e. where the mass of the first concentrate was very large. Grade improved significantly in subsequent concentrates (as the rate of both flotation and of concentrate removal decreased) but yields were too small to affect the overall concentrate grades significantly.

The rapid removal of concentrate at high flotation rates (70 % of the coal was recovered in the first 15 seconds of flotation) is unavoidable at conventional froth depths. Ostensibly, if greater froth residence times were available (froth was scraped off every five seconds initially) the entrained material would return to the pulp. However in many instances encountered in the flotation program froth rigidity would have largely precluded this. Furthermore, a study of the flotation results for this coal on a global basis (Section 5.5.4) suggested that flotation rate is not as powerful a factor as would be expected, though it undoubtedly had some effect. Its true effect could have been masked by poor gangue liberation.

c) Intrinsic frothing ability

The intrinsic frothing ability of Shellsol AB was investigated in flotation tests conducted without MIBC. Figure 5.23 shows that the oil produced remarkable recoveries at the 400 μ l dosage, indicating its ability to adopt both collecting and frothing roles. The 200 μ l dosage is clearly inadequate for both roles. In addition to some frothing ability inherent with pure aromatics, as shown by hexyl benzene, it is very likely that surfactant impurities in this aromatic oil are responsible for its especially good frothing characteristics,

chiefly through their role in hindering bubble-bubble coalescence. The absence of MIBC did not induce better concentrate grades (cf Figure 5.21).

Of the two conditioning methods tested in the absence of MIBC, lpdc again produced the better recoveries especially at the 200 μ l dosage where recoveries at hpdc were negligible. This appears in conflict with the fact that when using lpdc the oil was more poorly dispersed and therefore more limited in its availability to particles in the pulp. Recoveries would be expected to be poorer.

Other possible causes of the strange behaviour may be easily ruled out. The degree of oil dispersion does not affect bubble size as shown in Chapter 4. Frother (MIBC) was absent so changes in frothing performance as a result of its transfer to the oil phase were not relevant. Thus by elimination it is deduced that some physical attribute of the oil droplets and/or adsorbed oil lenses, controlled by the type of conditioning procedure selected, was responsible. The physical size of the oil droplets, and by association the thickness of the oil lenses on the coal particles, apparently had some influence on froth stability and hence on the recovery. As droplet size decreased so recovery decreased. A decrease in dosage (and hence possibly in the thickness of the oil adsorbing on the particles) induced a similar effect. The very poor recovery (about 5 %) at hpdc with 200 μ l of Shellsol AB (Figure 5.23) was attributed to these effects. An increase in dosage or a decrease in conditioning intensity both improved the recovery as may be seen from Figure 5.23.

Poor recoveries were also observed in other tests in which the Shellsol AB was finely dispersed, i.e. after 11pm, 11pm/f and hpdc (Figure 5.20). Nevertheless, Figure 5.20 shows that the recovery at hpdc was considerably better when MIBC was present than in its absence (Figure 5.23), all other conditions being equal. This reinforced the notion that a froth stability phenomenon was responsible for the poor recoveries. Again recovery was found to increase after milder dispersion conditions (lpdc).

An increase in dosage also overcame the froth stabilization deficiency, postulated to be induced by oil dispersion being too thorough, as may be seen from Figure 5.21. An increase in frother

dosage would also be expected to provide the necessary froth stability. This was found to be so with hexyl benzene (Figures 5.18 and 5.19).

5.4.3 Aliphatic/aromatic oil mixtures

5.4.3.1 Pegasol 3745

a) The effect of conditioning procedures

Figure 5.24 shows the flotation results achieved under various conditioning regimes with a 200 μl dosage of the 200-210°C Pegasol 3745 cut and with 36 μl of MIBC. With the exception of the 11pm test the hierarchy of flotation performance achieved by the different conditioning procedures was like that obtained for dodecane (Figure 5.10) at similar dosages. However, recoveries were somewhat better in all cases. The reason for this is not better dispersion or adsorption of the Pegasol 3745 oil onto coal: when used alone, it behaved in a manner typical of the aliphatic oils. This oil also had only a small influence on bubble size when used alone (Section 4.7.2.7). Its aromatic oil content can therefore only be a small contributory factor to the better overall performance observed at each conditioning procedure. However, the remarkable bubble reduction effect of the MIBC-Pegasol 3745 joint action (found in the bubble sizing testwork and discussed in Section 4.7.2.8.c) is believed to be chiefly responsible for the observed improvement in recoveries.

b) The effect of boiling range

i) Recovery

Figure 5.25 shows that at 400 μl dosages and with 18 μl of MIBC the lower boiling point cuts (180-190 and 200-210°C) behaved very similarly. All cuts gave good recoveries. The viscous 240-250°C cut produced significantly slower kinetics but only a slightly poorer final recovery. Coal recovery after 15 s (first concentrate) was only half that achieved with the lower boiling range homologues.

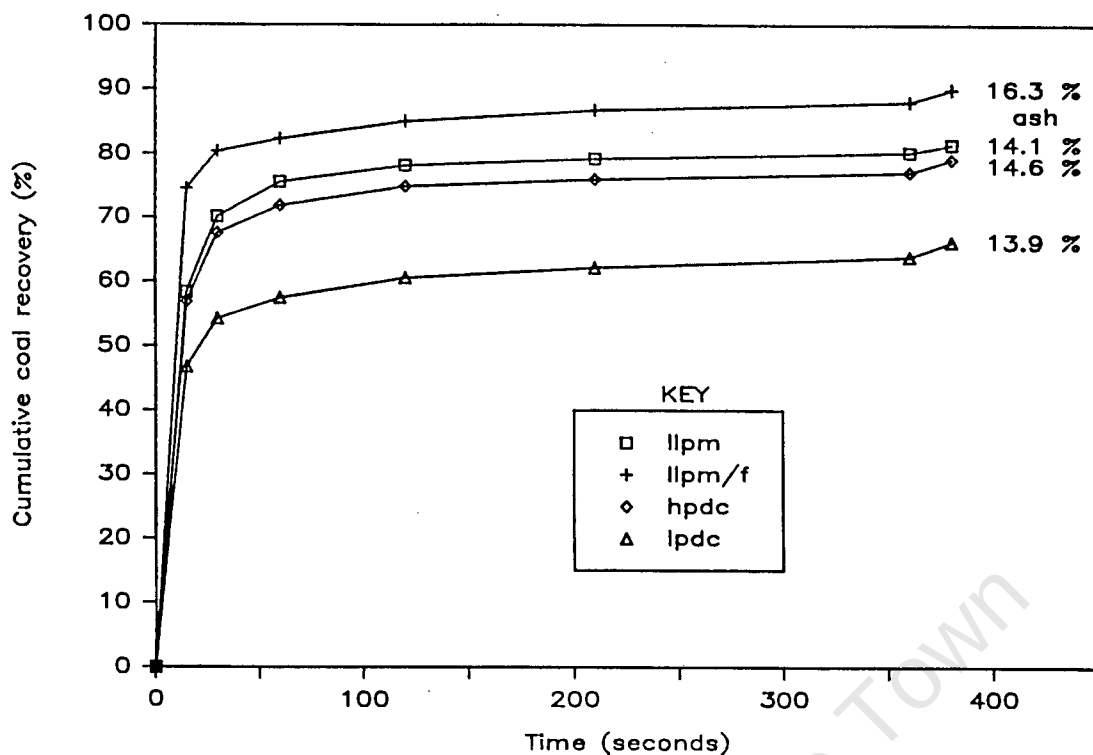


Figure 5.24 : The effect of various conditioning procedures on flotation performance using 200 μ l of Pegasol 3745 (200-210°C cut) and 36 μ l of MIBC per float. Milled Greenside No.2 seam unwashed coal ($\sim 500 \mu$ m).

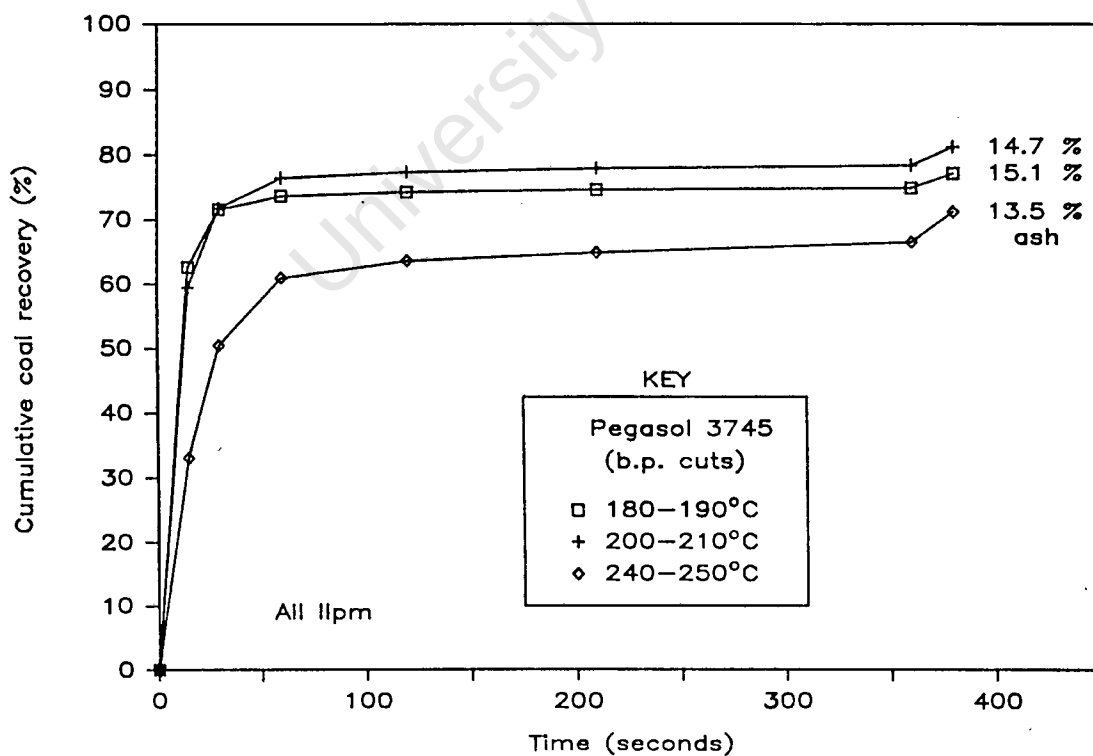


Figure 5.25 : Flotation performance with various Pegasol 3745 boiling range cuts at 1lpm. 400 μ l of oil and 18 μ l of MIBC per float. Milled Greenside No.2 seam unwashed coal ($\sim 500 \mu$ m).

The differences in flotation kinetics achieved with the various cuts is not easy to explain but is apparently related to the viscosity. Droplet size distributions of all the cuts were very similar (refer to Figure 2.12) so collector availability was not the explanation. Differences in degree of adsorption of the oils (in the absence of MIBC; since this was only added later) were also slight (see Figure 3.17). The presence of MIBC did enhance the adsorption of the cuts somewhat: in the presence of MIBC, adsorption of lower boiling range cuts was more pronounced than that of the 240-250°C cut (see Figure 3.25). However the 11pm conditioning procedure used ensured that oil adsorption would be complete before MIBC was added; and since oil is essentially irreversibly adsorbed, and flotation commenced soon after MIBC addition, there seems little chance that the system had readjusted.

It may be that differences in the flotation kinetics were the result of differences in the spreading characteristics of the oil homologues at the air-water interface in the presence of MIBC, because spreading affects bubble size. However, this postulate offers an incomplete explanation since bubble sizes were observed to change to only a small extent (Figure 4.22). This figure shows that the more viscous cut did produce a broader bubble size distribution than the other cuts, which ties in with the flotation results; but the difference appears very small in relation to the large difference in flotation rates.

It is suggested rather that a fluid-fluid coalescence interpretation of air bubble-oil coagulation, similar to the liquid-liquid coalescence mechanism reviewed in the literature survey (Section 5.2.3.2), offers the most plausible explanation for the reduced flotation rate observed at the higher oil viscosities. According to this theory, the rate of air bubble-oil droplet coalescence or rather coagulation will tend to decrease with an increase in oil viscosity. Bubble-oiled particle collection efficiencies would therefore be reduced, thereby decreasing flotation rates, yet the approximate equivalence of particle coverage (oil droplet size and adsorption are similar) and reasonably similar bubble sizes would ultimately lead to roughly equivalent final recoveries.

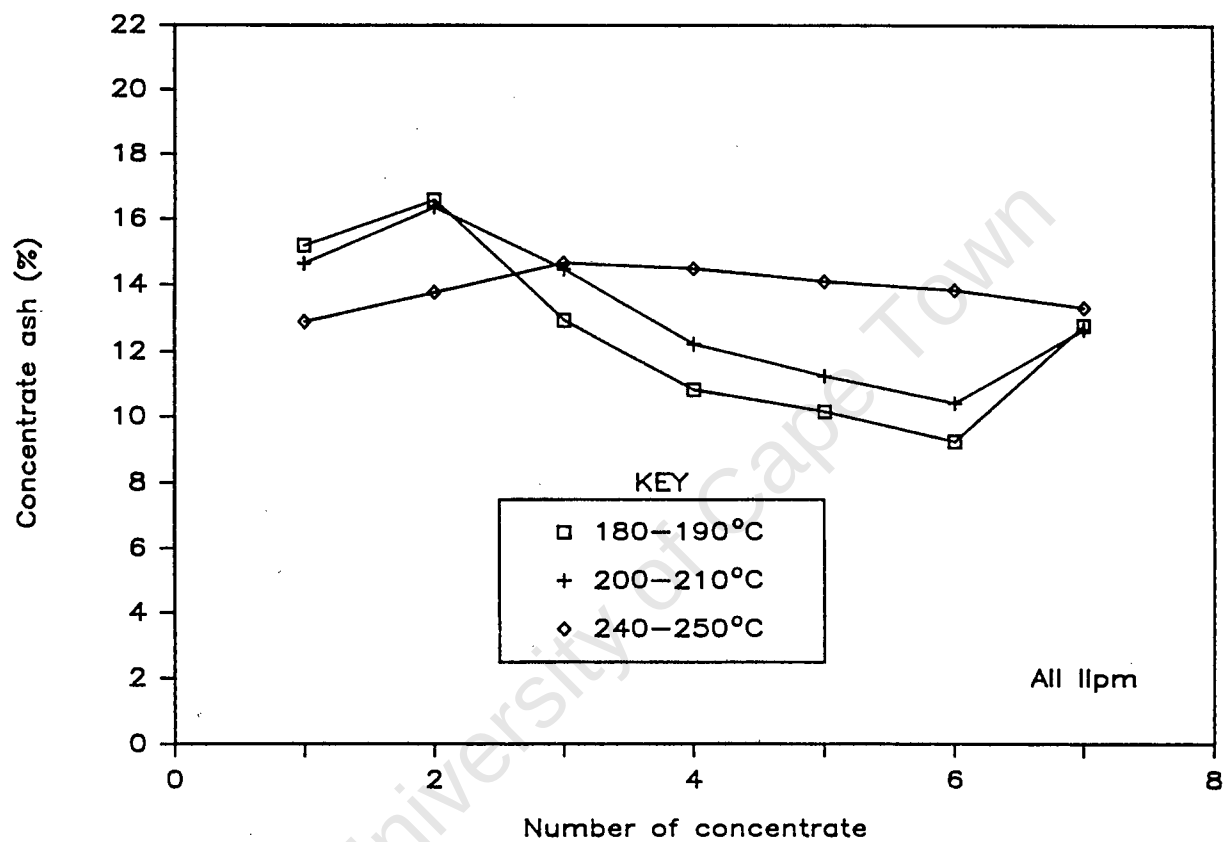


Figure 5.26 : Grades of successive concentrates obtained during flotation with various Pegasol 3745 boiling range cuts at 11pm. 400 μ l of oil and 18 μ l of MIBC per float. Milled Greenside No.2 seam unwashed coal (-500 μ m).

If this hypothesis is correct, oil viscosity would be an appropriate means of regulating flotation rate without sacrificing overall recovery.

ii) Grade

The effect of flotation rate on the grades of successive concentrates obtained with the Pegasol 3745 cuts is now considered. Figure 5.26 shows that fairly consistent concentrate grades were obtained throughout the flotation with the 240-250°C cut. This is in contrast to the other cuts which produced high ash contents initially (second concentrate in particular). Subsequent concentrates produced by the lower boiling range cuts were of far better grade, but the yields were too small to affect overall grades. The yields of these later concentrates was so small that entrainment of unwanted material was negligible. These later concentrates also had a high water content in relation to the solids content, which undoubtedly aided in the drainage of entrained material. The influence of froth water content on gangue drainage is considered further in Section 5.5.6.

Despite the apparently significant effect of rate, its actual effect was small. Nevertheless, the higher boiling range cuts produced somewhat better grades because they took longer to float the material, thereby reducing entrainment. The selectivities of the cuts are not different: the grades of the first two concentrates achieved with lower boiling range homologues were higher than those of the 240-250°C cut simply because more mass was floated.

Concentrate grades are largely determined by the proportion of middling material (in terms of ash) within the feed. No matter how the flotation parameters are altered flotation will only be able to produce a low-ash product with a well liberated coal. With the coal used in these tests, the proportion of middling material is large and, as the particles are dominated by hydrophobic carbonaceous material (see Section 3.5.3), they will be collected. Factors such as flotation rate can therefore only have a small impact on the grades, though its importance with well liberated feeds is widely acknowledged.

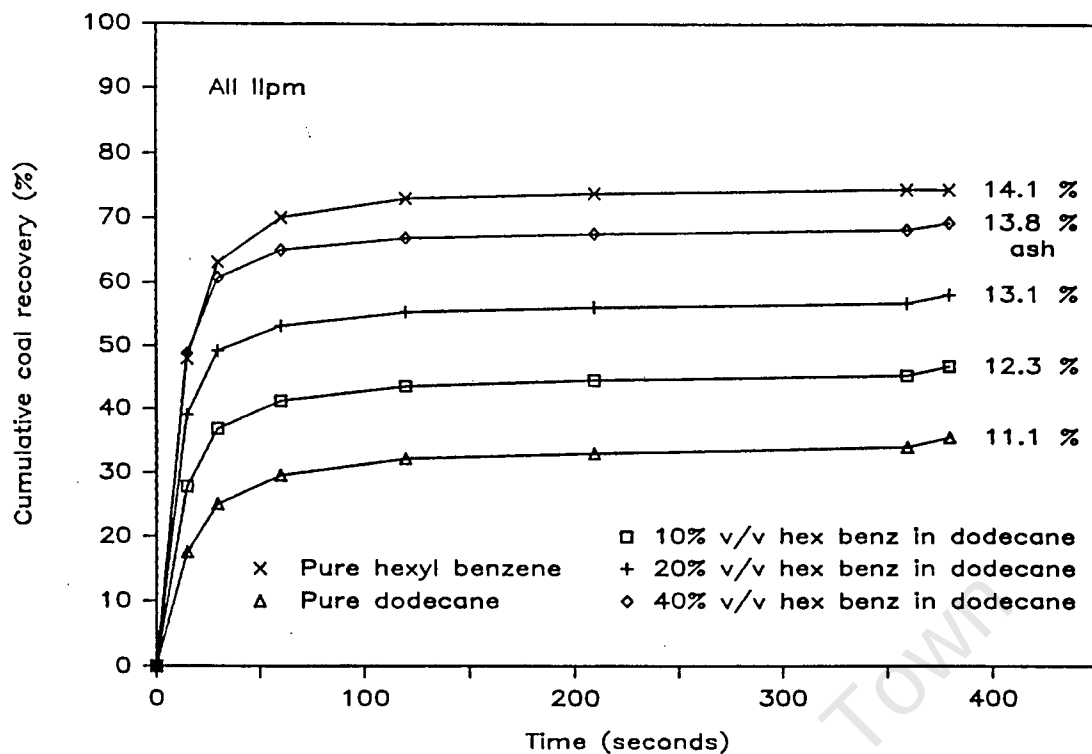


Figure 5.27 : Flotation performance obtained with various proportions of hexyl benzene in dodecane. 11pm conditioning procedure. 200 μ l of oil and 36 μ l of MIBC per float. Milled Greenside No.2 seam unwashed coal ($\sim 500 \mu$ m).

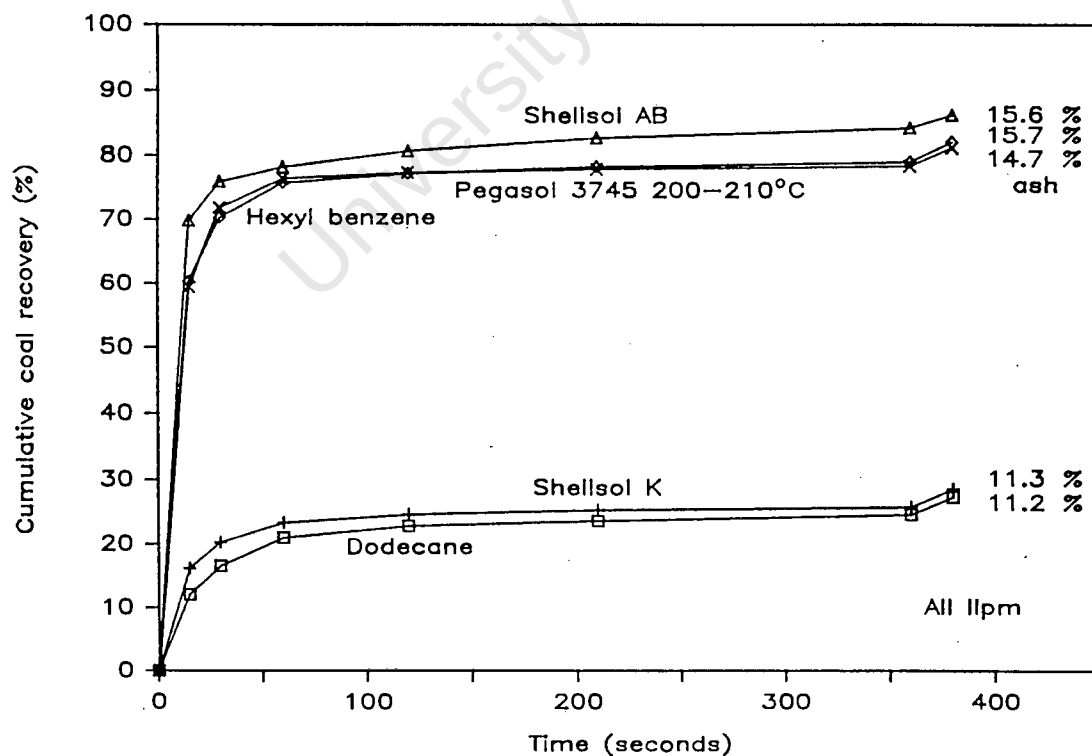


Figure 5.28 : Flotation performance with various collectors. 11pm conditioning procedure. 400 μ l of oil and 18 μ l of MIBC per float. Milled Greenside No.2 seam unwashed coal ($\sim 500 \mu$ m).

5.4.3.2 Hexyl benzene/dodecane mixtures

One means of controlling flotation rate would be by regulating the bubble size, which can be achieved chemically (through a suitable choice of collector oil) or physically (by altering impeller speed and aeration rate). The possibility of regulating flotation rate by using oils of different viscosities has already been discussed in Section 5.4.3.1.b.

The nature of the oil was also investigated as an alternative means of regulating flotation rate through its influence on bubble size. In these tests physical parameters were maintained at the same levels used in other tests. Since hexyl benzene was known to reduce bubble size, blends of this oil in dodecane were tested in the presence of an adequate frother concentration (36 μl of MIBC/float) to see if the rate of flotation could be controlled. Oil dosages were 200 μl . Figure 5.27 shows the results. Increasing proportions of hexyl benzene markedly increased the flotation rate: the 40 % mixture produced results practically the same as pure hexyl benzene. Unfortunately with all the blends a low initial rate was always symptomatic of a low overall recovery, in contrast to the results achieved with oils of higher viscosity, as discussed in the preceding section.

5.4.4 General collector comparisons

The above subsections deal with oils one-at-a-time and the effects of various parameters on flotation, in conjunction with the oils, are considered. In this subsection, a general comparison of the flotation performance tendencies of each oil type, at the same conditions, is presented.

5.4.4.1 Recovery

The flotation performance of the oils was found to be the reverse of that expected on the basis of the conclusions of Brown et al (1958), following their observations of the spreading characteristics of oils on wet coal. They proposed that oils which

spread spontaneously at the air-water interface (typically aromatic oils) would deprive coal of oil upon contact of an oiled particle with an air bubble. Flotation performance would therefore be expected to deteriorate. On this basis non-spreading oils (typically aliphatic oils) were believed to be better collectors. The results of the present testwork, as discussed in the preceding sections, clearly shows that (at the oil dosages used) this was not the case.

The results shown in Figure 5.28 typify those found throughout the testwork program. Figure 5.28 shows that at 400 μ l dosages (per float) of collector and with 18 μ l of MIBC, excellent recoveries (of the order of 80 %) were obtained using the predominantly aromatic oils. The aliphatic oils behaved poorly in comparison; cumulative coal recoveries were as low as 30 %. A notable exception was the Pegasol 3745 200-210°C cut, which contains only 20 % aromatics, but which produced flotation results much like those of the aromatic oils.

The marked difference between the aromatic and the aliphatic oils, both pure and commercial stocks, reflected the differences that were observed in the behaviour of each oil type with respect to dispersion, adsorption and effect on bubble size. An exception was the Pegasol 3745 oil, which had an approximately 80 % aliphatic content. This oil behaved very similarly to the predominantly aliphatic oils (dodecane and Shellsol K) in terms of dispersion and adsorption onto coal. However, its significant effect on bubble size (in the presence of MIBC) apparently caused the large difference in flotation results between it and the other aliphatic collectors.

The results of dispersion tests carried out at similar conditions (pre-mixing of the oils) revealed that the "pure" aliphatic oils and the Pegasol 3745 oil were well dispersed, albeit to less of a degree than the aromatic oils (Section 2.6.2). Amongst the aromatic oils, hexyl benzene was better dispersed than Shellsol AB, yet its flotation performance was no better. Dispersion was in all cases sufficient for good flotation performance.

In terms of adsorption, both Shellsol AB and hexyl benzene adsorbed to a significantly greater extent than did the dodecane, Shellsol K and Pegasol 3745 oils. Because of better dispersion and more extensive adsorption, it is reasonable to expect that the

aromatic oils would be better distributed on the solids within the pulp. Since their selectivity (and that of the aliphatic oils) is good, their flotation performance would be expected to be better than the aliphatic oils. Nevertheless the results obtained with the Pegasol 3745 suggest that the lower extent of adsorption reached by the predominantly aliphatic oils is still sufficient for effective flotation performance, provided that bubble/froth characteristics are appropriate.

The behaviour of the Pegasol 3745 oil emphasized the importance of bubble size and froth stability in relation to oil dispersion and adsorption. Clearly if the latter two phenomena do not arise, then flotation is impossible. However, although the degree to which both dispersion and adsorption onto coal found with the Pegasol 3745 oil was less than that achieved with the aromatic oils, the results obtained with the Pegasol 3745 in flotation testwork indicated that these levels are still sufficient for good flotation performance. This showed that flotation performance is dominated, but not dictated, by the effect of the oil, or the oil-frother combination, on bubble size and hence ultimately on the structure and stability of the froth phase.

Poor froth structure/stability is synonymous with reduced recovery. The influence of poor froth stability on the recovery of solids becomes increasingly marked as particle size increases. This is a widely acknowledged phenomenon and was clearly evident from visual observations of the concentrates recovered throughout the testwork program.

Table 5.5 shows the size distribution of the feed and of the overall concentrates for some of the flotation experiments shown in Figure 5.28. The froths produced when the Pegasol 3745 200-210°C cut, hexyl benzene (and hence presumably Shellsol AB) were used as collectors, yielded concentrates in which the size distribution of the solids was practically identical to that of the feed. In contrast, the weak froth produced when dodecane was used as the collector was only able to support the finer particle sizes: proportionately less of the coarser particles was recovered. 94 % of the particles in the concentrate were smaller than 300 μm , compared with 73 % in the feed; and 84 % passed 250 μm , compared to 64 % in the feed. Visual

similarity indicated that the Shellsol K concentrate would have exhibited similar characteristics.

Table 5.5 : Cumulative size distributions of the unwashed coal in the flotation feed and in the flotation concentrates. 400 μ l of oil and 18 μ l of MIBC. 11pm conditioning.

Size (wet)	Cumulative mass percent passing			
	Feed	Conc.	Conc.	Conc.
		H. Benzene	Pegasol 200-210°C	Dodecane
75	30.6	29.6	30.7	44.0
106	37.9	39.5	39.2	55.6
150	46.6	47.8	47.5	66.2
250	64.4	66.3	64.3	83.8
300	72.6	74.8	73.1	93.6
500	100.0	100.0	100.0	100.0

That poor recovery is a froth phenomenon and not a result of inadequate oil dosage has been clearly shown in tests in which the froth stability was increased by increasing the frother dosage and/or by using an appropriate conditioning procedure. At a 200 μ l dosage of dodecane, which is half that used in the test shown in Figure 5.28, but with the frother dosage increased to 36 μ l and using 11pm/f conditioning procedure, an excellent recovery was obtained (Figure 5.10). The particle size distribution of the concentrate produced was practically identical to that of the feed as may be seen in Table 5.2.

As has been pointed out in previous subsections, froth form and stability is dependent, inter alia, on the type of oil used as collector, the dosage of the oil, the dosage of the frother, the possibility of beneficial frother-collector interaction, the solid particle size distribution, the native hydrophobicity of the solid particles and the type of conditioning procedure employed.

5.4.4.2 Grade

As may be seen from Figure 5.28, the Pegasol 3745 (200-210°C cut) gave better grades at similar recoveries than both the commercial aromatic oil Shellsol AB and hexyl benzene, even though flotation was also rapid (most of the concentrate was produced in the first 15 s). Differences were small but may have been suppressed by inadequate gangue liberation.

The difference in the overall concentrate grade could be indicative of the somewhat better selectivity displayed by aliphatics towards coal particles which would be regarded as middlings because of their ash content. Aliphatics are strictly non-polar and unable to adsorb on a charged surface. The aromatic collectors, which are somewhat polar, are more readily able to adhere to a charged surface. However, these oils are only marginally less selective than aliphatic oils as shown by the selectivity testwork (Section 3.5 and Section 5.4.7 below).

With a well liberated coal feed, good grades should be obtained with both oil types. Though the aliphatic oils can be expected to have a small edge on the aromatic oils in respect to selectivity, the ability of aromatic oils to tolerate some surface oxidation, as well as their beneficial influence on bubble size, suggests that they would generally be a better choice of collector.

5.4.5 The effect of the timing of MIBC addition

The importance of the mode and timing of frother addition on flotation performance is discussed above in Section 5.2.3.5.a. In this flotation testwork, it was decided a priori to add MIBC separately from the oil since its preferential solubility in oil would have reduced its presence at the air-water interface and hence its frothing ability. Even if MIBC were added separately it would tend to migrate to the oil phase : frothing power and hence flotation performance would therefore be adversely affected by *early addition* of MIBC. At conditions where frother is added just prior to aeration, insufficient time would be available for much of the MIBC to migrate from the water to the oil or solid surfaces, or to dissolve into the oil itself.

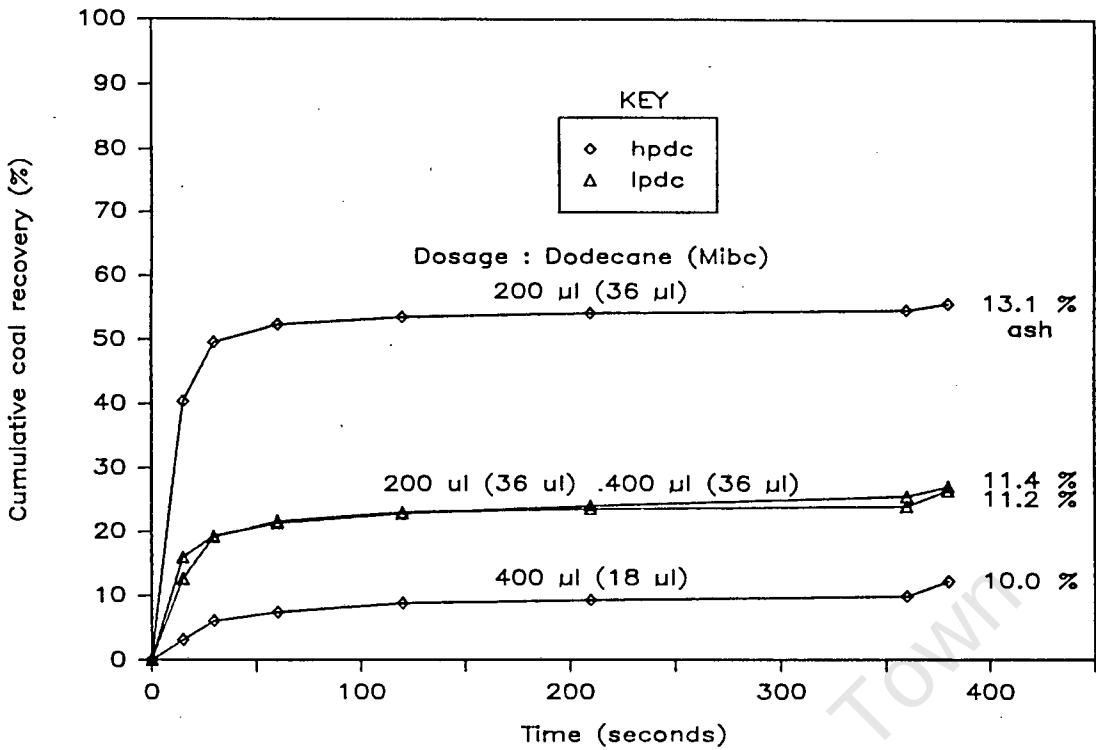


Figure 5.29 : Flotation performance with dodecane at 200 and 400 μl dosages under hpdc and lpdc regimes. MIBC was added 10 seconds after oil addition (early addition) at 18 and 36 μl dosages. Milled Greenside No.2 seam unwashed coal ($-500\ \mu\text{m}$).

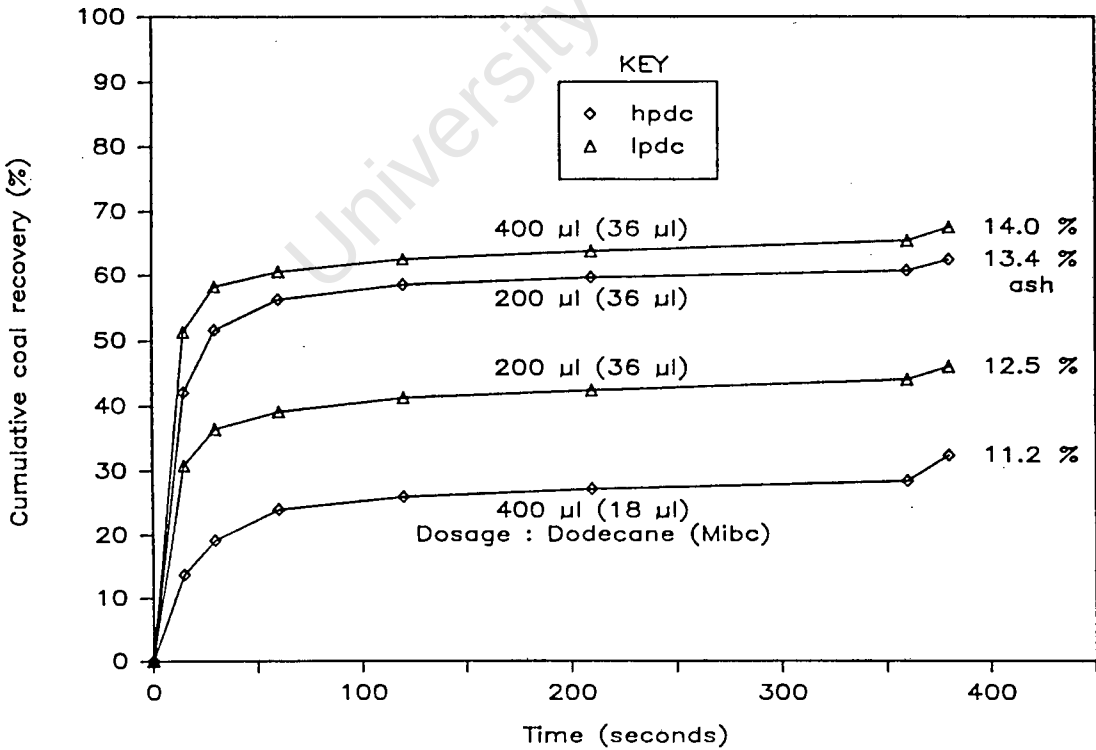


Figure 5.30 : Flotation performance with dodecane at 200 and 400 μl dosages under hpdc and lpdc regimes. MIBC was added 1 minute before aeration (late addition) at 18 and 36 μl dosages. Milled Greenside No.2 seam unwashed coal ($-500\ \mu\text{m}$).

It is of course possible to introduce the frother earlier, with the collector oil, as is often the case industrially. In a series of tests to investigate the effects of early addition, MIBC was added 10 seconds after addition of the collector oil. This was 5:43 minutes before commencing aeration as opposed to 1 minute before aeration. The conditioning regimes used with the latter mode of addition were lpdc and hpdc. The regimes used following early MIBC addition were similar in all respects bar the timing of MIBC addition: they are therefore designated "lpdc" and "hpdc" to distinguish them from the regular procedures.

A comparison of Figure 5.29 and Figure 5.30 shows that early MIBC addition was very detrimental to flotation performance, with the exception of the test at "hpdc", with 200 μl and 36 μl dosages of dodecane and MIBC respectively, in which the detrimental effect was less evident. In the other tests recoveries achieved after early MIBC addition were less than half those obtained following late MIBC addition. MIBC was evidently migrating to the oil phase thereby reducing its presence at the air-water interface and hence its frothing ability. The floats that showed the most negative percentage change in coal recovery were those where a large volume (400 μl) of oil was present and/or a low MIBC volume; which supports the above explanation. The floats in which the oil dosage declined relative to the MIBC dosage were considerably less affected, since there was less oil available and MIBC transfer rates were consequently reduced. Under these conditions, sufficient MIBC still remained in solution to sustain reasonable frothing performance.

It was expected that a sharp reduction in flotation performance would have been prevalent at "hpdc" since droplets were better dispersed thereby increasing oil-water surface area and presumably enhancing MIBC mass transfer. A comparison of Figures 5.29 and 5.30 shows that this effect was unexpectedly small at the 200 μl dosage of oil. This apparently anomalous behaviour is attributed to the induction of small air bubbles under this conditioning regime in an analogous fashion to that encountered at 11pm/f (Section 5.4.1.1.a). At "lpdc" where air bubbles are not induced by the impeller, flotation performance declined significantly, as expected. It is proposed that the small bubbles induced at "hpdc" competed with the oil for the adsorption of MIBC and in this way ensured that sufficient MIBC remained at the air-water

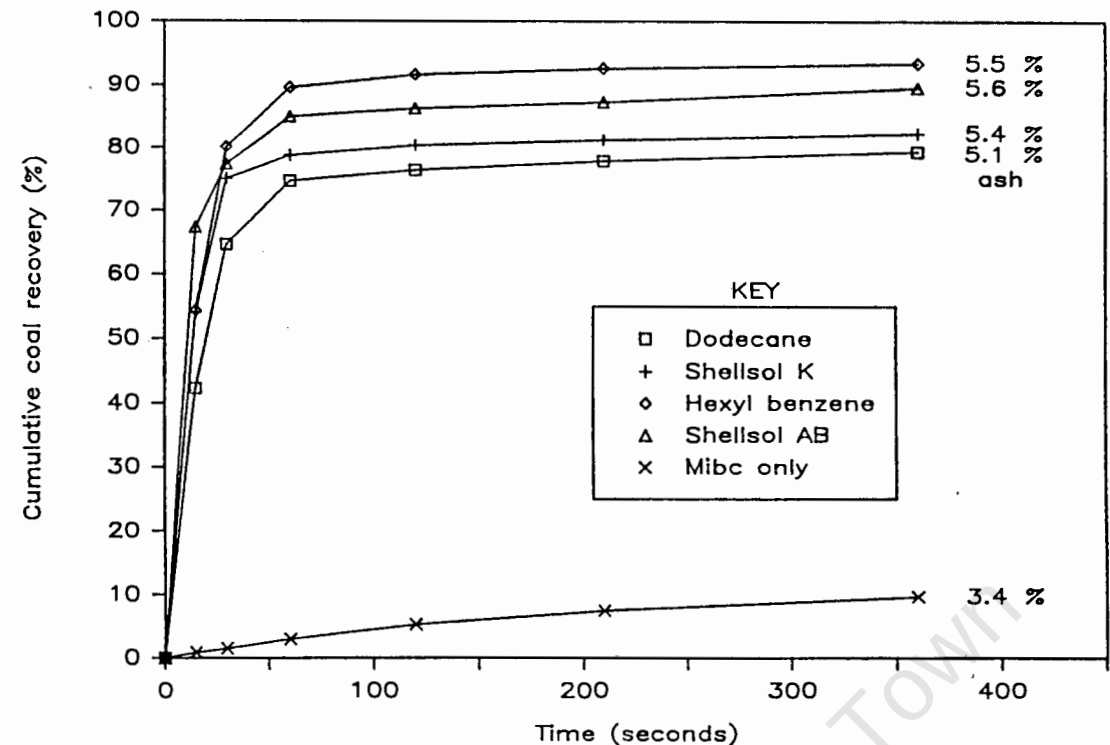


Figure 5.31 : Flotation performance with various collectors after 11pm conditioning. 400 μ l of collector and 18 μ l MIBC per float. Milled Greenside No.2 seam washed coal (-150 μ m).

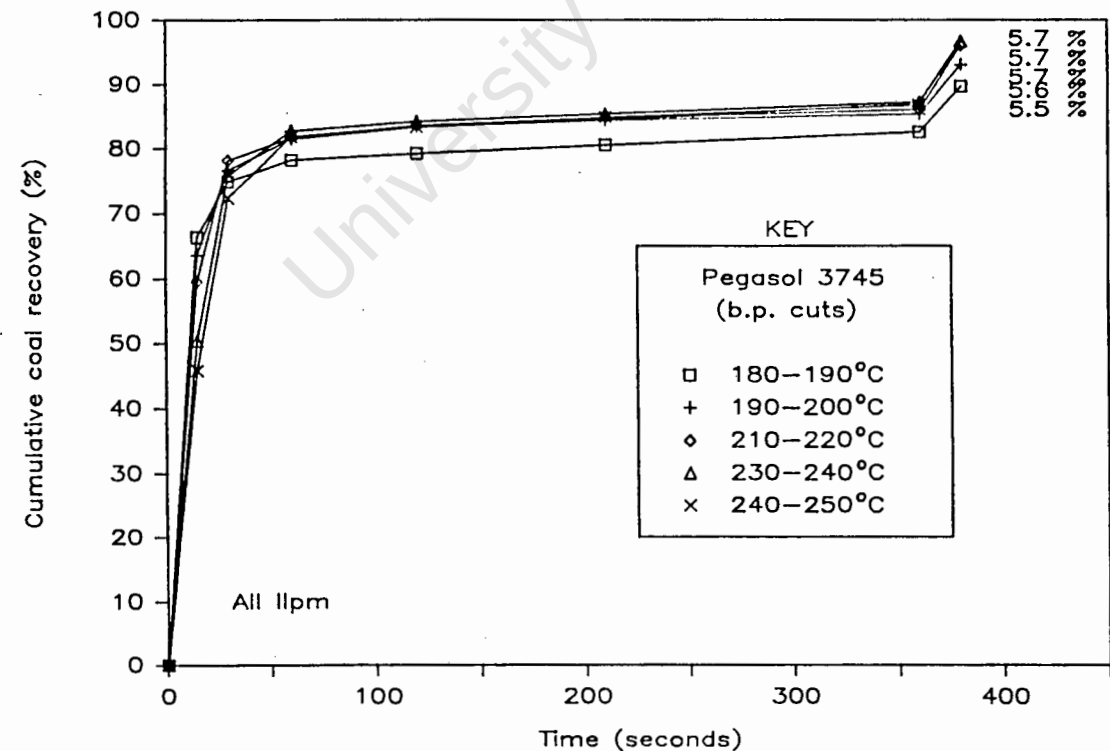


Figure 5.32 : Flotation performance with Pegasol 3745 boiling point cuts after 11pm conditioning. 400 μ l of Pegasol and 18 μ l MIBC per float. Milled Greenside No.2 seam washed coal (-150 μ m).

interfaces to facilitate frothing during subsequent aeration of the pulp. If the oil dosage was increased in relation to the MIBC dosage (the 400 μl /18 μl dodecane/MIBC test) then the harmful effect of MIBC dissolution in oil was clearly manifested, even at "hpdc".

The fall-off in flotation performance following early MIBC addition confirms the importance of MIBC at the air-water interface and the need to limit its adsorption by oil or coal, as discussed in Section 5.2.3.5.a.

5.4.6 Greenside washed and thickener underflow coals

Preliminary flotation testwork was conducted with the -150 μm fraction of the milled Greenside No. 2 seam washed (nominally 7 % ash) coal. Figure 5.31 shows that at 11pm conditions with a 400 μl oil dosage and with 18 μl of MIBC, trends were similar to those found with the unwashed (r.o.m.) coal, i.e. the aromatics performed better than the aliphatic oils. Differences were far less pronounced and all the oils gave good recoveries and very similar grades. The latter is not surprising since there is very little further liberation upon grinding the as-received washed coal sample. Grade-recovery curves were flat and similar indicating that the gangue is intimately associated with the coal.

The presence of a collector (oil) was essential to good flotation performance. Figure 5.31 shows that the coal was not readily floatable, despite being fine (-150 μm), in the absence of the oils even when 18 μl of MIBC was present. Only the cleanest and therefore most hydrophobic coal (normally the smallest particles) will float without the assistance of a collector. The collector is not only important for promoting coal floatability but is an important contributor to froth stability, particularly at frother dosages of the order of those conventionally used in flotation. Woodburn and Flynn (1984) have shown, in their investigation of the flotation performance of ultra-fine (-45 μm) coal, that kerosene addition has a marked effect on froth stability and thereby on flotation performance. The results in this thesis clearly support this, and furthermore show that it is also true of coarse coal particles.

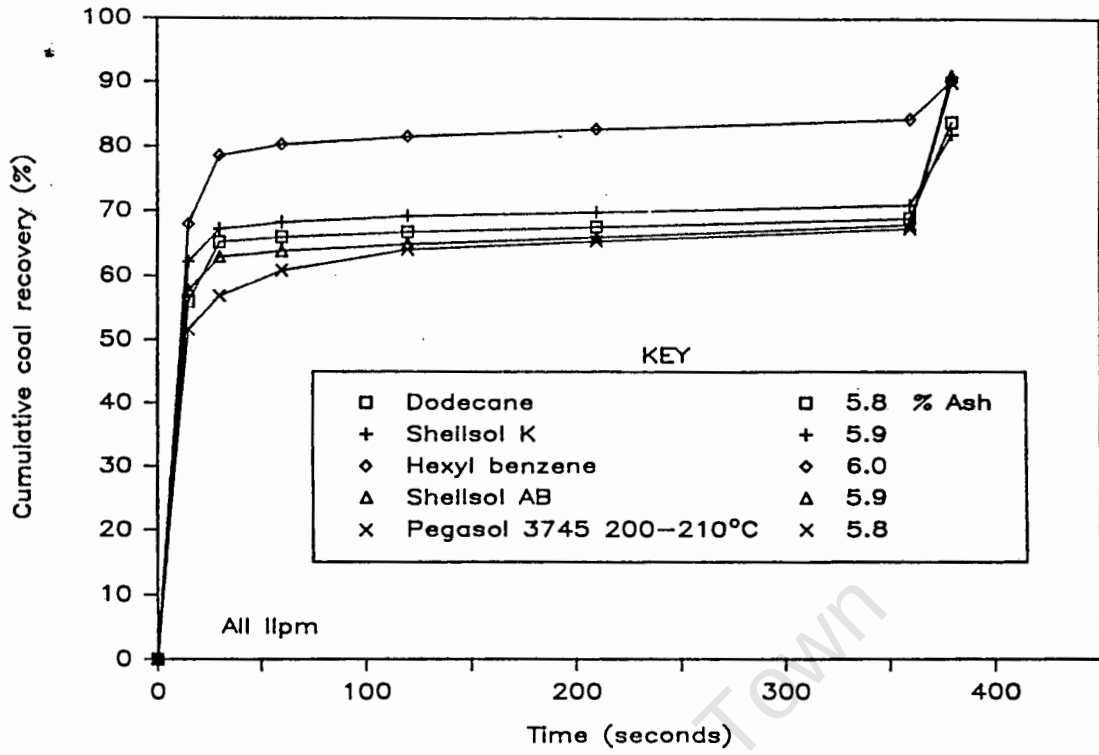


Figure 5.33 : Flotation performance with various collectors after 11pm conditioning. 400 μ l of collector and 18 μ l MIBC per float. Milled Greenside No.2 seam washed coal ($\sim 500 \mu$ m).

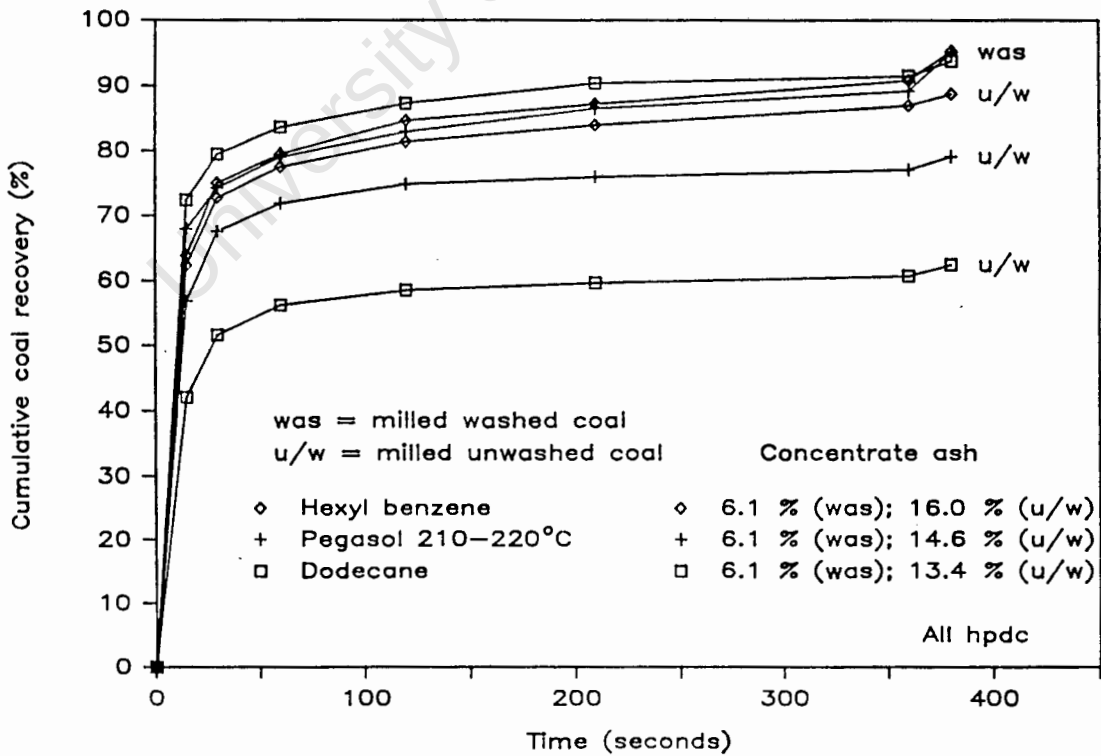


Figure 5.34 : Comparison of flotation performance of milled Greenside No.2 seam washed and unwashed coals of similar size distributions ($\sim 500 \mu$ m). hpdc conditioning procedure. 200 μ l dosage of oil and 36 μ l of MIBC per float.

Figure 5.32 shows that, at 11pm conditions, all the Pegasol 3745 boiling point cuts (400 μ l per float) gave practically identical and very good recoveries which corresponded to those obtained with the aromatic oils (Figure 5.31). However the higher the boiling point of the cut and hence the more viscous the oil the slower the flotation rate as represented by coal recovered in the first concentrate. As pointed out earlier, this was not a result of droplet size or of improved adsorption and frothing characteristics but presumably because of the effect of viscosity on oil-bubble coagulation/coalescence. The slower rates had no bearing on the grades produced which were all virtually identical because of the shortage of liberated gangue.

The more important reasons for the fairly similar performance achieved with all the oil types could be that :

1. the fineness of the coal (-150 μ m) had a positive effect on froth stability.
2. The coal had a much lower gangue content and was consequently more hydrophobic (oleophilic) and therefore more amenable to oil adsorption and so to flotation. The increased hydrophobicity of the coal surface would itself enhance froth stability by keeping bubble interfaces apart and therefore hindering their coalescence.

Additional tests were conducted with a -500 μ m fraction of the washed coal to determine whether particle size was the dominant influence. The size analysis for this fraction was very similar to that of the -500 μ m milled unwashed coal fraction (see Table 5.1). A low MIBC dosage (18 μ l/float) was selected to enable comparisons to be made with floats done with the unwashed coal, though this MIBC dosage was known to be inadequate with many of the oils.¹⁰ Figure 5.33 shows that apart from the detrimental effect of insufficient frother on the form of the froth (too dry - except with hexyl benzene), the actual amount of coal floated was similar irrespective of the collector oil type. The fineness of the feed was therefore not responsible for the similarity of the flotation performances.

¹⁰ This was also found by Eveson et al (1957) and Swanson et al (1984). Their work, which was reviewed in the literature survey, suggests a minimum dosage of 12 μ l.l⁻¹ for MIBC. (36 μ l/float).

To determine whether the similar flotation results obtained with the range of oil types were restricted to the 11pm condition (oil pre-mixed in water), testwork was conducted with the -500 μm washed coal fraction at hpdc (with sufficient frother to overcome the brittle froths, i.e. 36 μl per float). Figure 5.34 shows the performance of three typical oils (hexyl benzene, dodecane, and the Pegasol 3745 210-220°C cut) with both washed and unwashed coal samples. After the hpdc conditioning procedure the results obtained using the washed coal were still very similar irrespective of the oil type used, while the results with the unwashed coal showed significant variation despite the coals being of a very similar size range. With the unwashed coal, recovery varied from 60 % with dodecane to 90 % with hexyl benzene. Recoveries with the washed coal sample were all about 95 %. These results corroborate findings that all the collectors adsorb essentially equally on the washed coal. Conditioning procedures therefore have far less impact on the flotation performance of the washed coal.

However, as discussed in Section 5.4.4 above, complete oil adsorption is not a necessary criterion for good flotation performance. Providing that sufficient oil adsorption occurs, froth stability determines the flotation performance. Coal particles with a high native hydrophobicity will themselves contribute to the stability of the froth. Naturally, this character also results in all oil types adsorbing strongly onto the coal. Unwashed coals are less able to stabilize the froth and to adsorb certain oils because of an increase in hydrophilic character. Again, provided that the extent of the oil adsorption is sufficient to induce floatability, the deficiency of the coal in terms of froth stabilization can be corrected by the use of an adequate quantity of frother. Complete/very extensive oil adsorption is apparently not necessary.

Finally, flotation testwork was undertaken with a Greenside thickener underflow coal sample to check for the last time whether intrinsic coal properties or coal particle size were instrumental in causing the differences in flotation performance of the washed, fine coal (-150 μm) as opposed to the coarser, unwashed coal (-500 μm).

The thickener underflow coal had a very similar ash content to the unwashed coal sample but was much finer, with 75 % passing 150 μm (refer to Table 5.1 for the size analysis). In this testwork, a 200 μl dosage

of collector and 18 μl of MIBC were used per float. Hexyl benzene and dodecane were used to represent the aromatic and aliphatic oils respectively.

Figure 5.35 clearly shows that n-hexyl benzene performs far better as a collector than dodecane with this coal. The fineness of the coal was clearly an insufficient criterion for froth stability and consequently for coal recovery.

The results clearly reflect the increase in hydrophilic character of the coal surface on going from the washed to the thickener underflow coal. Dodecane was consequently less readily adsorbed as may be seen from Figure 3.19. On the other hand, hexyl benzene adsorbed to a significant extent thereby conferring strong hydrophobic character to the coal particles and so improving both the floatability and the froth stability, and hence the recovery. By analogy with earlier testwork with the unwashed coal, it is quite reasonable to expect aromatic oils to be more effective collectors than aliphatic oils for the thickener underflow coal. The coal floated poorly without collector, i.e. in the presence of MIBC only despite the predominance of fine particles in the feed. The surface character of the coal (either native or induced) is of greater importance.

5.4.7 Oil selectivity

The objective of this part of the work was to investigate whether the micro-scale selectivity evident in the adsorption studies was manifested during flotation. The adsorption work clearly showed that both aromatic and aliphatic oils were highly selective towards coal and scarcely adsorbed onto quartz. Both oil types also showed the ability to be selective towards r.o.m. coal fractions of low density (low ash content). The extent of oil adsorption decreased progressively as the density and hence ash content of the coal fractions increased (Section 3.5.3).

Droplet size distribution studies (Chapter 2) supported intuitive reckoning that oil dispersion improves with increased agitation intensity. It is also clear that for any given collector adsorption level (in terms of mass) a smaller mean droplet size will imply

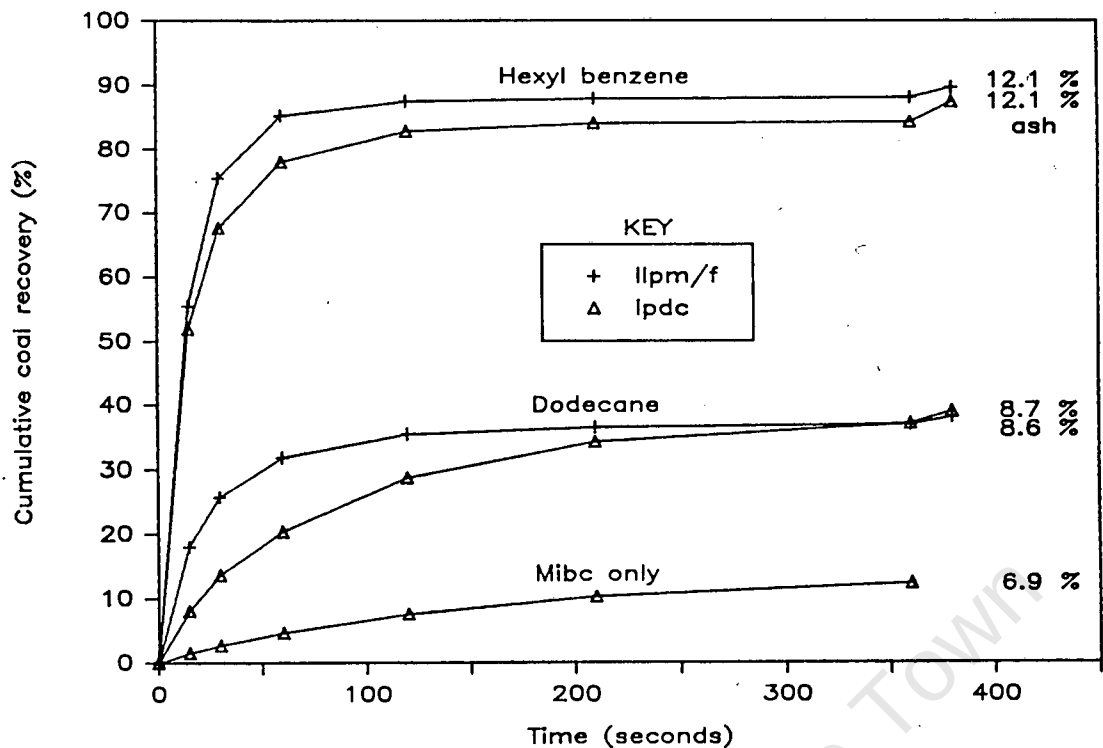


Figure 5.35 : Flotation performance with 200 μ l of dodecane (or hexyl benzene) and 18 μ l MIBC per float. Also 18 μ l of MIBC only. Greenside No.2 seam thickener underflow coal.

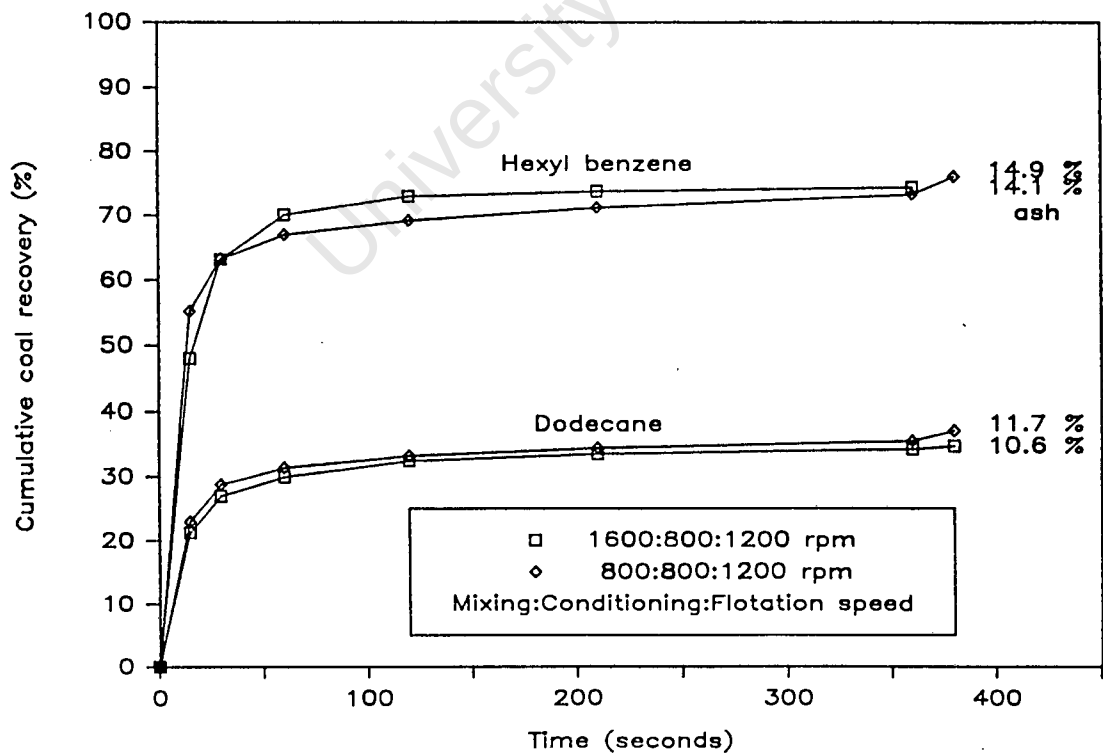


Figure 5.36 : Flotation performance produced by high and low impeller speeds during oil dispersion but low speeds during coal conditioning. 11pm conditioning procedure. 200 μ l of oil and 36 μ l of MIBC per float. Milled Greenside No.2 seam unwashed coal (-500 μ m).

increased (potential) coal coverage (on account of there being many more droplets). This would be expected to coincide with an increase in flotation recovery. An increase in selectivity would also be expected as smaller droplets could distinguish between and become attached to smaller areas of coal.

Testwork was conducted with the Greenside unwashed coal at various impeller speeds in order to verify this. Dodecane and hexyl benzene were selected as the oils to represent the aliphatics and the aromatics respectively. Dosages were 200 μl of the oils and 36 μl of MIBC.

Oil was dispersed at impeller speeds of 800 and 1600 rpm and coal conditioned at 800 rpm at 11pm conditions¹¹. This latter conditioning method was selected to ensure that the oils had sufficient opportunity to disperse before being contacted with the coal. Coal was conditioned at 800 rpm to preclude harmful "desorption" of collector as a result of coal attrition, which was evident when conditioning at 1600 rpm. After the frother was added (one minute before commencing aeration) the impeller speed was adjusted to 1200 rpm in all cases to eliminate changes in the rate or degree of MIBC mixing and to ensure similar bubble sizes.

Figure 5.36 shows that the grades were somewhat better with the better dispersed oil in both cases. However poor liberation of this coal sample made analysis of oil selectivity difficult. The influence of conditioning procedure, and by association of oil droplet size, on selectivity is considered in Section 5.5.8 below. The grades achieved by flotation were considerably poorer than those predicted by the density washability (see Figure 5.40). This was believed to be the result of a high proportion of middling (in terms of ash) coal which was nevertheless dominated by hydrophobic carbonaceous material.

To circumvent this problem, batch flotation tests¹² were conducted on feed mixtures consisting of Greenside unwashed coal (milled to -150 μm) and independent gangue minerals added in various proportions. The gangue added was either quartz or kaolin. Two gangue fractions were

¹¹ In all the other tests, impeller speed was kept constant at 1200 rpm.

¹² These experiments were conducted by F. Enous, a research assistant in the Chemical Engineering Department of the University of Cape Town. The results are interpreted here by the author.

thus present in the mixtures : one intimately associated with the r.o.m. coal and another which was added as a pure mineral.

The combined coal and (liberated) gangue mass was always nominally 300 g (some mass was lost in the flotation cell level control device). The actual proportions are listed in Table 5.6. Oil dosage was adjusted according to the mass of coal added, the level being 1500 g.t^{-1} . The oil used was Shellsol A, an oil very similar to Shellsol AB but with a lower boiling range ($165\text{--}185^\circ\text{C}$ as compared to $185\text{--}225^\circ\text{C}$). DIBK was used as the frother at a dosage of $36 \mu\text{l}$ ($12 \mu\text{l.l}^{-1}$). DIBK (5-nonanone) has a lower hydrophile-lipophile balance (H.L.B.) value than MIBC (because of its longer hydrocarbon chain) so the same type of behaviour can be expected in the flotation system.

The quartz used was 70 % $-70 \mu\text{m}$ in size and the kaolin $-50 \mu\text{m}$ (50 % $-2 \mu\text{m}$). The solid surface area within the pulp obviously increased enormously above that for a pulp consisting of coal alone, especially when the kaolin was used. The potential for oiling of the gangue minerals was therefore very enhanced.

It was necessary to have some idea of the proportion of gangue which was intimately associated with the coal in the concentrate in order to determine (or at least estimate) the amount of gangue in the concentrate that had been added as pure mineral. The former proportion was estimated by floating the same coal under the same flotation conditions but in the absence of any added quartz or kaolin. Thus 300, 270, 240, 210, 180 and 150 g of coal (see Table 5.6) were floated on their own using the same oil dosage, frother dosage, etc. The proportion of ash in the concentrates was somewhat lower in the floats conducted with less coal mass, as would be expected with the decrease in pulp density.

The frequency of particle interactions in floats containing added gangue was high because of the size distribution of the gangue. This is believed to have produced an effect similar to an increase in pulp density. For this reason it was felt that the *concentrate ash content* of the highest pulp density coal float, a value of 14 %, would provide a realistic and conservative indication of the amount of gangue recovered simply because of its intimate association with the coal. The range in ash contents was small, varying from 12.2 % at 150 g to 14.0 % at 300 g.

The higher ash level was also regarded as a good choice because the rate of flotation was higher in the presence of added gangue minerals; presumably because their fineness reduced bubble size and enhanced froth stability.

To simplify the calculations, the proportion of gangue in the coal recovered in the concentrate was universally assumed to be 14 %. Actual gangue mass (i.e. mineral matter content) would be somewhat higher (includes combustibles and water of hydration) but was not determinable. It was felt that the 14 % ash level could be applied universally as the recovery of coal in floats where no gangue was added was very similar to that in floats containing added gangue (Table 5.6).

In floats containing *added* gangue, ash-free coal recovery was determined by ashing the concentrates. The contribution of gangue intimately associated with the coal in the concentrate mass was calculated using the assumed gangue content (14 %).¹³ The actual concentrate masses were known so by difference the mass contributed by the added gangue (*including* water of hydration and combustibles) could be determined. The independent gangue minerals were obviously added on the basis of their mass in an unashed form. A sample calculation is given in Appendix 5.2.

Figure 5.37 and Figure 5.38 show the results of floats done with quartz and kaolin additions respectively. The proportion of coal collected remained about the same (as in the standard float carried out in the absence of any added quartz or kaolin) irrespective of the mass of gangue mineral added to the feed as shown in Table 5.6 below. This is indicative of the ability of the oils to seek out and adsorb onto hydrophobic carbonaceous surfaces irrespective of the presence of a very large gangue surface in the pulps.

It is quite obvious that only a very small proportion of the added gangue minerals reported to the concentrate. Figure 5.37 shows that virtually no quartz was found in the concentrate over the entire range of feed mixtures. The recovery of kaolin was higher than that of quartz. This was principally an entrainment effect rather than a reagent selectivity effect. When very finely milled quartz was used in

¹³ The mass of gangue intimately associated with the coal in the feed was also based on its ash mass. (This is conventional).

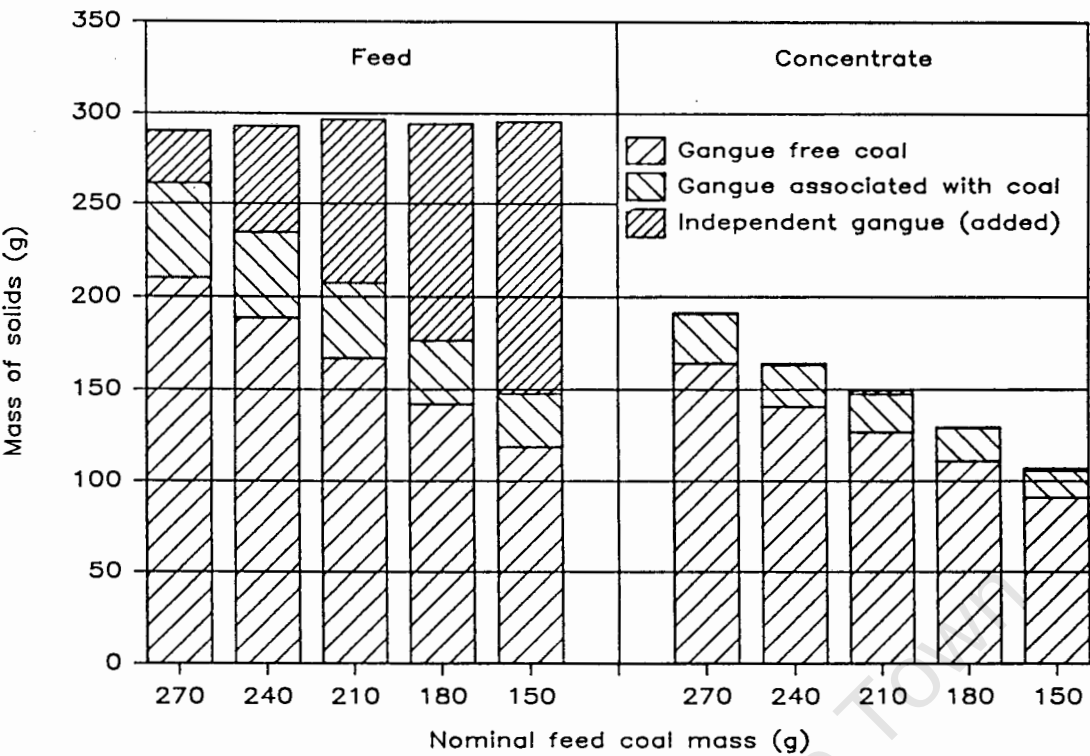


Figure 5.37 : Masses of gangue free coal, gangue associated with coal and independently added quartz in a flotation concentrate compared to their respective masses in the flotation feed. Greenside No.2 seam unwashed coal ($-150\ \mu\text{m}$) and quartz (70 % $-70\ \mu\text{m}$) added in various proportions to total 300 g (nominally).

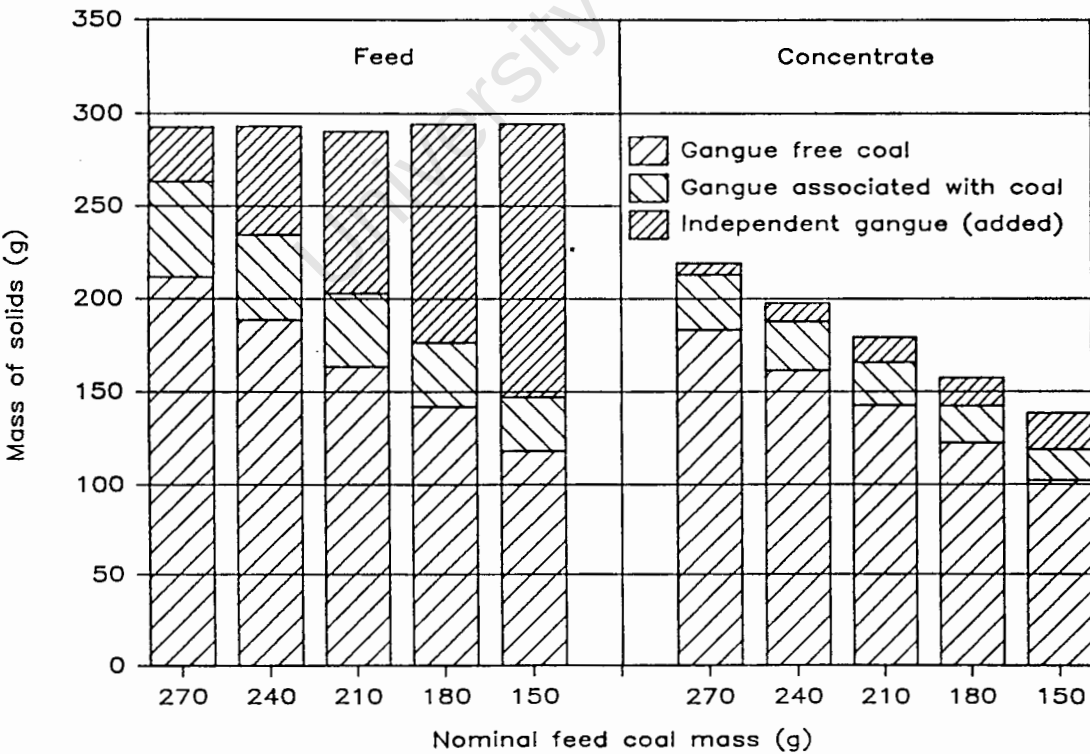


Figure 5.38 : Masses of gangue free coal, gangue associated with coal and independently added kaolin in a flotation concentrate compared to their respective masses in the flotation feed. Greenside No.2 seam unwashed coal ($-150\ \mu\text{m}$) and kaolin (50 % $-2\ \mu\text{m}$) added in various proportions to total 300 g (nominally).

conjunction with coal in the feed, the proportion of quartz reporting to the concentrate increased (see Appendix 5.3, Figure A5.1).

The proportion of gangue which was associated with the coal and which reported to the concentrates was relatively high. The fact that so little independent gangue was found in the concentrate emphasized again that poor flotation grades are not due to poor selectivity but rather due to poor liberation. Attempts to float just the quartz or the kaolin (no coal) at similar conditions and with similar reagent dosages produced no yield whatsoever. This confirmed that the oil does not collect these minerals. Independently added gangue found in the flotation concentrates was a result of factors other than selectivity; chiefly entrainment and possibly also sliming of coal particles.

Table 5.6 : Coal recoveries in floats with unwashed coal only and with different proportions of unwashed coal and added gangue.

Coal only			With added Quartz	With added Kaolin
Mass of coal added (coal only) (g)	Mass of coal recovered (ash free) (%)	Mass ratio of coal to added gangue (g:g)	Mass of coal recovered (ash free) (%)	Mass of coal recovered (ash free) (%)
300	79.8	300:0	79.8	79.8
270	81.7	270:30	78.3	86.6
240	81.0	240:60	74.5	85.6
210	80.7	210:90	75.9	87.3
180	77.5	180:120	78.1	86.4
150	75.1	150:150	76.7	86.4

Similar testwork was also carried out with both the Greenside washed coal and the Greenside thickener underflow coal in the presence and absence of added quartz and kaolin (see Appendix 5.3). Results again proved the selectivity of the oil.

The fact that an aromatic oil (Shellsol A) proved to be highly selective on a practical scale indicates, in the light of the adsorption results, that selectivity behaviour of oils with a higher aliphatic content can be expected to be at least equivalent (though their flotation performance in terms of recovery could be worse).

The flotation testwork therefore confirmed the macro-scale selectivity of the hydrocarbon oils and the fact that limited adsorption of these oils onto *liberated* gangue would have little impact on the grades.

5.5 RESULTS AND DISCUSSION : GLOBAL FLOTATION RESULTS

5.5.1 Introduction

The aims of this section are twofold :

1. To expose important relationships between various flotation parameters and overall flotation performance characteristics, for example the rate of flotation and the concentrate ash content.
2. To provide an objective overall view of the results of the individual flotation experiments. For example, it is difficult to assess the effect of certain variables on some aspects of flotation performance, such as grade, should the yields be dissimilar. In such cases, it is difficult to say precisely whether higher ash contents are the result of, say, increased flotation rates or merely a function of the increased concentrate yields.

In this section the results of all the flotation experiments with a particular coal sample are considered together. The mode of conditioning, reagent type, reagent dosage and so on are not isolated.

In order to evaluate the efficiency of the beneficiation achieved in the flotation experiments, it was necessary to define the liberation characteristics of the coal, i.e. to predict the ash levels for any particular mass of concentrate produced. Concentrate mass rather than mass yield (%) was used as a basis since it related better to variables such as concentrate water recovery.

In this work the liberation characteristics of the coal sample were defined by the float-sink (density separation) behaviour. The density washability so obtained is indicative of the best possible ash level obtainable in terms of the coal's physical liberation characteristics on a gravity basis. This is a lower limit and actual ash levels achievable by perfect flotation could (and usually would) be higher. Unless the particle surface is dominated by hydrophilic impurities, the collectors can be expected to collect the particle, as discussed in Section 3.5.3. Flotation washability (grade) is determined by the type and proportion of gangue at the surface of the composite particle.

The floatability (propensity to be floated) of a coal is not entirely dictated by its gangue (ash) content (Laskowski, 1986; Hornsby and Leja, 1984). Laskowski (1986) pointed out that the coal floatability is dependent additionally on surface characteristics such as the sort of hydrocarbon skeleton (rank) and the degree of surface oxidation. The proportion of hydrophilic gangue at the surface of the composite particle is nevertheless of great importance. Good physical liberation is therefore vital to beneficiation. If the surface of a coal is heavily oxidized, thereby inducing hydrophilicity, then the native floatability of the coal (potential yield) will be severely reduced. However, oxidation (or rank) *per se* do not affect the washability (grade) which is controlled by the proportion of gangue.

In terms of flotation washability¹⁴, extensively oxidized and low rank coals may show poor performance since the collectors which might be used to induce adequate floatability of these coals could also introduce a measure of floatability to the undesired gangue minerals. Collectors capable of adsorbing on hydrophilic oxidized (or low rank) coal surfaces can be expected to adsorb on hydrophilic gangue surfaces (though the latter, e.g. clays, will normally possess stronger hydrophilic character because of permanent surface charge).

The term "predicted ash" in the discussion which follows is synonymous with the "best possible ash level" as determined by the density washability curve. Ash content at a particular yield was chosen rather than the more conventional organic efficiency since the

14 The best grade achievable by flotation at any particular yield.

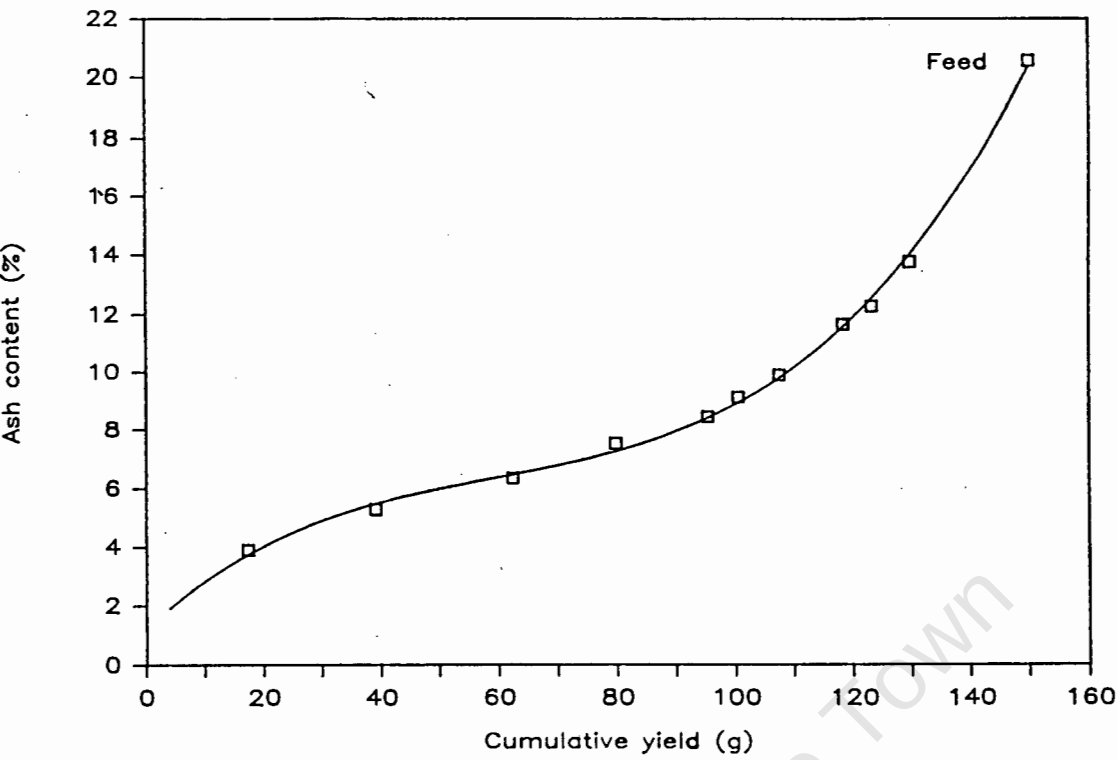


Figure 5.39 : The liberation characteristics of milled Greenside No.2 seam unwashed coal ($-500\ \mu\text{m}$) as defined by its float-sink behaviour (density washability).

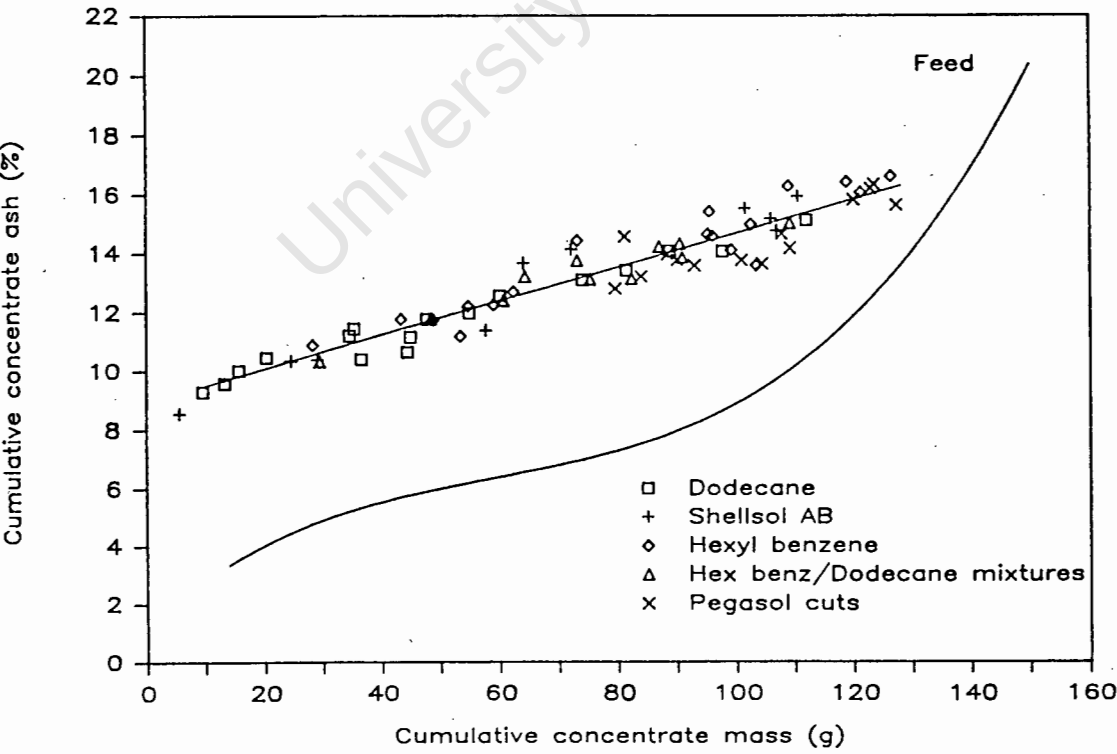


Figure 5.40 : A global comparison of concentrate grades achieved with the best grades possible at equivalent yields. Milled Greenside No.2 seam unwashed coal ($-500\ \mu\text{m}$).

experimental flotation procedure readily produced yield versus time data. Comparison of actual ash content with that predicted from the experimentally obtained yield (using the float-sink relation) was direct and easy.

5.5.2 Liberation characteristics as defined by float-sink behaviour

The liberation characteristics of the unwashed coal sample were defined and determined by its float-sink behaviour. The ash content of the coal fraction floating at any particular density was considered to represent the best possible grade which could be obtained at the corresponding mass yield.

The float-sink analyses were conducted using the centrifugal technique developed by Franzidis and Harris (1986). This technique allows for separation down to ultra-fine sizes (below 25 μm). The technique repeatability is good and is shown in Appendix 5.4.

Figure 5.39 gives the results of the float-sink analyses on a sample of milled Greenside unwashed coal with the size distribution given in Table 5.1. This is the size range which was used in the actual flotation testwork. The cumulative ash contents of the float fractions are plotted against the cumulative mass of these fractions. This latter mass includes the gangue content, i.e. it is not on an ash-free basis. The symbols in the Figure represent the actual experimental points.

In order to facilitate the prediction of the best possible ash levels for any particular concentrate yield a third order polynomial was fitted to the experimental points (by least squares regression). This is shown as a smooth curve in Figure 5.39. This equation is given below.

$$Y = 1.2327 + 0.18394X - 0.0024711X^2 + 0.00001397X^3 \quad [5.14]$$

where Y represents the concentrate ash and X the concentrate mass.

5.5.3 Comparison of flotation performance with best possible performance

Figure 5.40 shows the grades of the total concentrates obtained in flotation experiments conducted with the milled unwashed coal, for the various oils. The best possible grades for the corresponding mass

yields, as predicted by the float-sink function, are represented by the smooth curve.

As may be seen, the flotation results for the milled unwashed coal were well displaced from their best possible levels. Even when mass yields were low the grades were no nearer to their potential levels. In fact the actual and best possible ash contents only approached one another as the concentrate mass approached that of the feed (as they must do when just about everything floats - which obviously defeats the beneficiation process).

The reasons for the displacement of the actual results from those theoretically possible could be several, including :

1. Inadequate reagent selectivity.
2. Excessive quantities of middling material (in terms of desirable ash content) which are dominated by hydrophobic carbonaceous material. This controls the flotation washability.
3. Rapid rates of flotation and concentrate removal which encourage entrainment and allow insufficient time for froth drainage. This will reduce grades in relation to the flotation washability.
4. Froth phase characteristics, including the ability of the froth to support large particles, and its mixing and drainage dynamics.

In the light of the adsorption (Section 3.5) and flotation testwork (Section 5.4.7), the first possibility was excluded, i.e. collector selectivity was considered adequate in distinguishing between coal and gangue surfaces. But although the selectivity of all the oily collectors was found to be good, particles of a certain ash content, which would be regarded as middlings, have an inordinately large carbonaceous surface area in relation to that of the ash-forming gangue minerals. These particles would be collected and would account for some displacement from the best possible separation function. This would explain the poor grade found even at low yields. Additional displacement from the density washability relation would result from inappropriate flotation control and poor froth phase characteristics.

5.5.4 The effect of flotation rate on concentrate grades

In coal flotation, the bulk of the feed material is floated. This material bulk and the rapidity with which it floats leads to thick and abundant froths which cause problems with regard to cleaning, because of the accompanying high entrainment levels and the difficulty in gangue draining from the froth phase. The rate of flotation would thus be thought to be of considerable importance in determining concentrate grades.

In the discussion which follows, the rate of production of the first concentrate was used as a measure of the flotation rate. This concentrate was collected over the first 15 seconds of flotation and was invariably by far the largest concentrate. The trends reflected by this concentrate would therefore be indicative of the results for the concentrate as a whole. Even when subsequent concentrates had lower ash contents, their masses were usually too small to have a significant effect on the overall grades; these were largely determined by those of the first concentrates.

Figure 5.41 shows the grades of the first concentrates of the series of flotation experiments and the best possible grades (smooth curve) for the corresponding yields plotted against flotation rate. A comparison of the actual and best possible ash levels reveals that the relations are essentially parallel. In other words low flotation rates did not result in significantly improved grades and very high flotation rates were clearly not as detrimental to concentrate grades as might have been expected.

This parallelism is reflected in Figure 5.42 which shows mass-based flotation rates as opposed to Figure 5.41 which shows time based flotation rates. The former relationship was used to account for tests in which the first concentrate yield did not dominate the total yield. The ratio of first concentrate mass to total concentrate mass versus the difference between the actual and best possible ash levels for the first concentrate mass is shown. Again it is quite evident that flotation rate has far less of an impact on concentrate grades than was expected. However within a set of flotation experiments where only one

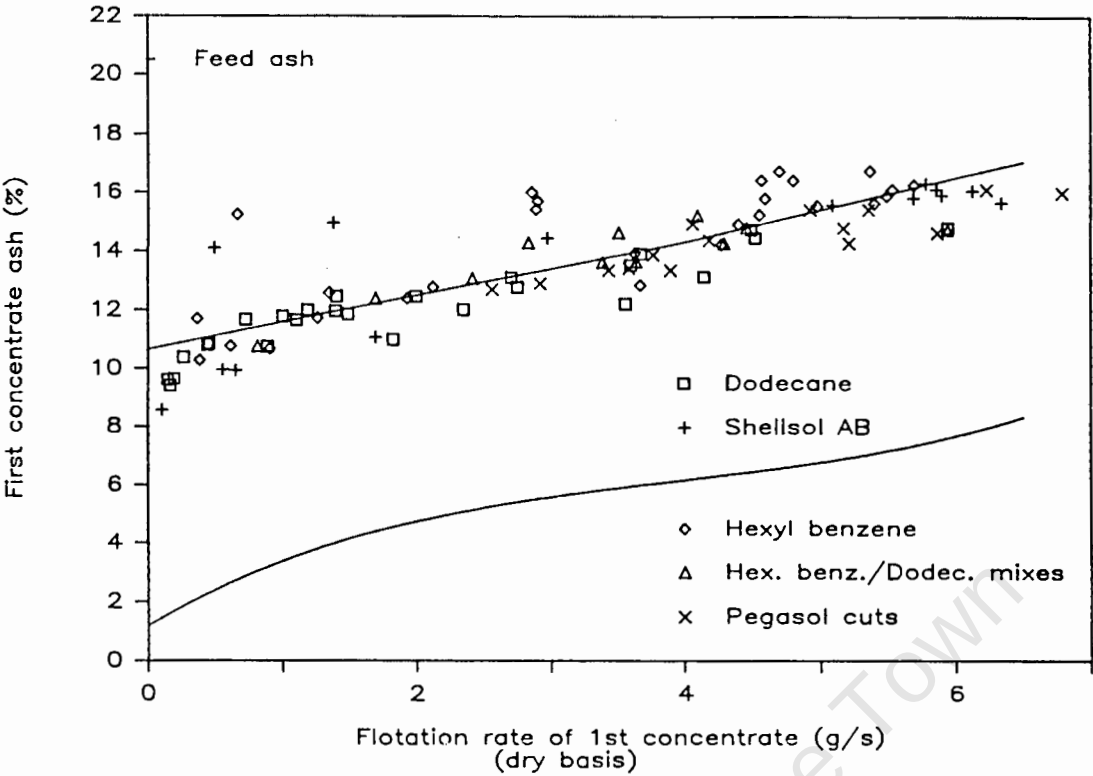


Figure 5.41 : A global evaluation of the effect of flotation rate on the grade of the first concentrate. Milled Greenside No.2 seam unwashed coal (-500 μ m).

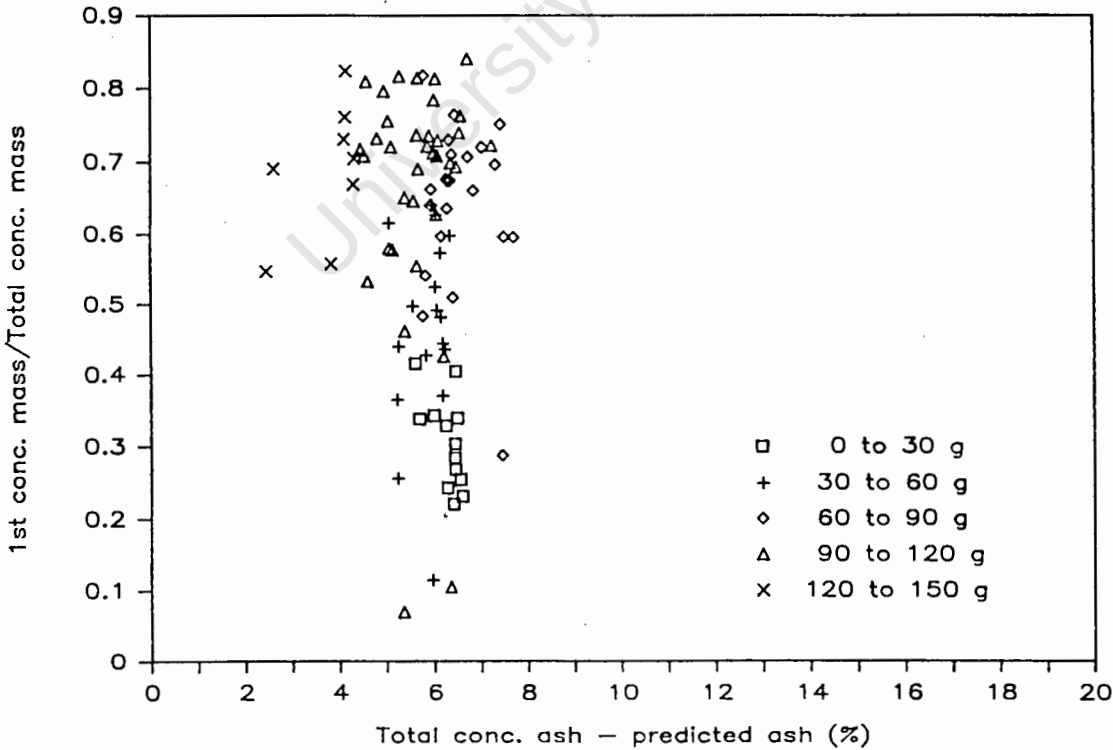


Figure 5.42 : A global evaluation of the difference between actual and best possible grades for a range of recoveries and recovery rates (mass basis). Milled Greenside No.2 seam unwashed coal (-500 μ m).

parameter was altered, different rates did have a small influence on the grades as indicated by the scatter in the data points.

The largest concentrates (120-150 g) apparently gave the best performance but this is only because the true characteristics of the coal feed must be approached by the concentrate as most of the coal is floated. Obviously beneficiation of the feed no longer occurred to any significant degree.

5.5.5 The relationship between water recovery and concentrate mass

The type of froth formed will have a significant influence on both grades and recoveries. A "dry" froth has little internal mixing and little drainage of water to facilitate the removal of entrained gangue material. Dry froths have been found to restrict recovery at fixed froth heights in this batch flotation testwork. Bensley and Nicol (1985) stressed that wet, mobile froths are essential to the recovery of coarse coal. During the flotation experiments the mass of water within the froth was measured and is referred to as the water recovered. Water recovery has two components :

1. The water recovered from the bubbles themselves, i.e. that water constituting the bubble film.
2. The interstitial water recovered from between the bubble films.

The increase in the number of bubbles and a decrease in their size within the froth phase dictates the froth water recovery and in turn the solid mass recovery. Obviously the more froth, the more solids can be supported; and the smaller the bubbles constituting this froth, the more loaded the froth is likely to be. In a general sense, the greater the water recovery the greater the concentrate yield.

Figure 5.43 shows this relationship. A straight line, passing through the origin, was fitted (using a least squares technique) to the experimental data. Obviously as the feed mass (150 g) is approached the relationship will approach this datum asymptotically but the linear relationship is valid over most of the range.

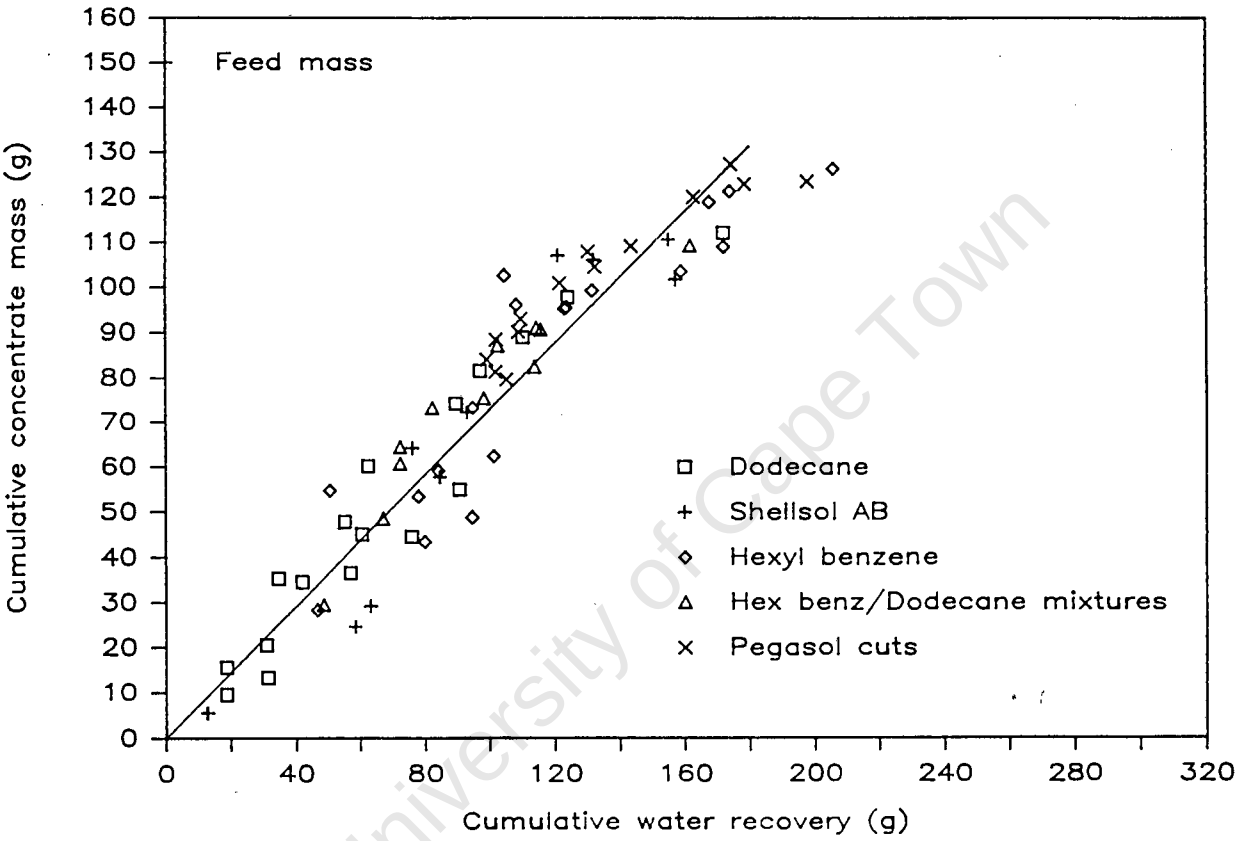


Figure 5.43 : A global appraisal of the relationship between mass yield (dry) of concentrate and the concentrate water recovery. Milled Greenside No.2 seam unwashed coal (-500 μm).

The line was made to pass through the origin. This should be so because if there is no water recovery, i.e. no froth phase, there will be no concentrate produced. This is a fact implicitly recognized by Trahar (1981) in his work on the contribution of flotation and entrainment to overall fines flotation. In sharp contrast, Warren (1985), whose work included some studies with coal, found that extrapolating the concentrate mass back to zero water recovery gave a definite positive intercept. This intercept was attributed to true flotation, while further yields, represented by the positive slope of the line, were attributed to capture by entrainment.

His assumption with regard to true flotation is that the bubble films possess a negligible mass and that almost the entire froth water mass is interstitial water in which entrained particles reside. It is open to speculation just how much water constitutes the bubble film and where the film ends and interstitial water begins. The number of bubbles, their very large cumulative surface area in the froth and the fact that their walls have a definite thickness suggests, to this author, that their contribution to the water recovery is not negligible.

While bubble films may have a small individual volume in two phase froths this is not necessarily the case in three phase froths. As the bubble (air cavity) moves through the pulp phase, solids become attached to its interface. In order to transfer to the froth phase a second air-water interface must be created. With solids already adhered at the original (inner) interface it seems reasonable, to this author, that the second interface must be displaced from the first one by more than a negligible distance because of the solids present. The bubble film would then not have negligible volume.

This hypothesis is supported by the findings of Flynn and Woodburn (1987) who measured the thickness of the hemispherical portion the lamellae of bubbles constituting the uppermost portion of the froth (using a conductance probe). They were only able to measure the thickness of the top-most lamellae (bubble films). These are the most well-drained since they possess the longest froth residence time and are not subject to any drainage-retarding effects induced by the close proximity to the lamellae of neighbouring bubbles. They found good agreement between the lamella thickness and the d_{95} size of the particles in the froth. In this author's work, particles of up to 500 μm

in diameter were present in the froth so that the findings of Flynn and Woodburn (1987) suggest that bubble lamellae could be several hundred microns thick and therefore not of negligible volume.

The film (lamellae) water is clearly closely associated with the collected solids and the bubbles to which they are attached. Additional interstitial water will undoubtedly exist due to entrapment, and will contain entrained solids. However it seems unreasonable to presume that most of the froth water is entrained. Warren's postulation would imply that all the coal in the flotation testwork shown in Figure 5.43 was "collected" by entrainment alone and not by direct bubble-particle attachment since the intercept is zero. This is unacceptable since direct bubble-particle attachment has been studied photographically and is widely accepted to dominate the collection mechanism in sub-aeration flotation cells. The reason for the positive intercept in Warren's work is not clear.

5.5.6 The relationship between water recovery and concentrate grade

Water recovery is indicative of the form of the froth. To evaluate the effect of froth water content on grade, it is necessary to compare the relationship between the actual grades and water recoveries with that between the predicted grades and the same water recoveries in order to compensate for the changes in concentrate mass induced by the other flotation parameters. Obviously the *apparent* trend is for concentrate ash to increase with water recovery, as increased water recovery implies a greater concentrate mass as shown in Figure 5.43. This in turn implies a higher ash content as shown by Figure 5.39.

It is therefore the difference between the actual and the predicted grades for a particular yield with respect to the accompanying water recovery which is important. If the two relations diverge with increasing water recovery then increased water recovery can be deduced to have a detrimental impact on concentrate grades. Converging curves would indicate the opposite, while parallel curves would mean no influence.

Figure 5.44 shows the results for the milled unwashed coal. The points are fitted to straight lines (by least-squares) to allow easier

comparison of the trends. It is not necessary that these lines pass through the origin as even the tiniest amount of coal floated would have some ash content, i.e. it would not be entirely carbonaceous material.

The predicted points give the grades for the concentrate mass which was actually recovered, as calculated from the float-sink cubic function (Equation 5.14). The actual and best possible grades for each concentrate mass are plotted against the actual water recovery to give the two relations. The scatter of the actual experimental points is more prevalent than that of the predicted points, indicating the influence of factors such as conditioning procedures and dosage on flotation performance (even when similar concentrate masses were produced).

As may be seen, the actual and predicted relations converge slightly with increased water recovery levels indicating that this is not harmful to grade. Increased interstitial water facilitates gangue drainage and enhances froth mobility, including internal mixing, which aids in froth cleaning. Increased froth water content might be expected to have an analagous effect, in terms of gangue drainage, to washing the froth with externally supplied water as in flotation columns. "Dry", brittle froths were observed to exhibit no signs of mixing or movement so that any gangue entrained was rigidly held and had no opportunity of returning to the pulp.

Warren (1985) believed that the wetter the froth the greater the entrainment and hence the poorer the grade. However, froth water content is dependent on bubble size, particle size and so on, i.e. on the form of the froth. This is not necessarily related to its solids content. Warren's supposition is contradicted by this author's work and by the very recent work of Woodburn et al (1988). His (Warren's) contention that "dry" froths produce the best grades appears highly improbable. Dry froths often produce less concentrate mass, and hence an *apparently* better grade.

5.5.7 The impact of the type of reagent oil

Though the figures discussed above have depicted flotation results achieved with the various collector oils, the influences of the oils themselves have not been explicitly considered. The impact of oil type

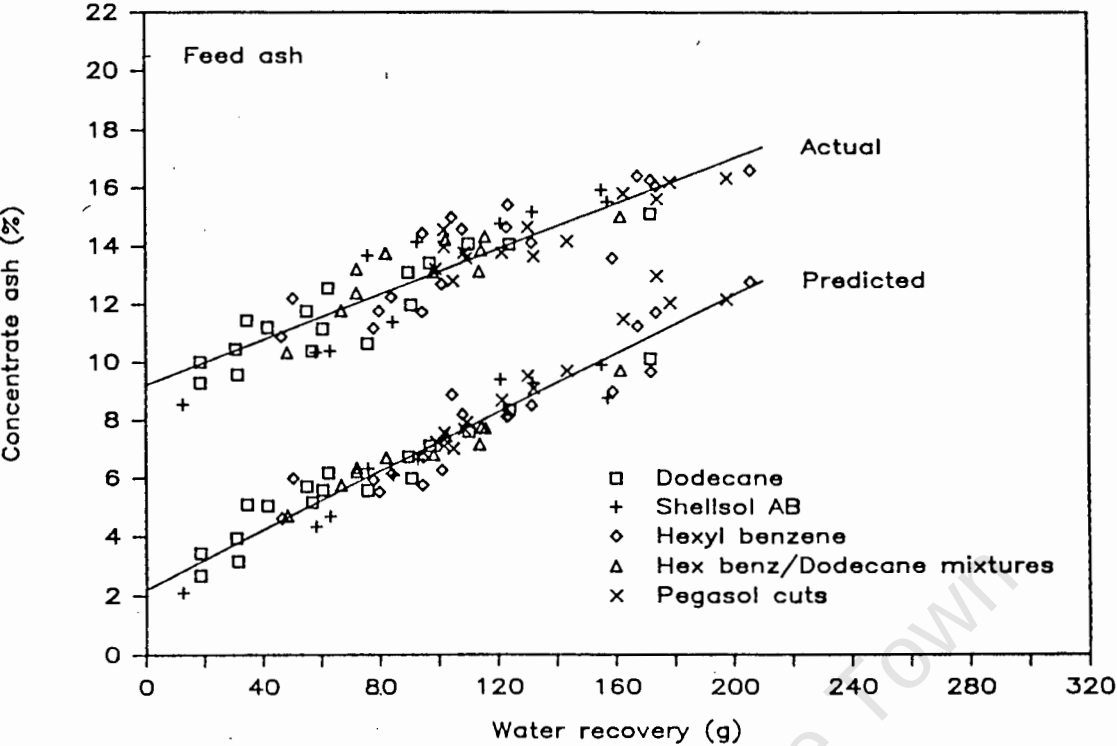


Figure 5.44 : A global evaluation of the relationship between concentrate grade and water recovery. Milled Greenside No.2 seam unwashed coal (-500 μ m).

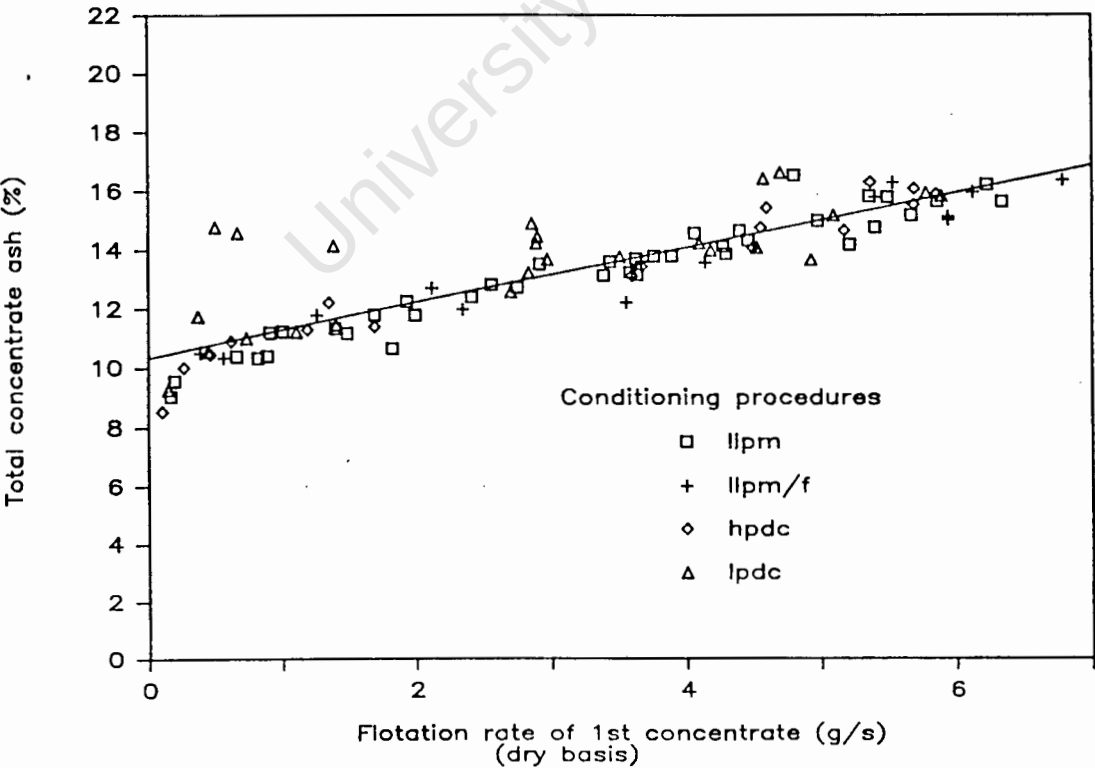


Figure 5.45 : A global appraisal of the effect of conditioning procedure on the concentrate grade over a range of flotation rates. Milled Greenside No.2 seam unwashed coal (-500 μ m).

is not easy to assess from a global point of view because of the widely divergent conditioning, dosage and other flotation aspects involved. However it is evident from the global studies that no reagent outclasses the others in terms of practical selectivity, as most experimental points essentially conform to the basic trends, with outliers having no consistent relation to oil type.

5.5.8 The effect of conditioning procedures on concentrate grades

The impact of conditioning procedures on the flotation performance is discussed in detail in Section 5.4 which is concerned with flotation results on an individual basis. However some major trends are evident from the global flotation studies. Figure 5.45 shows the relationship between concentrate grade and flotation rate for floats conducted under various conditioning regimes. The conditioning methods produced the full range of rates depending on other conditions selected, such as reagent dosage. However one method of conditioning stood apart from the others; and this was lpdc (low pulp density conditioning). Almost all the lpdc results lie on or above the general trend as represented by the straight line fitted through the experimental points (by least squares regression). In other words the grades of the concentrates produced after using this conditioning procedure were generally worse than when other conditioning procedures were used.

In this conditioning procedure the collector oils were added to a full flotation cell, where mixing conditions were comparatively mild. In all the other conditioning procedures, the oils were dispersed in a partially filled cell. Obviously the smaller droplets produced under these conditions enhanced the selectivity potential of the oil, as would be expected.

Lpdc is the least efficient approach to dispersing the oil and conditioning the pulp. This has been acknowledged by other workers. Glembotskii et al (1970) reported that direct oil addition to the pulp results in a large amount of oil floating to the surface and passing into the froth phase thereby necessitating an increase in oil dosages.

However lpdc is the conditioning procedure most often used in laboratory batch floats and most similar to the approach used

industrially (assuming the oil is not pre-emulsified). The results shown in Figure 5.45 support the view that emulsification or dispersion of the collector prior to addition to the pulp, or else very vigorous mixing of the oil within the pulp prior to entering the float cells, enhances flotation performance with respect to grade.

5.6 CHAPTER SUMMARY

The flotation testwork described in this chapter was carried out with three samples from the Greenside Colliery; being unwashed, washed and thickener underflow. Experiments were carried out with various collector oils, in the presence and absence of MIBC, and for a variety of conditioning procedures. The results are summarized below and interpreted in the light of the results of the investigations of the various sub-processes (dispersion, adsorption, effect on bubble size) presented in the previous chapters.

This section also includes a summary of the mechanisms of oiled coal particle and air bubble contact and attachment. Important points arising from the review of the literature relevant to this chapter are summarized in Section 5.2.5 above.

5.6.1 The impact of the type of collector oil

It has been stated that hydrocarbon oils are effective coal collectors only when they are retained as an independent oil phase. This will certainly be the case with high boiling point oils, and indeed, oils with boiling ranges between 200 and 250°C are widely acknowledged to be the most effective coal collectors. Most of the oils used in this testwork fell in this range.

Several workers consider viscosity to be an important appraisal criterion for flotation performance. In so far as it relates to the chemical nature of the oils in terms of Van der Waals bonding, polar interactions, fluid-fluid coalescence rates, etc., this is understandably so. It has also been proposed that oils which spread poorly are likely to be good collectors. Experimental results described in this chapter suggest that this could only be a valid proposition in

the absence of other important parameters affected by the oil, such as bubble size.

In terms of chemical constitution, the order of coal flotation activity is reported to be aromatic, naphthenic and iso-paraffinic. The origin of the crude oils from which commercial oils are produced is therefore important. In addition to the induced dipole-induced dipole interactions the possibility of polar interactions offered by aromatics is probably the reason for their improved flotation performance and also explains why partially oxidized hydrocarbon oils (with their polar functional groups) have been found to be successful coal collectors; particularly if the coal is oxidized. In this testwork a substantial difference in aromatic and aliphatic collector performance was discerned in experiments conducted with an unwashed coal. In terms of overall recoveries obtained, aromatic oils were superior collectors.

The predominantly aliphatic oils were not adsorbed to the same extent as aromatic oils onto the unwashed coal sample, as proved in adsorption studies. When adsorption was virtually complete as with the washed coal sample (with a similar size distribution to the unwashed coal), differences in flotation performance were small with all oil types and for a variety of conditioning procedures.

In terms of practical selectivity no oil produced significantly better results (grades). Flotation testwork confirmed the macro-scale selectivity of the hydrocarbon oils and the fact that limited adsorption of these oils onto *liberated* gangue would have little impact on the grades.

Though more extensive oil adsorption undoubtedly aided flotation recovery, the more limited oil adsorption shown by aliphatic oils is not necessarily indicative of poor recoveries. It is however a reflection of the hydrophilic character of the coal surface. Since this is believed to have a marked effect on froth stability, and adsorption of aliphatic oils on such coals is limited, good recovery, when using these oils, is dependent on froth stability. Factors which contribute to this are, amongst others, bubble size, particle size, particle hydrophobicity (either native or induced by oil and possibly "promoter" surfactants) and frother-induced electrical repulsion between bubble films. The latter effects hinder bubble coalescence. In practical terms good

recovery translates to the need for effective frother-collector joint action or an increase in frother dosage. If froth stability was ensured, aliphatic oils did produce good recoveries.

It was found that the effectiveness of the oils as collectors depends to a considerable degree on their influence on bubble size since this is an important contributory factor to froth phase structure and stability. Aromatic oils produced froths with smaller air cells. These froths were mobile (more water between the lamellae) and sufficiently stable to allow concentrate recovery. On the other hand, the aliphatic oils often produced froths with very large bubbles (sometimes polyhedral in nature) that were generally not sufficiently stable or free-flowing (with unwashed coals) to allow substantial concentrate recovery.

Froths must possess sufficient mechanical strength to be able to support coarse particles. The ability of the froth to sustain large particles is of great importance to improved yields since typical coal feeds are likely to possess a significant proportion of coarse material by mass. Aliphatic collectors required high frother (MIBC) additions to overcome their deficiency in this respect. The fact that higher frother dosages could improve performance emphasised that the extent of oil adsorption alone was not a sufficient criterion for predicting flotation performance.

Since the presence of aromatic oils produced smaller air bubbles these oils obviously altered air-water surface tension. All the oils tested are exceedingly insoluble in water and hence unable to congregate at the interface as individual molecules, as typical surfactants would. The mechanism by which the aromatics affect the interface chemistry lies in the manner in which the oils spread at the interface. A sufficiently thin film of oil would mimic soluble surfactant behaviour in terms of the lowering of surface tension if the air-water interface is replaced by water-oil and oil-air interfaces with cumulatively lower surface tensions (energy). The aromatic oils spread spontaneously to form a film at the air-water interface while the aliphatics exist as discrete, substantial droplets (lenses) at the interface, i.e. they do not spread spontaneously.

The inability of aliphatic oils to spread at the air-water interface resulted in their ineffectiveness in reducing bubble size.

Froth structure and stability were therefore not significantly enhanced by the use of these oils. Increased native hydrophobicity of the coal is believed to assist in compensating for the deficiency of aliphatic oils in this regard as was shown by tests with a coarse washed coal sample.

The aromatic oils, especially the commercially produced Shellsol AB, are capable of forming and sustaining a substantial froth phase in the absence of any frother. The pure aromatic oil investigated, hexyl benzene, still required MIBC to achieve the best possible flotation results. This indicated that, in addition to reduced bubble size, froth stability is dependent on reduced bubble coalescence rates. Although aromatic oils reduce bubble size, coalescence of oil films covering bubbles tends to collapse the froth unless this is counteracted by surface-active agents like frother. These agents induce electrical double layer repulsion between the oil films as well as between uncoiled bubble surfaces. The commercially produced Shellsol AB probably had an enhanced froth stabilizing ability because of the presence of trace surface-active impurities which are often associated with commercial aromatic stocks.

The presence of surface-active impurities in commercial oils can produce apparently anomalous behaviour. The largely aliphatic Pegasol 3745 oil produced excellent recoveries with unwashed coals in spite of its limited dispersion and adsorption characteristics in relation to the aromatic oils. This oil (Pegasol 3745) was observed to reduce bubble size significantly in the presence of MIBC. This action was attributed to a surface-active oil impurity rather than to its aromatic content as it did not occur to the same extent with predominantly aromatic oils. Since powerful surfactants (very polar or ionized) are virtually insoluble in strictly aliphatic oils, it is believed that commercial oils would have to have a significant aromatic content before such effects become apparent.

Flotation kinetics were reduced with higher boiling range Pegasol 3745 cuts, yet differences in the induced bubble sizes were insignificant. This was attributed to the increase in oil viscosity slowing fluid-fluid (oil-air) coalescence. However, similar thermodynamic (spreading/ adsorption) characteristics ensured that the cuts all produced similar final recoveries. An increase in oil viscosity

good proportion of MIBC molecules congregate at the air-water interface and so retain their frothing ability .

5.6.3 Beneficiation achieved by flotation in relation to feed liberation

The float-sink characteristics of a coal feed provide an excellent measure of the liberation characteristics of the coal feed as whole. A global evaluation of flotation results revealed that grades were much poorer than those theoretically possible for any given concentrate mass. However, expecting flotation grade to conform to the degree of liberation as represented by the float-sinks curve is not strictly appropriate since the surface of a particle with an undesirable ash content may still be dominated by hydrophobic carbonaceous material and hence be floatable. Further displacement from the floatability curve will be brought about by inappropriate flotation operating parameters.

Floatability is also influenced by the rank and degree of oxidation of the carbonaceous material. While changes in these latter two factors influence the floatability (yield) they do not directly harm the grade (flotation washability) at any given yield. However, the use of a collector/promoter which will adsorb on coal surfaces possessing some hydrophilic character may be harmful to grade in that it is also more likely to adsorb on polar/charged gangue surfaces.

5.6.4 The effect of flotation rate

A rapid flotation rate is generally acknowledged to decrease grades since it enhances entrainment. However in this testwork the grades, considered in a global sense, were not markedly affected by changes in flotation rate. The poor liberation of the feed and the consequent flotation of high carbonaceous content middling material, evidently masked its true effect. Flotation parameters enhancing rapid flotation merely lowered the grades slightly producing some scatter in the data but did not affect the global trend significantly.

5.6.5 Froth water content and its influence on concentrate grades

With any one coal feed, froth water content is governed to a large extent by the choice of collector oil, mainly because of the influence of the latter on bubble size. Froth mobility, including internal mixing, is dependent on a sufficiently high water content in relation to the solids content. In many instances the poor mixing (inherent stratification) within the froth (as dictated by the froth form and in particular its water content) precluded gangue drainage so that a large froth residence time would have been of no use in cleaning the froth. Dry froths showed no signs of mixing and evidently possessed insufficient interstitial water to promote gangue drainage.

5.6.6 The effect of conditioning procedures

With any one oil, conditioning procedures were found to have a marked influence on flotation performance under certain circumstances. This was a result of, inter alia, their influence on oil dispersion, the spreading of oil within the pulp and the possible induction of air by the impeller under certain conditioning regimes, leading to air nuclei/bubbles forming on the solids and promoting the adherence of bubbles produced later during aeration. Several workers, who between them studied a number of minerals, concurred that pre-aeration of the pulp during conditioning is beneficial to flotation.

Conditioning-induced performance variations will make it very difficult to evaluate the suitability of an oil as a coal collector in a limited batch flotation program. Under conditions of different dosage or even of a seemingly unimportant change in conditioning procedure, the difference in results can be remarkable. The most common way of introducing oil in batch flotation experiments, i.e. lpdc (where the cell is full so that agitation conditions are comparatively mild) generally produced poorer grades. This finding supports evidence that prior dispersion of oils improves grades as well as reducing dosages. An increase in pulp agitation intensity will also facilitate oil dispersion but the additional power required would make this economically disadvantageous. Furthermore, it may still be incapable of distributing oil as thoroughly as pre-dispersion if the coal adsorbs the oil rapidly and consequently as comparatively large droplets.

Generally, the flotation performance variations produced after various conditioning procedures could be compensated by increasing both collector and frother dosages, though again this is probably a less cost efficient approach.

The conclusions reached as a result of the flotation testwork are not included in this chapter but are deferred to Chapter 6 in which they are discussed as part of the conclusions for the thesis as a whole.

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CHAPTER 6

CONCLUSIONS

6.1 Introduction

Documented research on the action of insoluble collectors in flotation sub-processes is limited. Hence an inadequate understanding exists of the impact of insoluble collectors on flotation performance. In this thesis, the theoretical understanding of the action of oily hydrocarbon collectors in coal flotation has been consolidated and extended, particularly in respect of interfacial phenomena. The role of the frother was also explored, particularly when used in conjunction with an oily hydrocarbon collector. The theoretical analysis was supported with practical experimental work.

Special emphasis was placed on three pulp phase sub-processes; namely, the dispersion of the oil, the selective adsorption of the oil onto coal, and the effect of oil on the creation of air bubbles and their attachment to oiled coal particles. The objective was to try to explain the significant variations in coal flotation performance, observed when using various oils, in terms of the behaviour of the oils in these pulp phase sub-processes.

The limited knowledge available suggested a fairly broadly-based investigative approach using traditional coal flotation reagents. Aliphatic and aromatic oils, of both synthesis grade (pure) and commercial quality, were used as coal collectors: MIBC was used as frother, this being the most common commercial frother in coal flotation today. The coal used was from Greenside Colliery, which is located in South Africa's most important coal field, at Witbank.

For each sub-process investigated, the theoretical analysis and the results of the experimental work undertaken are discussed in one chapter of the thesis, which contains its own conclusions. Conclusions from each of these chapters are consolidated in the present chapter and correlated with the conclusions drawn from the flotation testwork.

6.2 General

Coal flotation results are generally well explained by the observed behaviour of the oily collector and MIBC (frother) in the pulp phase sub-processes. The action of both aliphatic and aromatic oils not possessing intrinsic surface-active constituents is well understood. However, the existence of surfactants as intrinsic constituents of some commercial oils (and therefore unquantifiable), complicates this understanding.

A specific study of froth phase phenomena involving the reagents was found to be unnecessary in most instances. Pulp phase sub-processes necessarily precede those in the froth phase and the influence of the oils on pulp phase bubble formation gives a good indication of their influence on the froth phase. The actions of the oil in all three sub-processes are inter-related as they are all governed by the intrinsic interfacial properties of the oil.

Aromatic stocks are recommended as coal collectors since they adsorb readily on somewhat hydrophilic coal surfaces yet remain highly selective. They are also capable of reducing bubble size significantly thereby contributing to excellent flotation recovery.

Mixing any oil in water (in the absence of a frother) and observing its effect on the size and number of bubbles created upon introduction of an air stream, is suggested as a means of gauging the likely flotation performance of the oil. The oil's behaviour at the air-water interface is indicative of its behaviour in other interface-related processes involving the oil such as dispersion and adsorption. This test is not foolproof as some commercial oils may induce excellent performance in combination with a particular frother or other added surfactant, but use of the frother in the test will mask the effect of the oil on bubble size reduction.

A thorough understanding of interfacial phenomena is essential for quantitative or even semi-quantitative prediction of flotation performance. However, the level of theoretical understanding of several coal flotation sub-processes remains insufficient for quantitative prediction of performance. Theoretical understanding of interfacial

phenomena is particularly limited in respect of dynamic and non-equilibrium conditions, which are typical of any flotation process. This is especially true of the theory concerning surfactant (such as frother) behaviour. These reagents strongly influence and may even control coal flotation.

In general, to arrive at models of the flotation sub-processes, equilibrium conditions and further simplifications such as planar and homogeneous solid surfaces must be assumed. In coal flotation the extreme heterogeneity of the coal surface is likely to elude quantitative description and will therefore restrict the understanding of interfacial phenomena involving coal to the semi-quantitative for the foreseeable future.

Despite the inadequacy of the theory for predictive purposes it is very useful for explanatory purposes.

Some of the more important observations and conclusions emanating from the study of the sub-processes are summarized below. This is followed by conclusions in respect of the influence of the sub-processes on (batch) coal flotation. Finally, recommendations for further work are given.

6.3 Oil dispersion

The dispersion of oil and its distribution amongst the coal particles within the pulp is a pre-requisite for the flotation of coals which are insufficiently hydrophobic to float in the absence of collector (oil).

Agitation conditions typical of laboratory batch flotation cells were found to be capable of adequately dispersing all the oils studied. In every millilitre of pulp water millions of oil droplets were produced (in the absence of solids) at oil dosages of 67 and 133 $\mu\text{l.l}^{-1}$ of water (1000 and 2000 g per tonne of coal in a 5 % m/m pulp). Mean droplet sizes were therefore small; mean diameters (based on volume) were not greater than 35 μm with any oil under even comparatively mild agitation conditions (full cell). In terms of droplet number, droplets of the order of a few microns in diameter dominated the droplet populations.

Volume-based droplet distributions (i.e. volume vs. diameter) were statistically well modelled by the normal distribution function in either its arithmetic or geometric (logarithmic) form. The latter form was rare and was restricted to aromatic oils under vigorous and/or prolonged agitation conditions, where both very small and considerably larger droplets co-existed in the population.¹

Aliphatic and predominantly aliphatic oils (both pure and commercially derived) produced very similar droplet size distributions at the same mixing conditions. This indicated similar oil-water interfacial properties as well as the absence of powerful surfactant impurities in the commercial aliphatic oils.

Aromatic oils were better dispersed than aliphatic oils at the same conditions, reflecting their lower oil-water interfacial tensions. Increasingly vigorous agitation conditions produced correspondingly smaller droplets, particularly with aromatic oils. Droplet numbers increased by up to two orders of magnitude.

Oil dispersion characteristics were assessed in the absence of solids. The presence of solids, with the accompanying adsorption of oil droplets, will limit the degree of oil dispersion, and distribution of oil within the pulp can be expected to be less thorough. However, this was not found to hamper flotation recovery at the oil dosages used. It did decrease grades to a small extent. Rapid oil adsorption onto coal is nevertheless expected to progressively prejudice oil distribution within the pulp as oil dosages are decreased. Thus, in the interests of economy and of selectivity it is suggested that oils are pre-dispersed or emulsified prior to addition to coal pulps.

MIBC (the frother used) did not promote and usually hindered oil dispersion, irrespective of whether it was added mixed in the oil or independently. An increase in mean droplet size may not necessarily be manifested in the presence of MIBC since more powerful (typically ionic) surface-active impurities often present in commercial oil stocks may override its influence. In the absence of the influence of other surfactants MIBC will always tend to reduce the degree of oil

¹ Frequency-based distributions lost all semblance of normality if the corresponding volume based distribution followed the arithmetic form of the function. Log-normal distribution forms were however retained.

dispersion. Its effect was particularly striking in very turbulent regimes. Under mild agitation conditions no effect was apparent. MIBC dosage was $12 \mu\text{l.l}^{-1}$ of water in both cases.

The effect of MIBC may be explained by the inherent surface-active properties of the molecule. The emulsifying tendencies of a surfactant can be determined from its calculated hydrophile-lipophile balance (H.L.B.) value. An H.L.B. value below 7 is indicative of a water-in-oil emulsifier. The value for MIBC is 6.05. However the oil-phase fraction used in flotation is too small to make the formation of an water-in-oil dispersion physically possible and the effect of MIBC is manifested as an increase in the mean oil droplet size.

A water-in-oil emulsifier accelerates the coalescence of oil in relation to the coalescence of water. The smaller the respective droplets, the faster their rate of coalescence and the more noticeable the effect of the emulsifier will be, which explains why the influence of MIBC is particularly prevalent in high shear regimes.

6.4 Oil adsorption

A technique was successfully developed for monitoring the dynamics of oil adsorption in turbulent coal pulps. Oil adsorption is monitored directly and therefore circumvents problems associated with indirect methods often used for evaluating potential oil adsorption on coal, such as contact angle and other coal wettability measurements.

Oil adsorption onto coal is a physi-sorption process since no specific chemical bonds are formed. Bonding arises through London-Van der Waals forces and, with some oils, by additional hydrogen bonding interactions. Though these bonds are individually weak, their cumulative effect for each long-chain oil molecule and finally for all the molecules present at the coal-oil interface of the adsorbed droplet is a strong bond. Oil droplet adsorption on coal is essentially an irreversible process.

The adsorption and spreading tendencies of the various oils can be readily ascertained or explained with the classical (Dupré) wetting relations. Oil adsorption is governed by the possibility of lowering the

energy of the system by replacing a water-coal interface with a lower energy oil-coal interface.

Despite favourable thermodynamic conditions of the final (adsorbed) state, the success of adsorption is governed by the ability to overcome a high energy "barrier" encountered during the approach of coal particle and oil droplet. This barrier is a result of the electrical double layer repulsion of the similarly charged oil droplets and coal particles. These interactions hinder the thinning and rupture of the aqueous phase separating the oil droplet and the solid particle.

Oil droplets and coal particles will both be negatively charged at a pH typical of unadjusted coal pulps (around pH 8). Several workers have found that positive oil droplet charge is only manifested at low pH (at least below pH 5) and that a positive charge for unbeneficiated coal occurs at even lower values or does not occur. Kinetic energy must be input to overcome the repulsion barrier.

Both oil types readily adsorbed on washed (low ash) coal wetted with water. On a coal surface with an increase in hydrophilic character (unwashed coal), aliphatic oils adsorbed to far less of an extent, indicating their inability to displace water from such coal surfaces. Aliphatic oils will readily wet these same surfaces if they are dry. Aromatic oils continued to adsorb to a large extent. These oils are capable of weak polar interactions as a result of unevenly distributed electron clouds. This allows the oils to interact with electro-positive hydrogen atoms and so adsorb on comparatively high energy (e.g. oxidized) coal surfaces. Tolerance of some hydrophilic character makes aromatic oils a better choice of collector - because of greater operational flexibility in flotation. Products of the oxidation of hydrocarbons constituting the oil also enable the oils to adsorb on comparatively high energy surfaces, by facilitating the development of a hydrogen-bonding mechanism.

A contact angle will always form between the oil droplet and the coal surface in an aqueous phase since none of the oils will spread spontaneously on any coal surface wet by water. Mechanical work is required to spread the oil. Conditioning prior to commencing flotation is therefore important.

Young's equation provides an adequate model of the final adhesion process but it is severely limited for predictive purposes since hysteresis, non-homogeneous solid surfaces, varying and variable surfactant adsorption densities, etc. make contact angle measurements of qualitative use only. Nevertheless contact angle measurements and Young's equation are the only means currently available to assess solid interfacial tensions.

A combination of the Gibbs adsorption equation and the Young equation is particularly useful in the theoretical understanding of the action of surfactants (of which frothers are usually the most important) in coal flotation. Unfortunately this equation assumes that equilibrium conditions are attained which would not generally be true in an actual flotation situation. The existing theory of surfactant behaviour in dynamic situations is inadequate or non-existent.

MIBC does not promote oil adsorption and slowed this if it was contacted with the coal prior to the oil. In the latter tests, final adsorption levels were similar and it is postulated that this occurred because MIBC was transferred from the coal-water interface to the oil-water interface or into the oil itself upon repeated contact of oil and coal surfaces.

All the oils studied were found to be highly selective towards hydrophobic carbonaceous material and would not adsorb on typical hydrophilic gangue minerals. Subsequent flotation tests verified this selectivity. So-called high ash particles were nevertheless collected since composite particles containing ash-forming minerals are often dominated by hydrophobic carbonaceous material. Flotation washability and density washability curves for the coal were therefore displaced from one another with flotation washability offering poorer results. Good physical liberation is vital to beneficiation by flotation.

Coarse particles of unwashed coal required several minutes of conditioning before the oils reached their final adsorption levels. Oil adsorption was faster on the equivalent size fractions of washed coal. Fine particles adsorbed oil very quickly because of their high specific surface area. Adsorption was usually complete in a matter of seconds. As adsorption is essentially irreversible, this action will starve many of the particles of oil, especially if the oil is not pre-dispersed. Oil

starvation will affect large particles in particular. These particles usually form a substantial portion of the discard/flotation feed streams in coal washing plants. The vastly disparate adsorption rates support the claimed advantages of split conditioning/flotation circuits.

Furthermore, the milder the agitation conditions, the more rapid oil adsorption was found to be. This indicated that the oil was adsorbed as fairly large droplets in mildly turbulent regimes. Distribution within the pulp would consequently be poorer, especially if the oil was not pre-dispersed: dispersion of the oil prior to its addition to the coal pulp should be standard practice.

Modelling the kinetics of oil adsorption on the basis of a postulated mechanism was not possible. Postulation of a mechanism was prevented by the insolubility of the oil (droplet size distribution), the ability of free oil droplets to coalesce with those adsorbed instead of adsorbing directly on the coal, and of large adsorbed droplets spawning daughter droplets in high shear regimes.

"Equilibrium" adsorption levels observed with aliphatic oils on unwashed coal are believed to be the result of insufficient adsorption sites rather than the result of a dynamic adsorption-desorption process. The oil droplets are essentially irreversibly adsorbed.

For simple curve fitting an n 'th order equation gave an excellent fit though for predictive purposes a second order reversible reaction equation is recommended. In this latter case, equilibrium adsorption levels have to be empirically determined.

As oil adsorption onto coal occurs, and selectively, it can be confidently stated that hydrocarbon oils are good collectors for coal since thermodynamics indicate that air-oil coalescence/coagulation will always occur (because the surface tensions of the oils are less than that of water).

6.5 The effect of the oil on bubble size

The size distribution of bubbles produced within the pulp at fixed aeration rate has a pronounced effect on flotation rate and froth form and stability.

Testwork showed that several oils decrease the size of air bubbles formed considerably and even surpass MIBC in this role at conventional dosages. The aromatic oils (both pure and commercial) fall into this category. They alter air-water interfacial behaviour by spontaneously spreading at this interface as it is thermodynamically favourable to do so. The air-water interface is effectively replaced by oil-water and air-oil interfaces of lower cumulative interfacial tension (energy).

This reduction in bubble size caused by the presence of aromatic oils is not dependent on the presence of true surfactants as the pure hexyl benzene, which is free of surfactants, reduces bubble size in a very similar manner to the commercially produced aromatic oil, Shellsol AB.

Dodecane, Shellsol K and Pegasol 3745 have very little or no influence on air bubble size since they do not spread spontaneously at this interface. These oils remain as lenses at the interface.

Because spreading phenomena dictate bubble size, the degree of oil dispersion and the oil dosage were found to have little effect on bubble size.

In investigating the joint action of oil and MIBC on bubble size (at conventional dosages) it was found that MIBC dictates the mean bubble size when used in conjunction with dodecane and Shellsol K (aliphatic oils). On the other hand, the aromatic oils (Shellsol AB and hexyl benzene) dictate bubble size when used in conjunction with MIBC, and MIBC plays no apparent role, i.e. the sizes are similar to those produced by the oils in the absence of MIBC.

An anomaly occurs with the Pegasol 3745 boiling range cuts, the joint action of oil and MIBC induces smaller bubbles than are obtained with either reagent in isolation (at the same dosages). This behaviour is attributed to a lowering of the interfacial tension by mutual "complexing" of some surface-active oil impurity and MIBC at the air-water interface.

The frequency-based bubble size (diameter) distributions were statistically well-modelled by the normal distribution either in its arithmetic or in its geometric (logarithmic) form.

6.6 Flotation results

The conclusions which follow apply to the oil-coal-MIBC systems studied in this thesis. Other frothers or additional surfactants (such as cationic promoters) may induce other results.

All the oils floated washed coal well. In general, aliphatic oils were poorer collectors of unwashed coal than any aromatic oil (under identical conditions). This is certainly true of aliphatic oils with little or no aromatic content. However, Pegasol 3745, a predominantly aliphatic oil with about 20 % aromatic content, behaves anomalously. This is discussed in more detail below.

Both recovery and grade were dependent on conditioning procedure, oil dosage and MIBC dosage. The conditioning procedure often had a marked influence on flotation performance. This was a result of, inter alia, its influence on oil dispersion, oil spreading and distribution within the pulp and the induction of air by the impeller at reduced cell volumes. Suitable increases in oil and/or MIBC dosage can help to overcome these effects but will increase the costs of beneficiation.

The mode of addition of MIBC was also found to be important. The preferential solubility of MIBC in oil will limit its accumulation at the air-water interface if it is added mixed in the oil. This suggests that MIBC addition should be independent of the oil and as late as possible prior to commencing flotation. Tests showed that early addition of MIBC could severely restrict flotation recovery. It should therefore not be added during any conditioning step. Use of a preferentially water-soluble frother may be another alternative.

The necessary activity of MIBC at the air-water interface implies that its dosage must be in accordance with its concentration in the pulp water and not according to the mass of solids in the pulp.

Tests showed that the extent of oil dispersion and of adsorption onto coal was sufficient at the oil dosages used to render the coal particles floatable. The hydrophobic character of the particles is however an insufficient criterion for recovery. In addition, froth stability is necessary. Stability is enhanced by, amongst other factors, increased particle hydrophobicity, a decrease in bubble size, a decrease

in particle size and the presence of surfactants which hinder bubble coalescence.

Results achieved with the aliphatic oils clearly demonstrate the need for froth stability. While recoveries of unwashed coal were often poor, an increase in the MIBC dosage boosted yields remarkably. It was shown that this could not be attributed to increased dispersion nor to increased oil adsorption; nor to any collecting ability of MIBC. On the other hand, the recovery of washed coal at the usual reagent dosages was excellent because the increased native hydrophobicity of the particles themselves contributed to froth stability. (It also consequently enhanced oil adsorption).

The influence of the oil on bubble creation and consequently on froth stability was the sub-process which dominated flotation performance. This explains why the Pegasol 3745 oil, which is 80 % aliphatic, performed excellently as a coal collector although its extent of adsorption and of dispersion were not as good as those of the aromatic oils. In the presence of MIBC it markedly reduces bubble sizes. The behaviour induced by the Pegasol 3745 oil also confirms that the extent of dispersion and adsorption of aliphatic oils was sufficient since it behaved in a very similar manner to dodecane and Shellsol K in these respects, yet produced excellent recoveries.

This anomolous behaviour (attributed to surface-active oil impurities) indicates the potential problems which might arise in predicting or maintaining coal flotation performance when commercial oil stocks are used. A substantial aromatic content is believed to be necessary to induce anomalous behaviour since powerful surfactants will not dissolve in essentially pure aliphatic oils.

Despite the ability of the aromatics to reduce bubble size, froth stability is additionally aided by the presence of a true surfactant, like a frother. In tests with unwashed coal, with a pure aromatic oil (hexyl benzene) and no MIBC, a froth did develop and up to 40 % of the coal was recovered. However recovery could be doubled if MIBC was used. In the absence of MIBC, the coalescence of the oil films which cover the bubbles tends to collapse the froth. Surface-active agents like MIBC counteract or hinder this by inducing electrical double layer repulsion between adjacent oil films.

Commercially-produced Shellsol AB was able to maintain substantial froths at appropriate dosages (2000 g.t^{-1}) in the absence of MIBC. This was attributed in part to bubble size reduction and in part to the stabilizing effect of inherent surface-active constituents.

However, in general, adequate froth stability is dependent on the joint presence of both the oil and the MIBC. A deficiency in either usually produces poorer performance. *The correct choice of collector oil is also important to froth stability, and thus to recovery, chiefly because of its influence on bubble size.*

Flotation rate was found to decrease significantly with an increase in the boiling range (and hence viscosity) of the essentially homologous series of Pegasol 3745 cuts. Final recoveries were however similar, reflecting the similarity of oil dispersion and of adsorption onto coal. The decrease in rate could not be attributed to a differences in the sizes of bubbles induced: these were all similar. The decrease was attributed to a decrease in the rate of oil-air coalescence (oiled particle-air bubble contact) as the viscosity of the oil increased.

A high rate of flotation is widely acknowledged to contribute to poor grades because of encouraging entrainment. The inadequate liberation of the coal samples used in this thesis (which are typical of South African coal fines) apparently masked the effect of rate, which had unexpectedly little influence on the concentrate grades. Very low rates as well as very low recoveries failed to improve the grades significantly. It was shown that this was not a selectivity problem.

An increase in the froth water content induced more mobile froths which were more easily removed. The increased water content is also believed to improve the drainage of gangue from the froth and thereby improve concentrate grades. This conclusion was reached after a global assessment of the water recovery and grade results. This approach is essential since increased yield accompanies an increase in water recovery. The latter is indicative of froth form and stability. Grades apparently decrease but this is a result of the increased yield and not of the water recovery *per se*.

6.7 Recommendations

1. Interfacial phenomena control the flotation process. This suggests that flotation performance may be advantageously regulated by making use of other surfactants (e.g. frothers and promoters). A better choice of frother or the use of a promoter could be used to enhance both the dispersion and the adsorption of oils, especially the aliphatic oils. The latter effect would in turn promote froth stability (and by association recovery) by rendering the particles more hydrophobic. It would be useful to study these effects as well as the mode of reagent addition since the best mode of addition to the pulp may also be expected to vary with the type of frother employed.

It is suggested that particular emphasis be placed on non-ionic surfactants since many commonly used frothers fall into this category. While some practical work in this field has been published there is still considerable scope for research, particularly with regard to the flotation of South African coals.

2. There is much scope for more theoretical investigations, notably with respect to surfactant behaviour and in particular to its behaviour in dynamic/non-equilibrium conditions typical of the flotation process. At present only qualitative deductions and predictions are possible.
3. A systematic evaluation of the effect of the oil-coal-frother interactions on the form and stability of the froth would be useful to quantify some of the observations made in this regard in this thesis.
4. Flotation results, when considered in the light of the known suitability of oils as collectors, point to inadequate coal liberation as the major reason for unsatisfactory grades. This suggests the need for on-going investigation of the liberation characteristics of South African coals to determine whether large-scale recovery of low ash (7 %) coal would ever be practically possible and whether further comminution would be economical or not.

REFERENCES

- Adamson, A.W., Physical Chemistry of Surfaces, 1st ed., Interscience Publishers, New York, 1960.
- Adamson, A.W., Physical Chemistry of Surfaces, 2nd ed., Interscience Publishers, New York, 1967.
- Agar, G.E. and Barrett, J.J., "The use of flotation rate data to evaluate reagents", *CIM Bulletin*, 76(851), March 1983, pp. 157-162.
- Ahmed, N. and Jameson, G.J., "The effect of bubble size on the rate of flotation of fine particles", *International Journal of Mineral Processing*, 14, 1985, pp. 195-215.
- Al Taweel, A.M., Delory, B., Wozniczek, J., Stefanski, M., Andersen, N. and Hamza, H.A., "Influence of the surface characteristics of coal on its floatability", *Colloids and Surfaces*, 18 (1), 1986, pp. 9-18.
- Anfruns, J.P. and Kitchener, J.A., "The absolute rate of capture of single particles by single bubbles", in Flotation, A.M. Gaudin Memorial Volume, Vol. 2, ed. Fuerstenau, M.C., American Institute of Mining, Metallurgical and Petroleum Engineers, Inc., New York, 1976, pp. 625-637.
- Aplan, F.F., in Fine Coal Processing, eds. Mishra, S.K. and Klimpel, R.R., Noyes Publications, Park Ridge, New Jersey, 1987.
- Aronson, M.P., Zettlemoyer, A.C. and Wilkinson, M.C., "On the properties of certain four phase oil-water-solid-vapour configurations. 1. Comments on the stability of a four phase contact line", *The Journal of Physical Chemistry*, Vol. 77, No. 3, 1973, pp. 318-322.
- Aronson, M.P., Zettlemoyer, A.C., Codell, R.B. and Wilkinson, M.C., "The static profiles of several solid/oil/water/vapour configurations. II. Partially submerged drops", *Journal of Colloid and Interface Science*, Vol. 54, No. 1, June 1976, pp. 134-148.
- Aston, J.R., Deacon, M.J., Furlong, D.N., Healy, T.W. and Lau, A.C.M., "The chemistry of non-ionic surfactants in coal preparation processes", Proceedings of the 1st Australian Coal Preparation Conference, ed. Swanson, A.R., 1981, pp. 358-378.
- Bailey, R. and Gray, V.R., "Contact angle measurements of water on coal", *J. Appl. Chem.*, 8, April 1958, pp. 197-202.
- Bailey, R. and Whelan, P.F., "The influence of pulp temperature on the froth flotation of four British fine coals", *Journal of the Institute of Fuel*, 25, January 1953, pp. 304-308.

Banarjee, A., Roy, A.R., Sarkar, G.G. and Lahiri, A., "Kinetics of coal flotation", *Journal of the Institute of Fuel*, July 1962, pp. 298-302.

Baranov, L.A. and Gubaidulin, Sh.Sh., "Time required for adhesion of flotation reagent drops to oxidized coal particles", *Soviet Min. Sci.*, Vol. 7, No. 4, 1971, English translation by Plenum Publishing Corporation, New York, 1972, pp. 427-430.

Bensley, C.N. and Nicol, S.K., "The effect of mechanical variables on the flotation of coarse coal", *Coal Preparation*, Vol 1, 1985, pp. 189-205.

Bernstein, D.F., Higuchi, W.I. and Ho, N.F.H., "Kinetics of flocculation and/or coalescence of dilute oil-in-water emulsions", *Journal of Pharmaceutical Sciences*, Vol. 60, No. 5, May 1971, pp. 690-694.

Bhargava, A., Francis, A.V. and Biswas, A.K., "Interfacial studies related to the recovery of mineral slimes in a water-hydrocarbon liquid-collector system", *Journal of Colloid and Interface Science*, Vol. 64, No. 2, April 1978, pp. 214-227.

Bitter, J.H., "Conditioning of the pulp and its influence upon the results of flotation", 5th International Coal Preparation Congress, Section A : Paper 3, Pittsburgh, 1966, pp. 37-44.

Botha, P.H., "An investigation of the flotation of three South African coals", *J. S. Afr. Inst. Min. Metall.*, Nov. 1980, pp. 395-400.

Boudart, M., Kinetics of Chemical Processes, Prentice-Hall, New Jersey, 1968.

Brodnyan, J.G., "Emulsion particle size II. Determination of the distribution function using the ultracentrifuge", *Journal of Colloid Science*, Vol. 15, 1960, pp. 563-572.

Brookes, G.F. and Bethell, P.J., "Zeta potential, contact angle and the use of amines in the chemical dewatering of froth-floated coal", *Powder Technology*, 40, 1984, pp. 207-214.

Brown, D.J., Gray, V.R. and Jackson, A.W., "The spreading of oil on wet coal", *J. Appl. Chem.*, 8, November 1958, pp. 752-759.

Burkin, A.R. and Bramley, J.V., "Flotation with insoluble reagents. I. Collision and Spreading in the coal-oil-water system", *J. Appl. Chem.*, 11, August 1961, pp. 300-309.

Burkin, A.R. and Bramley, J.V., "Flotation with insoluble reagents. II. Effects of surface-active reagents on the spreading of oil at coal-water interfaces", *J. Appl. Chem.*, 13, October 1963, pp. 417-422.

Buys, I.E., "Comparison of froth flotation and oil agglomeration for fine and ultrafine coal beneficiation", B.Sc. Honours thesis, University of Cape Town, 1987.

Campbell, J.A.L. and Sun, S.C., "Bituminous coal electrokinetics", *Transactions Society of Mining Engineers, AIME*, Vol. 247, June 1970a, pp. 111-114.

Campbell, J.A.L. and Sun, S.C., "Anthracite coal electrokinetics", *Transactions Society of Mining Engineers, AIME*, Vol. 247, June 1970b, pp. 120-122.

Celik, M.S. and Somasundaran, P., "Effect of pretreatments on flotation and electrokinetic properties of coal", *Colloids and Surfaces*, 1, 1980, pp. 121-124.

Chibowski, E., Holyz, L. and Staszczuk, P., "Flotation response of sulphur wetted with n-alkanes", *Polish Journal of Chemistry*, 59, 1985, pp. 1167-1172.

Cooper, F.A., "The size-frequency distribution of emulsion particles", *J. Soc. Chem. Ind.*, 56, Dec. 1937, pp. 447T-453T.

CRC Handbook of Chemistry and Physics, 61st edition, ed. Weast, R.C., CRC Press, Boca Raton, 1980-81.

Crossley, H.E., (Discussion), in Jowett, A. (1958) *op. cit.*, "The influence of the adsorption of frothing agent on the percentage recovery of coal from flotation pulps", *Journal of the Institute of Fuel*, 31, July 1958.

Davies, J.T. and Rideal, E.K., Interfacial Phenomena, Academic Press, London, 1961.

Davis, S.S. and Burbage, A.S., "Electron micrographs of water-in-oil-in-water emulsions", *Journal of Colloid and Interface Science*, Vol. 62, No. 2, November 1977, pp. 361-363.

Davis, S.S. and Burbage, A.S., "Particle size analysis of multiple emulsions (water-in-oil-in-water), in Particle Size Analysis, ed. Groves, M.J., Heyden, 1978, pp. 395-409.

Dell, C.C., "The effect of solids concentration on flotation", *Coal Preparation*, May-June 1968, pp. 101-103.

Deraguin, B.V. and Dukhin, S.S., "Theory of flotation of small and medium size particles", *Trans. Inst. Min. Metall.*, 70, 1961, pp. 221-245.

Dibbs, H.P., Sirois, L.L. and Bredin, R., "Some electrical properties of bubbles and their role in the flotation of quartz", *Canadian Metallurgical Quarterly*, Vol. 13, No. 2, 1974, pp. 395-404.

DMEA, (South African Department of Mineral and Energy Affairs), South African Discard and Duff Coal National Inventory, 1985, Aurora Printers for Government Printer, Pretoria, 1987.

Dmitrieva, G.M., Solnyshkin, V.I. and Schmidt, O.V., "The influence of certain non-polar reagents on the flotation of chalcopyrite", in Flotation Agents and Effects, ed. Solnyshkin, V.I., English translation Keter Press, Jerusalem, 1970, pp. 25-32.

Douglas, H.W., "The electrophoretic behaviour of certain hydrocarbons and the influence of temperature thereon", *Transactions of the Faraday Society*, Vol. 39, 1943, pp. 305-311.

Du Plessis, H.G., Reinecke, C.F. and Van Nierop, J.G., "The influence of oxygen containing surface groups on selective oil agglomeration properties of coal", Proc. Int. Conf. Coal Sci., Pergamon, Sydney, 1985, pp. 521-524.

Eveson, G.F., Ward, S.G. and Worthington, F., "Froth flotation of low rank coal : I. The adsorption of phenol from aqueous solutions by coals of various rank", *Journal of the Institute of Fuel*, December 1956, pp. 540-545.

Eveson, G.F., Ward, S.G. and Worthington, F., "Froth flotation of low rank coal : II. A statistical investigation of six factors influencing froth flotation", *Journal of the Institute of Fuel*, June 1957, pp. 298-309.

Fickling, R., "An investigation into the froth flotation of four South African coals", M.Sc. Thesis, University of Cape Town, 1986.

Finch, J.A. and Smith, G.W., "Bubble-solid attachment as a function of bubble surface tension", *Canadian Metallurgical Quarterly*, Vol. 14, No. 1, 1975, pp. 47-51.

Finch, J.A. and Smith, G.W., "Contact angle and Wetting", *Minerals Sci. Engng.*, Vol. 11, No. 1, January 1979, pp. 36-60.

Firth, B.A., Swanson, A.R. and Nicol, S.K., "The influence of feed size distribution on the staged flotation of poorly floating coals", *Proc. Australas. Inst. Min. Metall.*, No. 267, September 1978, pp. 49-53.

Firth, B.A., Swanson, A.R. and Nicol, S.K., "Factors governing the selection of coal flotation circuits", 9th International Coal Preparation Congress, New Delhi, 1982, pp. C3-2 to C3-11.

Flint, L.R., "Factors influencing the design of flotation equipment", *Miner. Sci. Engng.*, Vol. 5, No. 3, 1973, pp. 232-241.

Flint, L.R. and Howarth, W.J., "The collision efficiency of small particles with spherical air bubbles", *Chemical Engineering Science*, Vol. 26, 1971, pp. 1155-1168.

Flynn, S.A. and Woodburn, E.T., "A froth ultra-fine model for the selective separation of coal from mineral in a dispersed air flotation cell", *Powder Technology*, 49, 1987, pp. 127-142.

Franzidis, J-P and Anderson, G.V.M., "A technique to study the adsorption of oily collectors onto coal and gangue minerals", *Adsorption Science and Technology*, 3, 1986, pp. 303-316.

Franzidis, J-P and Harris, M., "A new method for the rapid float/sink analysis of coal fines", *J. S. Afr. Inst. Min. Metall.*, 86(10), 1986, pp. 409-414.

Franzidis, J-P, "Flotation of South African coals", CSP Progress Report, Dept. of Chemical Engineering, University of Cape Town, 1986, (unpublished).

Franzidis, J-P, "Flotation of South African coals", CSP Progress Report, Dept. of Chemical Engineering, University of Cape Town, 1987, (unpublished).

Fuerstenau, D.W., Rosenbaum, J.M. and Laskowski, J., "Effect of surface functional groups on the flotation of coal", *Colloids and Surfaces*, 8, 1983, pp. 153-174.

Fuerstenau, D.W., Williams, M.C. and Urbina, R.H., "The physical and chemical properties of coal and their role in coal beneficiation", Coal Science Conference, Sydney, Australia, 28 Oct.-1 Nov. 1985.

Fuerstenau, M.C., "Mineral-water interfaces and the electrical double layer", in Principles of Flotation, ed. King, R.P., South African Institute of Mining and Metallurgy, Johannesburg, 1982.

Garrett, E.R., "Stability of oil-in-water emulsions", *Journal of Pharmaceutical Sciences*, Vol. 54., No. 11, Nov. 1965, pp. 1557-1570.

Gaudin, A.M., Flotation, Mc-Graw Hill, New York, 1932.

Geidel, T., "Probability of attachment between mineral grains and air bubbles and its relation to flotation kinetics", *Aufbereitungs-Technik*, Nr. 5, 1985, pp. 287-294.

Glembotskii, V.A., Dmitrieva, G.M. and Sorokin, M.M., Nonpolar Flotation Agents, English translation Keter Press, Jerusalem, 1970, available from U.S. Department of Commerce, Clearinghouse for Federal Scientific and Technical Information, Springfield, Va. 22151.

Groves, M.J., "Dispersion problems in the size analysis of emulsions", *Proc. Soc. Analyt. Chem.*, Vol. 5, No. 8, August 1968, pp. 166-167.

Groves, M.J. and Freshwater, D.C., "Particle size analysis of emulsion systems", *Journal of Pharmaceutical Sciences*, Vol. 57. No. 8, Aug. 1968, pp. 1273-1291.

Hallworth, G.W. and Carless, J.E., "Stabilization of oil-in-water emulsions by alkyl sulphates : The influence of the nature of the oil on stability", *J. Pharm. Pharmac.*, 1972, 24, Suppl., pp. 71P-83P.

Harkins, W.D. and Beeman, N., "Emulsions : Stability, area per molecule in the interfacial film, distribution of sizes and the orientated wedge theory", *Journal of the American Oil Chemists' Society*, Vol. 51, June 1929, pp. 1674-1694.

Harris, M.C., Franzidis, J-P., Moody, D. and Buys, I.E., "Flotation and dewatering of fine coal. Part 1: The characterization and flotation of coal fines from the Rietspruit Colliery", Dept. of Chemical Engineering, University of Cape Town, 1986, (unpublished).

Harris, M., "Liberation characteristics of Greenside No. 2 seam coal", M.Sc. Thesis, University of Cape Town, 1987.

Harris, P.J., "Frothing phenomena and frothers", in Principles of Flotation, ed. King, R.P., South African Institute of Mining and Metallurgy, Johannesburg, 1982.

Haung, H.H. and Miller, J.D., "Kinetics and thermochemistry of amyl xanthate adsorption by pyrite and marcasite", *International Journal of Mineral Processing*, 5, 1978, pp. 241-266.

Herdan, G., Small Particle Statistics, Elsevier, Amsterdam, 1953.

Hornsby, D.T. and Leja, J., "A technique for evaluating floatability of coal fines, using methanol solutions", *Coal Preparation*, Vol. 1, 1984, pp. 1-19.

Horsfall, D.W., Zitron, Z. and De Korte, G.J., "The treatment of ultrafine coal, especially by froth flotation", *J. S. Afr. Inst. Min. Metall.*, Vol. 86, No. 10, Oct. 1986, pp. 401-407.

Horsley, R.M. and Smith, H.G., "Principles of coal flotation", *Fuel*, 30, 1951, pp. 54-62.

Janczuk, B., "The effect of n-alkanes on the force of air bubble detachment from a quartz surface in water", *Powder Technology*, 34, 1983, pp. 243-247.

Janczuk, B., "Effect of n-alkanes on wettability of graphite", *Fuel*, Vol. 65, January 1986, pp. 113-116.

- Jessop, R.R. and Stretton, J.L., "Electrokinetic measurements on coal and a criterion for its hydrophobicity", Letter to the Editor, *Fuel*, Vol. 48, No. 1, 1967, pp. 317-320.
- Jiang, Z.W. and Holtham, P.N., "Theoretical model of collision between particles and bubbles in flotation", *Trans. Inst. Min. Metall.* (Section C: Mineral Process. Extr. Metall.), 95, December 1986, pp. C187-C194.
- Jowett, A., "The influence of the adsorption of frothing agent on the percentage recovery of coal from flotation pulps", *Journal of the Institute of Fuel*, 31, July 1958, pp. 308-318.
- Kirchberg, H. and Töpfer, E., "The mineralization of air bubbles in flotation", 7 th International Minerals Processing Congress, Part 4 : Flotation kinetics, 1964, ed. Arbiter, N., Gordon and Breach, New York, pp. 157-168.
- Kirk-Othmer Encyclopaediae of Chemical Technology, 3 rd Edition, John Wiley and Sons, New York, 1978.
- Klassen, V.I. and Mokrousov, V.A., An Introduction to the Theory of Flotation, translated by Leja, J. and Poling, G.W., Butterworth and Co., London, 1963.
- Klassen, V.I., Plaksine, I.N. and Vlasova, N.S., "Theoretical bases of the action of reagents in coal flotation", Third International Coal Preparation Congress, Section E - Paper E2, Liege, 1958.
- Klimpel, R.R. and Hansen, R.D., "Chemistry of Fine Coal Flotation", in Fine Coal Processing, Eds. Mishra, S.K. and Klimpel, R.R., Noyes Publications, Park Ridge, New Jersey, 1987.
- Kruyt, H.R., Colloid Science, Vol. 1, Elsevier, Amsterdam, 1952.
- Laskowski, J., "Particle-bubble attachment in flotation", *Minerals Sci. Engng.*, Vol. 6, No. 4, October 1974, pp. 223-235.
- Laskowski, J.S., "Flotation of difficult-to-float coals", 10 th Int. Coal Prep. Congress, Vol. 1, Canadian Inst. of Mining and Metallurgy, Alberta, 1986.
- Laskowski, J.S. and Miller, J.D., "New reagents in coal flotation", in Reagents in the Minerals Industry, eds. Jones, M.J. and Oblatt, R., Published by the Institution of Mining and Metallurgy, London, 1984, pp. 145-154.
- Leja, J. and He, B.Q., "The role of flotation frothers in the particle-bubble attachment process", in Principles of Mineral Flotation, the Wark Symposium, eds. Jones, M.H. and Woodcock, J.T., Symposia Series No. 40, Australasian Inst. Min. Metall., 1984, pp. 73-89.

Leja, J. and Schulman, J.H., "Flotation Theory : Molecular interactions between frothers and collectors at solid-liquid-air interfaces", *Transactions AIME, Mining Engineering*, Feb. 1954, pp. 221-228.

Lekki, J. and Laskowski, J., "On the dynamic effect of frother-collector joint action in flotation", *Transactions IMM, Section C*, Vol. 80, September 1971, pp. C174-C180.

Lekki, J. and Laskowski, J., "A new concept of frothing in flotation systems and general classification of flotation frothers", 11th Int. Min. Proc Congress, 1975, pp. 427-448.

Lemberger, A.P. and Mourad, N., "Deaggregation in oil-in-water emulsions I : Influence of electrolytes", *Journal of Pharmaceutical Sciences*, Vol. 54, No. 2, 1965, pp. 229-232.

Levenspiel, O., Chemical Reaction Engineering, 2nd ed., John Wiley and Sons, New York, 1972.

Lloyd, P.J., Stenhouse, J.I.T. and Buxton, R.E., "Comparison of the errors due to sampling and to analysis by Coulter Counter", in Particle Size Analysis, ed. Groves, M.J., Heyden, London, 1978, pp. 367-377.

Loveday, B.K., "Analysis of froth flotation kinetics", *Trans. Instn. Min. Metall. (Section C : Mineral Process. Extr. Metall.)*, 75, No. 718, 1966, pp. C219-C225.

Lucassen-Reynders, E.H. and Lucassen, J., "Thin films, contact angles, wetting", The Scientific Basis of Flotation, ed. Ives, K.J., Nato ASI Series, Martinus Nijhoff Publishers, The Hague, 1984.

Mackenzie, J.M.W., "Electrokinetic properties of Nujol-flotation collector emulsion droplets", *Transactions Society of Mining Engineers, AIME*, Vol. 244, 1969, pp. 393-400.

Mackenzie, J.M.W., "Zeta-potential studies in mineral processing: Measurement, techniques and applications", *Minerals Sci. Engng.*, 3(3), 1971, pp. 25-43.

Mackenzie, J.M.W. and Matheson, G.H., "Kinetic and dynamic relationships in coal flotation", *Transactions Society of Mining Engineers, AIME*, 226, March 1963, pp. 68-75.

Mahajan, O.P. and Walker, P.L., "Water adsorption on coals", *Fuel*, 50, 3, 1971, pp. 308-317.

Malyuk, O.P., Sorokin, M.M. and Glembotskii, V.A., "The influence of the viscosity and the chemical composition of petroleum oils on the flotation of iron-bearing minerals", Flotation Agents and Effects, ed. Solnyshkin, V.I., English translation Keter Press, Jerusalem, 1970.

McMichael, A.Q., "The study and simulation of a unit flotation cell within a closed grinding circuit", M.Sc. Thesis, University of Natal, Durban, 1985.

Miller, I. and Freund, J.E., Probability and Statistics for Engineers, Prentice-Hall, Englewood Cliffs, 1965.

Mima, H. and Kitamori, N., "Stability and flocculation of oil droplets in dilute emulsions", *Journal of Pharmaceutical Sciences*, Vol. 55, No. 1, 1966, pp. 44-48.

Mishra, S.K. and Holmes, R.L., "Evaluation of hydrocarbon oils as collector for fine coal flotation", *Australian Coal Miner*, February 1981, pp. 28-33.

Mishra, S.K., "Improved recovery of fine coal by flotation", in Fine Coal Processing, eds. Mishra, S.K. and Klimpel, R.R., Noyes Publications, Park Ridge, New Jersey, 1987, p. 117.

Mugele, R.A. and Evans, H.D., "Droplet size distribution in sprays", *Industrial and Engineering Chemistry*, Vol. 43, No. 6, June 1951, pp. 1317-1324.

Mühle, K., Schulze, H.J., Stechemesser, H. and Ivanauskas, A., "Study of the basic steps in flotation and flocculation" *Trans. Inst. Min. Metall. (Section C : Mineral Process. Extr. Metall.)*, 91, September 1982, pp. C112-C116.

Mullins, J.D. and Becker, C.H., "A study of some factors influencing the stability of pharmaceutical emulsions", *Journal of the American Pharmaceutical Association Scientific Edition*, Vol. 45, No. 2, 1956, pp. 105-110.

Narsimhan, G., Nejjfelt, G. and Ramkrishna, D., "Breakage functions for droplets in agitated liquid-liquid dispersions", *AIChE Journal*, Vol. 30, No. 3, May 1984, pp. 457-467.

Neave, H.R., Elementary Statistics Tables, George Allen and Unwin Ltd, London, 1981.

Ng, F.L., "Surface phenomena influencing attachment and subsequent transfer of coal particles from an aqueous to a hydrocarbon phase", PhD Thesis submitted to the University of New South Wales, August 1982.

Parfitt, G.D., Principles of the Colloidal State, Monograph of The Royal Institute of Chemistry, London, 1967.

Petukhov, V.N., "The relationship between the physico-chemical properties of coal vitrinites and the adsorption capacity and flotability of the coal", *Khimiya Tverdogo Topliva*, No. 1, Vol. 13, English translation by Allerton Press Inc., 1979, pp. 7-13.

Picard, J.L., "Coal preparation washing processes: A technology review", CANMET Report No.85-2E, Canadian Government Publishing Centre, Ottawa, 1985, p. 52.

Pooley, F.D., "Some aspects of the flotation behaviour of coals with an insoluble collector", *Trans. Inst. Min. Metall., Section C*, Vol. 76, December 1967, pp. C282-84.

Rajagopal, E.S., "Statistical theory of particle size distributions in emulsions and suspensions", *Kolloid-Zeitschrift*, 162, 2, February 1959, pp. 85-92.

Ralston, J., "Thin films and froth flotation", *Advances in Colloid and Interface Science*, 19, 1983, pp. 1-26.

Rehfeld, S.J., "Stability of hydrocarbon-in-water emulsions during centrifugation. Influence of dispersed phase composition", *Journal of Colloid and Interface Science*, Vol. 46. No. 3, March 1974, pp. 448-459.

Robinson, J., "Relationship between particle size and collector concentration", *Institute of Mining and Metallurgy Bulletin*, Part 636, 1959, pp. 45-62.

Schulze, H.J., Physico-chemical elementary processes in flotation, Elsevier, Amsterdam, 1984.

Shaw, D.J., Introduction to Colloid and Surface Chemistry, 3rd ed., Butterworths, London, 1985.

Sherman, P., *J. Pharm and Pharmacol.*, 16, 1964. Quoted by Garrett, E.R., (1965) *op.cit.*

Shotton, E. and Davis, S.S., "A note on the stability of emulsions at high dilution", *J. Pharm. Pharmac.*, 1968a, 20, pp. 825-829.

Shotton, E. and Davis, S.S., "The use of the Coulter Counter for particle size analysis of some emulsion systems", *J. Pharm. Pharmac.*, 1968b, 20, pp. 430-438.

Sikdar, S.K. and Randolph, A.D., "Evaluation and calibration of the Model T Coulter Counter used in the population mode", *Analytical Chemistry*, Vol. 48, No. 9, August 1976, pp. 1415-1418.

Singleton, W.S. and Brown, M.L., "Effect of saline electrolyte on particle sizes in fat emulsions by electronic counting", *The Journal of the American Oil Chemists' Society*, Vol. 42, No. 4, 1965, pp. 312-314.

Smit, F.J. and Bhasin, A.K., "Relationship of petroleum hydrocarbon characteristics and molybdenite flotation", *International Journal of Mineral Processing*, 15, 1985, pp. 19-40.

Smith, H.G., Abbott, J. and Frangiskos, A., "Particle-bubble attachment in coal flotation", Paper 13, 2nd Symposium on Coal Preparation, Leeds, 21-25 October 1957.

Smith, H.G. and Duckmanton, B., "Further contact angle studies at coal surfaces", Paper No. 15, 2nd Symposium on Coal Preparation, University of Leeds, 1957, pp. 379-392.

Smitham, J.B. and Firth, B.A., "The distribution of insoluble collector on fine coal particles", *Proc. Australas. Inst. Min. Metall.*, No. 283, September 1982, pp. 29-35.

Sorokin, A.F., Kalakutskii, B.T., Kukolev, Ya.B., Tsiperovich, M.V. and Blokhin, V.W., "Use of oxidized hydrocarbons for flotation of coals", *Koks i Khimiya*, No. 1, 1979, English translation by Allerton Press, 1979, pp. 12-15.

Špetl, F. and Dedek, F., "New ideas on the kinetics of the flotation process", Fifth International Coal Preparation Congress, Section A: Paper 2, Pittsburgh, 1966, pp. 25-35.

Sprow, F.B., "Distribution of drop sizes in turbulent liquid-liquid dispersion", *Chemical Engineering Science*, Vol. 22, 1967, pp. 435-442.

Steedman, N.G. and Krishnan, S.V., "Oil agglomeration process for the treatment of fine coal", in Fine Coal Processing, eds. Mishra, S.K. and Klimpel, R.R., Noyes Publications, Park Ridge, New Jersey, 1987, p. 183.

Steenberg, E., "The depression of the natural floatability of talc : The mechanism involved in the adsorption of organic reagents of high molecular mass", D.Sc. Thesis submitted to the University of Potchefstroom, South Africa, 1982.

Stephens, M.A., "EDF Statistics for Goodness of Fit and Some Comparisons", *Journal of the American Statistical Association*, Vol. 69, September 1974, pp. 730-737.

Sullivan, D.M. and Lindsey, E.E., *Ind. Engng. Chem. Fundls.*, 1, 1962. Quoted by Sprow (1967) *op.cit.*

Sutherland, K.L., "Kinetics of the flotation process", *J. Phys. Chem.*, 1948, pp. 394-425.

Swanson, A.R., Firth, B.A. and Roberts, T., "The interaction between pulp density and frother addition in coal flotation", *Proc. Australas. Inst. Min. Metall.*, No. 289, February 1984, pp. 45-50.

Taylor, S.R., Miller, K.J. and Deurbrouck, A.W., "Surface chemical problems in coal flotation", *AIF Conference Proceedings*, Vol. 70, 1981, pp. 344-356.

Torza, S. and Mason, S.G., "Coalescence of two immiscible liquid drops", *Science*, Vol. 163, February 1969, pp. 813-814.

Trahar, W.J., "A rational interpretation of the role of particle size in flotation", *International Journal of Mineral Processing*, 8, 1981, pp. 289-327.

Troesch, H.A., "Die Zertäubung von Flüssigkeiten", *Chem.-Ing.-Tech.*, 26, 1954. Quoted by Groves and Freshwater (1968) *op. cit.*.

Tyurnikova, V.I. and Naumov, M.E., Improving the effectiveness of flotation, English translation Technicopy Ltd., Stonehouse, Glos. England, 1981.

Vlasova, N.S., Kushnereva, V.G. and Barsukova, Y.A., "Influence of the degree of oxidation of coals on the adsorption of n-aliphatic alcohols", *Coke Chem. (USSR)*, No. 6, 1973, pp. 5-7.

Walstra, P. and Oortwijn, H., "Estimating globule-size distributions of oil-in-water emulsions by Coulter Counter", *Journal of Colloid and Interface Science*, Vol. 29, No. 3, March 1969, pp. 424-431.

Ward, C.R. and Burdon, R.G., "Process development and selection for fine coal treatment", in Fine Coal Processing, eds. Mishra, S.K. and Klimpel, R.R., Noyes Publications, Park Ridge, New Jersey, 1987, pp. 65-71.

Warren, L.J., "Determination of the contribution of true flotation and entrainment in batch flotation tests", *International Journal of Mineral Processing*, 14, 1985, pp. 33-44.

Wen, W.W. and Sun, S.C., "An electrokinetic study on the amine flotation of oxidized coal", *Transactions Society of Mining Engineers, AIME*, Vol. 262, June 1977, pp. 174-180.

Wen, W.W., "Electrokinetic behaviour and flotation of oxidized coals", Ph.D. thesis, Pennsylvania State University, 1977. Quoted by Ng (1982) *op. cit.*

Whelan, P.F., "Froth-flotation reagents for coal : Distillation fractions of commercial oils and some simple phenolic compounds", *Journal Appl. Chem.*, 3, July 1953, pp. 289-301.

Whelan, P.F. and Brown, D.J., "Particle-bubble attachment in froth flotation", *Trans. Instn. Min. Metall.*, London, 65, 1955-6, pp. 181-192.

Williams, E.K., "The role of dispersion of insoluble reagents in the flotation of fine particles", Eng.Sc.D. thesis submitted to Columbia University, 1965.

Woodburn, E.T., Flynn, S.A., Cressey, B.A. and Cressey, G., "The effect of froth stability on the beneficiation of low-rank coal by flotation", *Powder Technology*, 40, 1984, pp. 167-177.

Woodburn, E.T., Stockton, J.B. and Robbins, D.J., "Factors influencing the structure of a 3-phase coal flotation froth", Column Flotation '88, Proceedings of an International Symposium on Column Flotation, ed. Sastry, K.V.S., Published by the Society of Mining Engineers, Inc., Littleton, Colorado, 1988, pp. 113-127.

Zisman, W.A., Contact Angle, Wettability and Adhesion, Advan. Chem. Series, No. 43, ed. Gould, R.F., 1964, p. 1.

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APPENDIX 1

SOME OIL SURFACE TENSIONS AND OIL-WATER INTERFACIAL TENSIONS

Oil	γ_{oa} mN.m ⁻¹	γ_{ow} mN.m ⁻¹	Temp. °C	Source
<i>Aliphatics</i>				
<i>Alkanes (paraffins)</i>				
n-Decane	23.9	51.2	-	2
n-Dodecane		52.1	25	1
n-Hexadecane		53.3	25	1
<i>Cyclo-alkanes (naphthenes)</i>				
Cyclohexane	24.9	51.0	-	2
<i>Aromatics</i>				
Benzene	30.2	34.1	-	2
Toluene	31.0	35.7	-	2
Ethyl benzene		37.0	25	1
n-Propyl benzene	29.0	40.0/38.4	-	2,1
n-Butyl benzene		40.1	25	1
Tetralin	36.3	38.6	-	2
<i>Impure oils</i>				
Light petroleum (120-160°C)	23.2	46.4	20	3
Light liquid paraffin	30.2	53.1	20	3
Peanut oil		23.6	30	4
Cod liver oil		9.5	30	4
Glyceryte ricinoleate		5.9	30	4

Source : 1. Rehfeld (1974)
 2. Glembotskii et al (1970)
 3. Hallworth and Carless (1972)
 4. Mullins and Becker (1956)

APPENDIX 2.1

QUALITATIVE VOLUME (MASS) BALANCES

A volume balance was used to verify that most of the dispersion droplets were accounted for in the analysis. Results are approximate because an imprecisely known volume of dispersion was added to 100 ml of Isoton in the Coulter Counter beaker.

Only data from the runs which included a 70 μm tube analysis could be used as these were the only instances in which an accurately known volume of the dispersion was analyzed by the Coulter Counter. (In other experiments analysis was based on particle number).

Example : For 200 μl of dodecane at 1200 rpm :

Cumulative volume measured by the Coulter Counter (see Data Appendix 1)

$$= 4172796 \mu\text{m}^3 \text{ in } 0.5 \text{ ml of dispersion}$$

$$= 4.17 \times 10^{-3} \mu\text{l in } 0.5 \text{ ml}$$

Actual dilutions :

200 μl of dodecane was mixed in 1 litre of water; Approximately 4 ml of this dispersion was added to 100 ml of Isoton II

$$\text{Hence vol. dodecane in 1 ml} = \frac{200 \mu\text{l} \times 4 \text{ ml} / 1000 \text{ ml}}{(100 + 4)}$$

$$= 7.69 \times 10^{-3} \mu\text{l}$$

$$\text{so volume in } 0.5 \text{ ml} = 3.85 \times 10^{-3} \mu\text{l}$$

This is in reasonable agreement with the volume measured.

Balances calculated for other reagents at other conditions also proved to be in acceptable agreement.

APPENDIX 2.2

MEANS OF THE PARTICLE SIZE INTERVALS

Calculation of higher order mean for use with normal distributions (from Herdan, 1953, p. 47) :

For the size interval x_1 to x_2 :

$$\text{Average volume} = \frac{\pi/6 \int_{x_1}^{x_2} x^3 \cdot dx}{\int_{x_1}^{x_2} dx} = \frac{\pi(x_2^4 - x_1^4)}{24(x_2 - x_1)}$$

[Assumes spherical droplets]

Now : Volume diameter = $[6/\pi \cdot (\text{Average volume})]^{1/3}$

$$\begin{aligned} \text{Therefore : Vol. diameter} &= \left[\frac{x_2^4 - x_1^4}{4(x_2 - x_1)} \right]^{1/3} \\ &= \left[\frac{(x_2^2 + x_1^2)(x_2 + x_1)}{4} \right]^{1/3} \end{aligned}$$

A comparison of the means of the size intervals is given overleaf.

Comparison of size interval means

Channel threshold diameter (μm)	Geometric mean diameter (μm)	Volume mean diameter (μm)	Arithmetic mean diameter (μm)
1.26			
1.59	1.415	1.431	1.425
2.00	1.783	1.803	1.795
2.52	2.245	2.270	2.260
3.17	2.826	2.857	2.845
4.00	3.561	3.601	3.585
5.04	4.490	4.540	4.520
6.35	5.657	5.720	5.695
8.00	7.127	7.207	7.175
10.08	8.980	9.080	9.040
12.70	11.314	11.440	11.390
16.00	14.255	14.413	14.350
20.20	17.978	18.181	18.100
25.40	22.651	22.898	22.800
32.00	28.510	28.826	28.700
40.30	35.911	36.308	36.150
50.80	45.246	45.751	45.550
64.00	57.019	57.652	57.400
80.60	71.822	72.616	72.300
101.60	90.493	91.502	91.100

APPENDIX 2.3COULTER COUNTER MODEL TA II : CALIBRATION SETTINGS70 μm tube

Step gain : 1
 Size calibration : 276.7
 Aperture matching switch : 8 - 40 K
 K value : 4.10
 Lowest channel (1) edge : 0.794 μm
 Active channels : 14 (3 upwards)
 Calibration material : 3.07 μm S.V.T. lattices

280 μm tube

Step gain : 1
 Size calibration : 262.9
 Aperture matching switch : 4 - 20 K
 K value : 16.18
 Lowest channel (1) edge : 3.17 μm
 Active channels : 13 (4 upwards)
 Calibration material : 19.71 μm Polystyn particles

$$K = \frac{d}{\left[\frac{2^w}{A} \right]^{1/3}}$$

Where :

d = diameter of calibration material
 w = no. of right hand calib. channel
 A = size calibration control setting

APPENDIX 2.4

GOODNESS-OF-FIT TESTS

Two statistical goodness-of-fit tests were used to determine whether the observed droplet distributions were in fact well modelled by a normal (or log-normal) distribution function. The null hypothesis in each case was that the dispersions were normal (or log-normal). If the calculated test statistic exceeded the critical value given for the test then the null hypothesis was rejected, i.e. the dispersions could not reasonably be assumed to be normal (or log-normal) in character. Tests were carried out at the 5 % significance level, i.e. there was a 5 % probability of rejecting the hypothesis when it was in fact true.

Kolmogorov - Smirnov test

The advantage of this test is that it can be used for very small samples where a Chi-square test does not apply (as in this case). The One Sample Kolmogorov-Smirnov test is based on the maximum absolute difference, D , between the values, e_i , of the cumulative distribution of a random sample of size n and those, p_i , of a specified theoretical distribution. (Cumulative probability tables are available for the normal distribution function). If the statistic D exceeds the critical Kolmogorov-Smirnov value then the null hypothesis for goodness of fit is rejected. Critical values may be found in Miller and Freund (1965).

Stephens' tests

These goodness-of-fit tests use statistics based on the empirical distribution function (EDF). One case which is relevant to this data was selected, i.e. the test for normality where the theoretical distribution's mean and variance are estimated from the sample data.

The test statistic used is D' , a modification of the Kolmogorov-Smirnov statistic, suggested by Stephens (1974), i.e.

$$D' = D(\sqrt{n} - 0.01 + 0.85/\sqrt{n})$$

(This modification is only applicable to the case where the mean and standard deviation are estimated from the sample data).

Critical values for the test statistic may be found in Stephens (1974).

Four worked examples for the four dispersions showing the greatest deviation (visually) follow. A worked example for a log-normal distribution is included. Note that the geometric mean and standard deviation are used.

Reagent : Dodecane 800 rpm 2 min

(200 μ l in 1 litre of water)

$$\mu = \bar{x} = 42.15 \mu\text{m}$$

$$\sigma = s = 12.59 \mu\text{m}$$

x_i	$(x_i - \mu)/\sigma$	Cum. e_i **	Cum. p_i	$ \text{Cum. } e_i - \text{Cum. } p_i $
6.35	-2.844	0.0023	0.0000	0.0023
8.00	-2.713	0.0035	0.0111	0.0076
10.08	-2.547	0.0054	0.0228	0.0174
12.70	-2.339	0.0096	0.0424	0.0328
16.00	-2.077	0.0188	0.0728	0.0540
20.20	-1.743	0.0409	0.1257	0.0848
25.40	-1.330	0.0918	0.2146	0.1228
32.00	-0.806	0.2090	0.3484	0.1394
40.30	-0.147	0.4404	0.5930	0.1526 *
50.80	0.687	0.7549	0.8648	0.1099
64.00	1.736	0.9591	0.9951	0.0360
80.60	3.054	0.9989	1.0000	0.0011

** These values are those of the experimentally observed cumulative distribution, and may be found in Data Appendix 1.

Data intervals : 12

$$* = D : 0.1526$$

$$D' : 0.5645$$

Kolmogorov - Smirnov 5 % critical D value : 0.375

Stephens 5 % critical D' value : 0.895 (from Stephens, 1974)

Therefore the null hypothesis for goodness-of-fit is accepted.

Reagent : 20 % hexyl benzene in dodecane 1200 rpm 2 min
(200 μ l in 1 litre of water)

$$\mu = \bar{x} = 23.42$$

$$\sigma = s = 11.32$$

x_i	$(x_i - \mu)/\sigma$	Cum. e_i	Cum. p_i	$ \text{Cum. } e_i - \text{Cum. } p_i $
1.26	-1.958	0.0250	0.0082	
1.59	-1.928	0.0268	0.0156	
2.00	-1.892	0.0294	0.0269	
2.52	-1.846	0.0322	0.0410	
3.17	-1.789	0.0367	0.0613	
4.00	-1.716	0.0427	0.0912	
5.04	-1.624	0.0526	0.1359	0.0833
6.35	-1.508	0.0571	0.1964	0.1393
8.00	-1.362	0.0869	0.2708	0.1839
10.08	-1.178	0.1190	0.3606	0.2416
12.70	-0.947	0.1711	0.4671	0.2696
16.00	-0.655	0.2546	0.5966	0.3420
20.20	-0.284	0.3897	0.7514	0.3617 *
25.40	0.175	0.5675	0.9069	0.3394
32.00	0.758	0.7764	0.9809	0.2045
50.80	2.419	0.9962	0.9898	

Data intervals : 16

$$* = D : 0.3617$$

$$D' : 1.520$$

Kolmogorov - Smirnov 5 % critical D value : 0.328

Stephens 5 % critical D' value : 0.895

Therefore the null hypothesis for goodness-of-fit is *rejected*.

Reagent : Hexyl benzene 1200 rpm 2 min
(200 μ l in 1 litre of water)

$$\ln \mu_g = \ln \bar{x}_g = \ln 11.25$$

$$\ln \sigma_g = \ln s_g = \ln 2.10$$

x_i	$\ln x_i$	$(\ln x_i - \ln \mu_g)$ $\ln \sigma_g$	Cum. e_i	Cum. p_i	$ \text{Cum. } e_i - \text{Cum. } p_i $
1.26	0.2311	-2.9507	0.0016	0.0000	0.0016
1.59	0.4637	-2.6372	0.0041	0.0293	0.0252
2.00	0.6931	-2.3281	0.0099	0.0592	0.0493
2.52	0.9243	-2.0164	0.0217	0.1059	0.0842
3.17	1.1537	-1.7072	0.0436	0.1607	0.1171
4.00	1.3863	-1.3937	0.0823	0.2215	0.1392
5.04	1.6174	-1.0823	0.1401	0.2842	0.1441 *
6.35	1.8485	-0.7708	0.2206	0.3554	0.1348
8.00	2.0794	-0.4596	0.3228	0.4353	0.1125
10.08	2.3105	-0.1481	0.4404	0.5311	0.0907
12.70	2.5416	0.1634	0.5636	0.6360	0.0724
16.00	2.7726	0.4747	0.6808	0.7423	0.0615
20.20	3.0057	0.7889	0.7852	0.8361	0.0509
25.40	3.2347	1.0976	0.8643	0.9148	0.0505
32.00	3.4657	1.4089	0.9207	0.9611	0.0404
40.30	3.6964	1.7199	0.9573	0.9831	0.0258
50.80	3.9279	2.0319	0.9788	0.9950	0.0162

Data intervals : 17

$$* = D : 0.1441$$

$$D' : 0.6224$$

Kolmogorov - Smirnov 5 % critical D value : 0.318

Stephens 5 % critical D' value : 0.895

Therefore the null hypothesis for goodness-of-fit is accepted.

Reagent : Dodecane 1200 rpm 2 min
(400 μ l in 3 litres of water)

$$\mu = \bar{x} = 35.45$$

$$\sigma = s = 7.53$$

x_i	$(x_i - \mu)/\sigma$	Cum. e_i	Cum. p_i	$ \text{Cum. } e_i - \text{Cum. } p_i $
10.08	-3.369	0.0004	0.0235	0.0231
12.70	-3.021	0.0013	0.0441	0.0428
16.00	-2.583	0.0049	0.0780	0.0731
20.20	-2.025	0.0212	0.1361	0.1149
25.40	-1.335	0.0901	0.2359	0.1458 *
32.00	-0.458	0.3228	0.4406	0.1178
40.30	0.844	0.7389	0.8220	0.0831
50.80	2.039	0.9793	0.9638	0.0155
etc.				

Data intervals : 8

$$* = D : 0.1458$$

$$D' : 0.4547$$

Kolmogorov - Smirnov 5 % critical D value : 0.457

Stephens 5 % critical D' value : 0.895

Therefore the null hypothesis for goodness-of-fit is accepted.

APPENDIX 3.1EVALUATION OF GLC RESULTS FOR PURE AND INDUSTRIALLY DERIVEDOILS.

The adsorption technique developed was readily extended to encompass industrially derived oils. The technique remained the same with the exception of the approach to the GLC analysis. With pure oils the chromatogram analysis was based on the areas or heights of two peaks : the collector peak and the internal standard peak. The advantage of height is clear for small peaks where peak area approaches that of any tail which is produced especially if the baseline is slightly displaced. The Vista 401 Data System used allowed results obtained on one basis to be recalculated in terms of the other. Results could therefore be cross-checked.

When analyzing the industrial oils a multitude of peaks representing the various constituents were found in the chromatogram. The peaks representing the oil were spread out over several minutes and varied widely in size. The baseline was therefore often not entirely accurate especially if collector peaks were present where the baseline drifted upwards because of the instrument temperature programming. This drift varied slightly from run to run and was not readily quantifiable. Total peak and particularly area based counts could therefore be inaccurate. However the chromatograms of all the industrially derived oils had a dominant peak. Analysis was based on the height of this peak. The oils used in the testwork were all insoluble in water so that monitoring the rate of disappearance of one constituent peak should be representative of the disappearance of the oil itself. To be on the safe side this supposition was tested.

Results for an arbitrary run (with Pegasol 3745 210-200°C cut) are shown in the table below. The actual peak heights were recorded and these values were normalized with that of the dominant (reference) peak as well as with the internal standard peak. Ratios remained reasonably constant and confirmed that the entire droplet is adsorbed and that no

constituent of the oil is preferentially adsorbed or passed into solution.

As the peak counts become very low (approach the threshold count) so a small error in the count from a slightly misplaced baseline becomes very exaggerated. However, the concentration values are correspondingly low so that a change in the peak ratio would have little effect on the measured concentration value. In determining actual concentration a peak is compared to that of the internal standard peak. The internal standard is of fixed concentration so that its peak count per unit volume is constant. The I.S. peak count is large in comparison to the small counts of collector oil peaks found towards the end of an adsorption run. A small error in the numeric count of these peaks therefore had virtually no effect on the calculated concentration.

Another advantage of using a single dominant peak (rather than integrating the individual peak counts) is accuracy, especially at low concentrations. As the concentration drops so the count produced by each constituent peak drops. At some point the counts of the minor constituent peaks fall below the threshold level which must be set to eliminate noise. These peaks are therefore not included in the integration with obvious loss of accuracy. Selecting a dominant peak which is always detectable obviates this problem.

The conclusion was that a dominant peak within the chromatogram of an industrially derived oil was an acceptable means of representing the oil in its entirety.

PEGASOL 3745 210-220 C CUT : Height basis

Sample	Peak at 6.7 min		Peak at 7.3 min		Peak at 7.7 min		Peak at 7.9 min		IS peak
	Count	Count IS count	Count	Count IS count	Count	Count IS count	Count	Count IS count	
22/4/1	158	0.0948	364	0.2185	94	0.0564	120	0.0720	1666
22/4/2	163	0.0980	376	0.2260	93	0.0559	123	0.0739	1664
22/4/3	141	0.0810	325	0.1868	80	0.0460	107	0.0615	1740
22/4/4	98	0.0581	227	0.1346	57	0.0338	75	0.0445	1686
22/4/5	76	0.0447	181	0.1065	44	0.0259	63	0.0371	1700
22/4/6	63	0.0373	135	0.0799	33	0.0195	48	0.0284	1689
22/4/7	44	0.0255	104	0.0602	26	0.0151	38	0.0220	1727
22/4/8	25	0.0148	54	0.0320		0.0000		0.0000	1686

Sample	Peak at 7.3 min		Peak at 7.3 min		Peak at 7.3 min		Peak at 7.3 min	
	Count/ 7.3 min count	Concen. of constit.* (ppm)	Count/ 7.3 min count	Concen. of constit.* (ppm)	Count/ 7.3 min count	Concen. of constit.* (ppm)	Count/ 7.3 min count	Concen. of constit.* (ppm)
22/4/1	0.4341	9.48	1.0000	21.85	0.2582	5.64	0.3297	7.20
22/4/2	0.4335	9.80	1.0000	22.60	0.2473	5.59	0.3271	7.39
22/4/3	0.4338	8.10	1.0000	18.68	0.2462	4.60	0.3292	6.15
22/4/4	0.4317	5.81	1.0000	13.46	0.2511	3.38	0.3304	4.45
22/4/5	0.4199	4.47	1.0000	10.65	0.2431	2.59	0.3481	3.71
22/4/6	0.4667	3.73	1.0000	7.99	0.2444	1.95	0.3556	2.84
22/4/7	0.4231	2.55	1.0000	6.02	0.2500	1.51	0.3654	2.20
22/4/8	0.4630	1.48	1.0000	3.20	0.0000	0.00	0.0000	0.00

* Assumes IS concentration = 100 ppm and response ratio = 1.

APPENDIX 3.2

LINEARITY OF DETECTOR RESPONSE

A linearity check of response of the detector over the range of concentrations envisaged was vital as the detector response is only checked with a single standard. Non-linear behaviour would necessitate a calibration curve. This is difficult to obtain as detector response tends to drift slightly from day to day and to change with small fluctuations in the gas flowrates. Fortunately detector response is linear with respect to changes in concentration and volume.

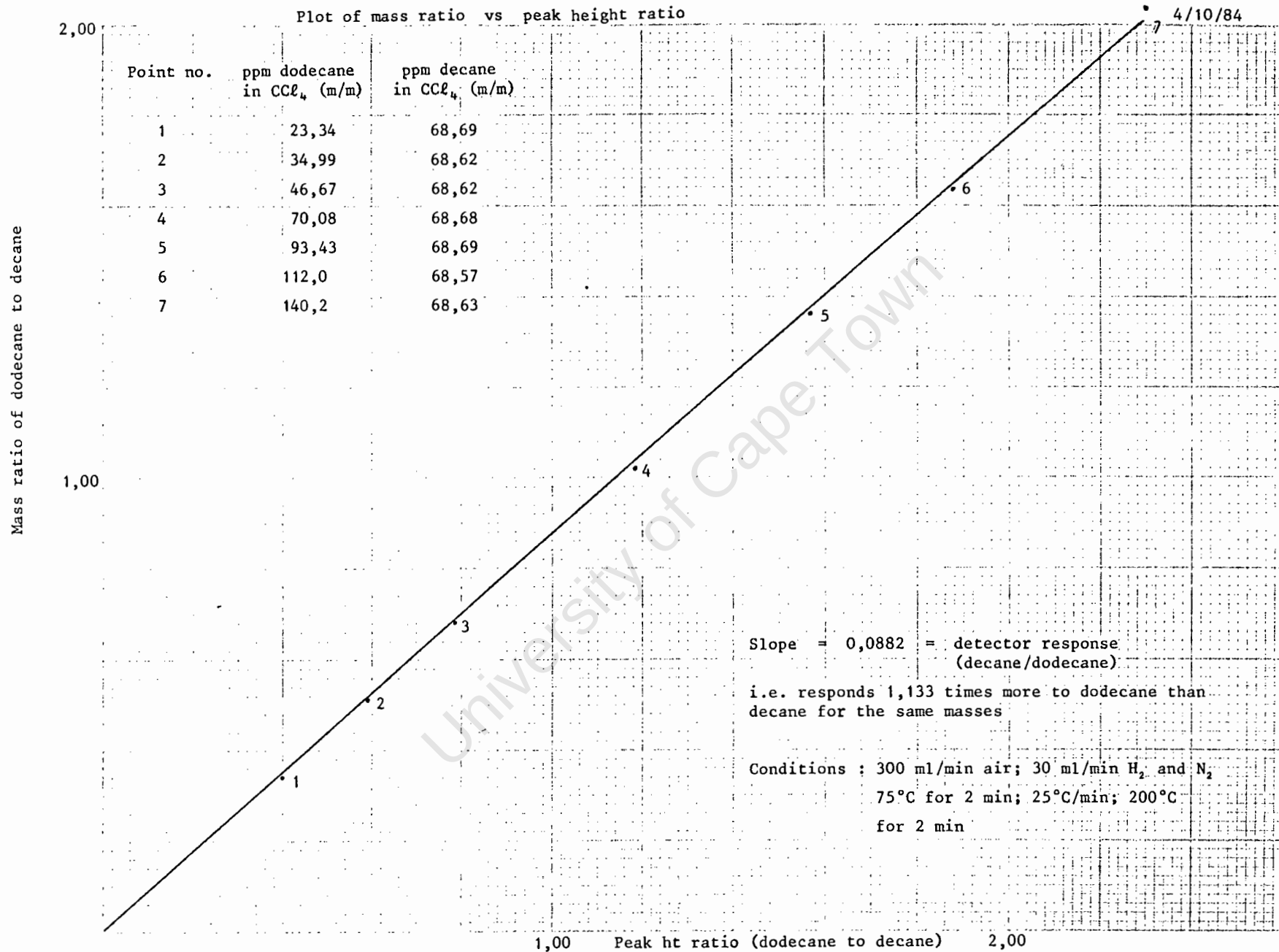
A3.1 Linearity with respect to concentration

Refer to the graph on the following page. Note that the response ratio of 1,133 is particular to this set of samples. The response ratio changes with changes in gas flowrates, etc. but is always linear over the concentration range.

A3.2 Linearity with respect to sample volume

Standard: 70,08 ppm dodecane / 68,68 ppm decane in CCl_4 .

Volume (approx.)	Peak ratio
1 μl	0,863
3 μl	0,868
5 μl	0,879



APPENDIX 3.3

OIL LOSS FROM THE ADSORPTION VESSEL

1. INTRODUCTION

Both the liquid extraction and the GC techniques give excellent reproducibility but a loss of oil mass, in terms of the mass initially added, always manifested itself (refer to Figures 3.11 and 3.12 in Chapter 3).

This appendix documents the testwork done in an attempt to discover the reason for the mass loss. The loss of dodecane from the vessel was investigated. Procedural errors which could account for this loss were investigated first.

These were:-

- 1) Extraction not 100 % efficient;
- 2) Reagent adsorbing onto the reactor walls;
- 3) Reagent not properly dispersed;
- 4) Syringe needle excluding large droplets;
- 5) Incorrect internal standard;
- 6) Inaccurate dispensing of reagent.

2. RESULTS OF INVESTIGATIONS INTO SOURCES OF PROCEDURAL ERROR

2.1 Extraction efficiency tests

Test 1

Internal standard: 0,0584 g decane added to 117,95 g CCl_4
= 495,1 ppm (mass ratio not mass fraction).

0,0577 g dodecane was added to 90,45 g of tap water, and emulsified by shaking vigorously in a closed vessel. Thereafter 117,01 g of the internal standard was added to the dodecane-water emulsion, shaken, and the liquid layers allowed to separate and clarify.

For complete extraction:

0,0577 g dodecane would be found in

$$117.01 - 0.0584 \times \frac{117.01}{117.95} \text{ g CCl}_4$$

i.e. 0,0577 g in 116,95 g CCl₄;

or 493,4 ppm dodecane in CCl₄ layer.

GLC analysis results:

peak ht ratio

(dod/dec)

1,102

1,103

1,106

1,108

mean = 1,1045

concentration dodecane = conc. decane x response

ratio x peak height ratio

= 495,1 x 0,90 x 1,1045

= 492 ppm

(cf. 493,4 actual).

Test 2

Tests were repeated with *distilled water* in closed vessels. Dodecane and water were emulsified by shaking prior to addition of the CCl₄ internal standard. A control was done simultaneously: here dodecane and water were not emulsified prior to CCl₄ addition.

Experiment	Actual conc.	Measured conc.	Error
1	191,5 ppm	205,2 ppm	+ 7,2 %
2	401,9	424,6	+ 5,6 %
Control	776,6	782,5	+ 0,8 %

Repeated analyses:

1	206,0 ppm	+ 7,6 %
2	422,8	+ 5,2 %
Control	777,9	+ 0,2 %

Error defined as :
$$\frac{\text{Measured conc.} - \text{actual conc.}}{\text{actual conc.}} \times 100$$

The repeat analyses verified the repeatability of the GC technique. The analyses of the control runs verified that the instrument was also accurate. From these experiments it appears that any error occurring is always on the positive side, i.e. the measured concentration is larger than the actual concentration. However when tests were done with the reactor (open vessel) mass losses were appreciable, i.e. the measured concentration of dodecane was much less than the added concentration. This is illustrated in the following test.

2.2 Reagent adsorbing on reactor walls

Dodecane was added by syringe, the mass of which was noted before and after injection to eliminate any dispensing errors. Two samples were withdrawn after 5 minutes of agitation and the remaining reactor contents were poured out into another vessel and extracted with 159,0 g of a new CCl_4 I.S. (249,9 ppm). Reactor walls and the impeller were then washed with 44,9 g of ethanol I.S. (235,3 ppm) to remove adsorbed dodecane.

2.2.1 Expected oil mass in vessel

0,0466 g dodecane was added to 496.8 g water. Mass dodecane in extraction vessel (this excludes the volume of samples and residue) may be calculated as follows:-

$$\frac{\text{Original mass dodecane}}{\text{Original mass water}} \times \text{mass water in extraction vessel}$$

(Assumes complete mixing).

$$\text{i.e. } \frac{0,0466}{496,8} \times 485,75 = 0,04556 \text{ g.}$$

$$\text{theoretical conc. in CCl}_4 \text{ layer : } \frac{0,04556}{159} = 286,5 \text{ ppm}$$

Similarly the theoretical residual dodecane in the 1,1 g of water still adhering to the vessel walls and impeller is :

$$\frac{0,0466}{496,8} \times 1,1 = 1,032 \times 10^{-4} \text{ g}$$

This would appear in the 44,9 g of EtOH I.S., assuming all dodecane is rinsed out. Concentration would then be 2,30 ppm.

However the conc. measured in the ethanol extract was 27,5 ppm which corresponds to $1,23 \times 10^{-3}$ g of dodecane or 2,6 % of the original dodecane mass. This indicates a small degree of adsorption onto the vessel walls, but not enough to account for the significant mass loss.

2.2.2 Analysis of samples withdrawn at 5 minutes

Theoretical conc. in the CCl ₄ extract	Measured conc.	Error
Sample 1 : 110,2 ppm	79,4 ppm	- 27,9 %
Sample 2 : 109,3	80,4	- 26,4 %

Analysis of extract from remaining reactor contents

Theoretical conc. in the CCl ₄ extract	Measured conc.	Error
286,5 ppm	188,4 ppm	- 34,2 %
"	191,4	- 33,2 %
"	197,0	- 31,2 %

The "theoretical concentration" is the concentration of dodecane expected in the CCl₄ layer, assuming complete extraction of the dodecane from the water sample withdrawn from the reactor. The volumes of water and CCl₄ used vary from sample to sample and so the theoretical concentration itself changes from one sample to another.

The theoretical concentration is not that of dodecane in the reactor water. However the error obviously applies equally to this. "Measured concentration" is the concentration of dodecane in the CCl_4 layer measured by the GC technique.

2.2.3 Adsorption onto reactor walls

Adsorption onto the stainless steel walls appeared minimal but this was checked at several impeller speeds. Alcohol was used to remove the dodecane-water emulsion remaining adhered to the vessel.

Abs. EtOH detector calibration std.: 307,03 ppm dodecane.

263,17 ppm decane.

Abs. EtOH I.S.: 221,10 ppm decane in EtOH.

Results:

1240 rpm	2,51 % of original	43,5 mg dodecane adsorbed
1510 rpm	0,9 %	"
1810 rpm	0,6 %	"

The conclusion is that adsorption of dodecane by the vessel walls and impeller was very small and therefore only partly responsible for the mass loss exhibited. The loss seemed to be directly related to the fact that the vessel was open, but before considering evaporative and other physical effects, the remaining sources of procedural error were investigated.

2.3 Inadequate dispersion of dodecane

Non-uniformity within the vessel seemed unlikely as samples withdrawn from various locations all exhibited similar dodecane concentrations. However various agitation methods were tried. These included strong axial mixing which was used to eliminate any tendency towards stratification as a result of the water-dodecane density difference. Results are listed below.

Theoretical conc.	Measured conc.	Error	Conditions
105,5 ppm	84,7 ppm	- 19,7 %	Turbine - 1810 rpm
144,2	118,2	- 18,0	" "
127,7	84,5	- 33,8	Propeller (co-axial) 2250 rpm
123,4	78,7	- 36,2	"
130,4	95,6	- 26,7	Prop.(off centre, angled) 2250
145,9	106,8	- 26,8	"

The turbine impeller gave the least mass loss. The co-axially mounted propeller resulted in a large mass loss and proved that poor axial mixing was not responsible for the error in measured dodecane concentrations. The less vigorous the agitation the greater the mass of oil lost.

2.4 Sampling syringe excluding some dodecane droplets

This possible source of error is unfounded as the mass loss was still manifested when the entire reactor contents were extracted. Furthermore droplet size analysis work on a Coulter Counter showed that no dodecane droplets larger than about 50 μm (diameter) were present. This size is considerably less than the needle bore. (400 μm).

2.5 Incorrect internal standard

This possibility is also unfounded as several new standards were prepared and the mass loss continued.

2.6 Inaccurate dispensing of dodecane

It is possible that less dodecane was added than was believed to be added. Dodecane was generally added with a "Gilson Pipettman". The accuracy and consistency of this device were tested over 10 successive pipettings - all using a new tip.

Consistency:

Mass pipetted

0,0406 g	SD : $4,75 \times 10^{-4}$ g
0,0418	mean : 0,04109 g
0,0409	
0,0411	CoV : 1,16 %
0,0405	
0,0405	
0,0412	
0,0415	
0,0411	
0,0417	

Accuracy:Volume set to 58 μ l

$$\text{Mean vol. dispensed: } \frac{0,0419}{0,75} = 54,8 \mu\text{l}$$

Slightly less dodecane was added but the difference is too little to affect the measured concentrations appreciably. Furthermore the mass loss persisted when an accurately measured mass of dodecane was used.

3. OPEN VESSEL CONSIDERATIONS

An interesting development is that the mass loss is apparently time dependent - a fact which would confirm that the previous possibilities for error do not account for the mass balance discrepancy; and point to some physical process as the cause. Furthermore, losses increased with a decrease in impeller speed (agitation intensity).

3.1 Time dependence of mass loss

Theoretical conc.	Measured conc.	Error	Time
111,49 ppm	97,31 ppm	- 12,72 %	1.5 min
104,95	78,58	- 25,13 %	3
108,86	80,82	- 25,76	5
106,60	69,31	- 34,98	8
125,60	72,01	- 42,66	12

(continued)

90,24	88,54	- 1,9 %	0.5 min
94,42	88,43	- 6,3	1
97,09	88,76	- 8,6	1.5
94,45	81,66	- 13,5	2
94,21	78,26	- 16,9	3
101,08	78,68	- 22,2	5

3.2 Loss with respect to impeller speed

Test 1:

Dodecane pipetted from above water surface. 58 μ l dodecane in 500 ml of tap water. 5 minutes of dispersion (also for Test 2).

Theoretical conc.	Measured conc.	Error	Conditions
163,3 ppm	96,6 ppm	- 40,8 %	1240 rpm
175,1	101,2	- 42,2	"
162,0	114,0	- 29,6	1510 rpm
164,4	122,1	- 25,7	"
147,0	107,2	- 27,1	1810 rpm
137,0	98,4	- 28,2	"
144,4	105,0	- 27,3	"
(New I.S.)			

Test 2:

Dodecane injected below water surface to stop surface tension affecting mixing. 58 μ l dodecane in 500 ml of tap water.

Theoretical conc.	Measured conc.	Error	Conditions
162,8 ppm	101,7 ppm	- 37,5 %	1240 rpm
157,8	102,6	- 35,0	"
129,9	90,9	- 30,0	1510 rpm
148,1	106,1	- 28,4	"
184,4	143,0	- 22,5	1810 rpm
129,2	89,3	- 23,1	"

These tests clearly show that the mass loss increased at low impeller speeds. This effect is discussed in the following section.

3.3 Evaporation of Dodecane

It seemed highly unlikely that evaporation was responsible for the mass loss as dodecane and other hydrocarbon oils used in the testwork have very low vapour pressures. However in view of the increased mass loss at reduced impeller speeds it appeared that evaporation did in fact contribute to the loss. Oil droplets are very small resulting in a very large oil surface area.

Obviously oil droplets churning around in the water would have little opportunity to evaporate. However those droplets adsorbing on the reactor walls above the water interface because of splashing would be exposed to air and have time to evaporate. The quantity evaporating would be tiny but in view of the small masses added such a loss could be significant.

Apart from splashing, it also appeared that some other physical escape route, which in turn promoted evaporation, was in operation. The possibility existed that the very hydrophobic collectors spread or "creep" up the stainless steel of the reactor walls in much the same manner as they spread over a quiescent water surface. This hypothesis was confirmed by arranging a solvent trap, consisting of a groove machined into the top of the reactor and filled with solvent, and noting an increasing concentration of collector in the solvent as time passed.

To eliminate the possibility of oil creep or of droplets being splashed on the vessel sides, experiments were done where CCl_4 was added to the reactor water *before* dodecane addition so that the dodecane would be captured immediately and entirely. Against this control, other tests were done where the dodecane was emulsified normally and the CCl_4 then added after a given time for emulsification had elapsed.

Testwork was done with a slower impeller speed to reduce splashing and spitting (as a result of an increased liquid level caused by the CCl_4 addition) and the dodecane agitated for a longer period to encourage the loss of dodecane.

Test 1:Control :

- 1) Water and CCl_4 agitated for 1 minute.
 - 2) 7 minutes agitation after dodecane addition.
 - 3) 1240 rpm.
- Mass CCl_4 added : 132,6 g
 Mass dodecane added : 0,0459 g
 Loss of mass after run : 13,9 g. (evaporation of CCl_4)

Theoretical conc. (assuming 13,9 g of CCl_4 evaporated)

$$\frac{0,0459}{(132,6 - 13,9)} = 386,7 \text{ ppm}$$

Measured conc. a) 347,7 ppm or - 10,1 % error
 b) 348,4 or - 9,9 % error.

Experiment :

- 1) 7 minutes agitation of water-dodecane.
- 2) 1 minute with CCl_4 .
- 3) 1240 rpm.

Mass dodecane added = 0,0456 g
 Theoretical conc. = 348,3 ppm
 Measured conc. a) 277,9 ppm or - 20,2 % error
 b) 277,7 ppm or - 20,3 % error.

The conclusion is that even in the extreme case where all the mass lost after a control run is attributed to CCl_4 evaporation alone, there is still a significant difference between the control and the experimental cases indicating a definite loss of dodecane from the system. If on the other hand the mass loss is at least in part attributable to "spitting" of the CCl_4 -water-dodecane system, then errors in the control tests were small while the experimental tests continue to manifest a large dodecane mass loss.

4. CONCLUSION

It was concluded that procedural errors were too small to account for the fairly consistent and relatively large loss of oil from the adsorption vessel. Mass loss was large in terms of the mass added but in actual terms was small, being of the order of 0.01 g in the minute prior to addition of solids.

The fact that mass loss was not apparent in a closed vessel pointed strongly to an actual physical loss from the reactor. The loss from an open vessel was time and agitation dependent supporting this conclusion.

Loss was apparently due to evaporation, partly from the water surface and from dispersion splashed on the vessel walls; and partly from the oil film which creeps up the vessel walls. Loss from the water by oil adsorption on the submerged vessel walls contributed only a very small part to the overall mass loss from the water.

APPENDIX 3.4INDEX OF EXPERIMENTAL CONDITIONS DURING THE ADSORPTION RUNS

The aim of this index is to direct the reader to the appropriate spreadsheet in Data Appendix 2 for more detailed results. In this index the asterisked runs were those conducted with the first of two samples of washed coal obtained from Greenside Colliery. In the thesis, these runs are carefully distinguished from those done using the later sample.

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INDEX FOR ADSORPTION RUNS

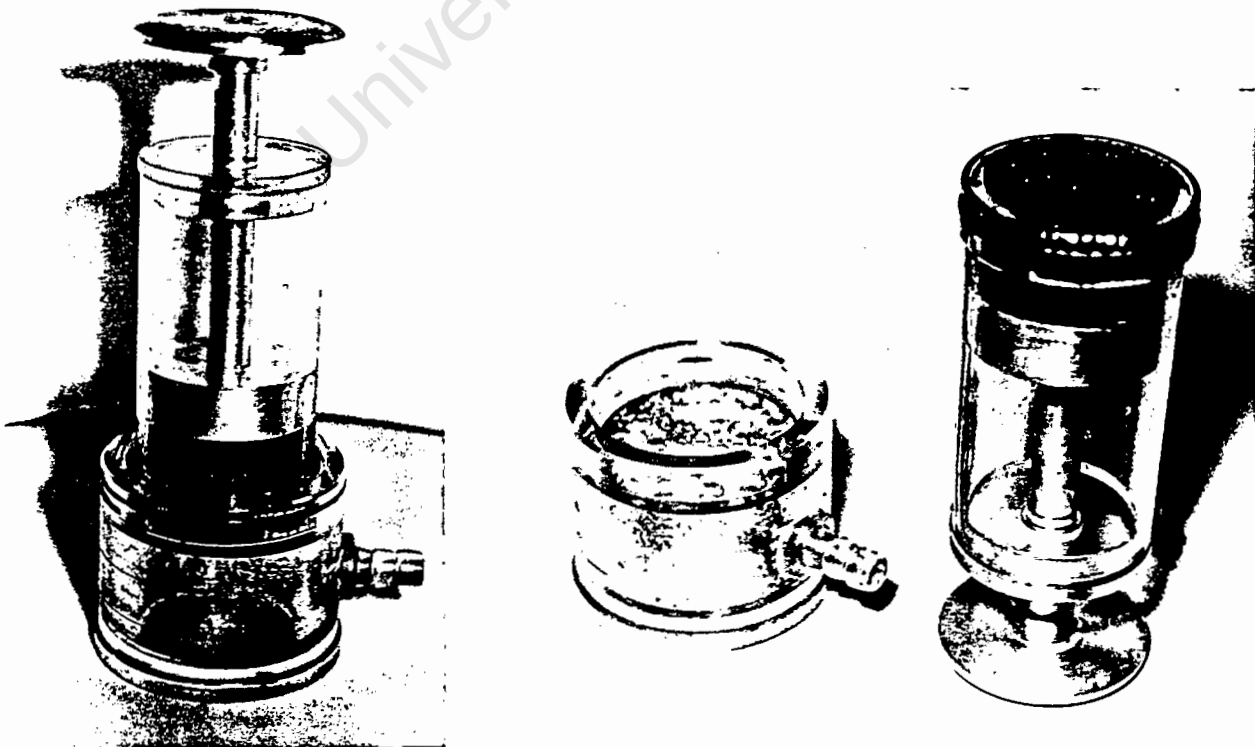
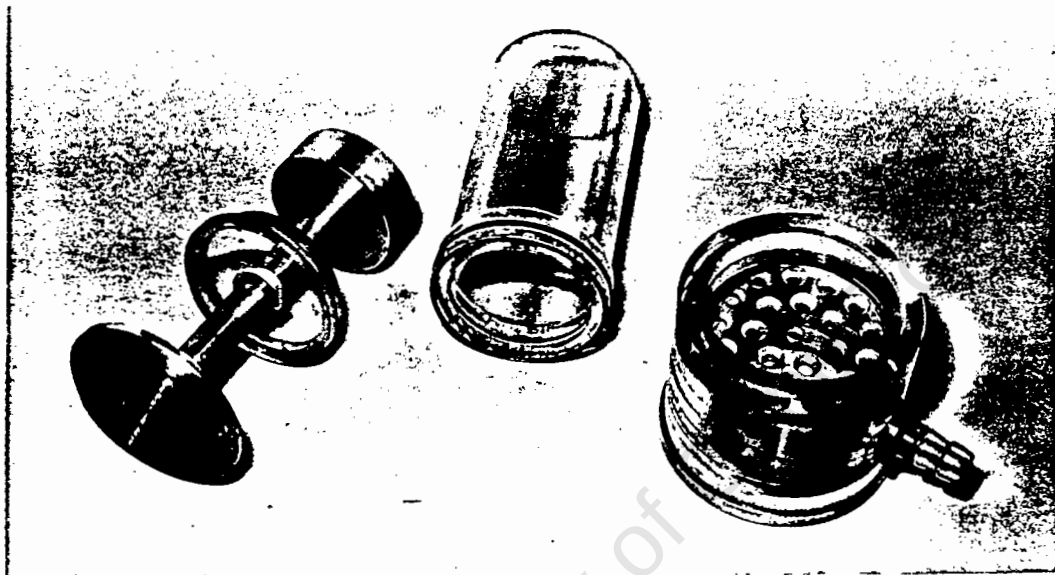
Run no.	Collector oil	MIBC	Coal used	Diam. (um)	Imp. spd. (rpm)	Comments
1	Dodecane		G/s No.2 Washed *	500-600	1650	
2	Dodecane		G/s No.2 Washed *	500-600	1650	repeat run
3	Dodecane		G/s No.2 Washed *	250-300	1650	
4	Dodecane		G/s No.2 Washed *	250-300	1650	rep.
5	Dodecane	yes	G/s No.2 Washed *	500-600	1650	
6	Dodecane	yes	G/s No.2 Washed *	500-600	1650	rep.
7	Dodecane		G/s No.2 Washed *	500-600	1650	175.5ul
8	Dodecane		G/s No.2 Washed *	250-300	1650	175.5ul rep.
9	Dodecane		Quartz	500-600	1650	
10	Dodecane		Quartz	500-600	1650	
11	Dodecane	yes	Quartz	500-600	1650	
12	Dodecane	yes	Quartz	500-600	1650	
14	Dodecane		Vryheid CC +1.3 -1.4 SG u/w	425-600	1650	
15	Dodecane		Vryheid CC +1.7 SG u/w	425-600	1650	
16	Dodecane		Vryheid CC -1.3 SG u/w	425-600	1650	
17	Dodecane		Vryheid CC +1.4 -1.5 SG u/w	425-600	1650	
18	Dodecane		Vryheid CC -1.3 SG u/w	425-600	1650	rep.
19	Dodecane		Vryheid CC +1.3 -1.4 SG u/w	425-600	1650	
20	Dodecane		Vryheid CC +1.7 SG u/w	425-600	1650	
21	Dodecane		Vryheid CC +1.5 -1.7 SG u/w	425-600	1650	
22	Dodecane		Vryheid CC +1.4 -1.5 SG u/w	425-600	1650	
23	Dodecane		Vryheid CC -1.3 SG u/w	425-600	1650	
24	Dodecane		Vryheid CC +1.3 -1.4 SG u/w	425-600	1650	10 min run
25	Shellsol K		Vryheid CC +1.3 -1.4 SG u/w	425-600	1650	
26	Shellsol K		Vryheid CC +1.3 -1.4 SG u/w	425-600	1650	rep.
27	Decane		G/s No.2 Washed *	500-600	1650	2 min dispersion
28	Hexadecane		G/s No.2 Washed *	500-600	1650	2 min dispersion
29	Tetradecane		G/s No.2 Washed *	500-600	1650	2 min dispersion
30	Dodecane		G/s No.2 Washed *	500-600	1650	
31	Dodecane		G/s No.2 Washed *	500-600	1650	
32	Dodecane		G/s No.2 Washed *	500-600	1650	
33	Hexadecane		G/s No.2 Washed *	500-600	1650	
34	Dodecane		G/s No.2 Washed	500-600	1650	10 min run
35	Dodecane		G/s No.2 Washed	500-600	1650	10 min run
37	Dodecane		Tchikondeni Washed	500-600	1650	
38	Dodecane		G/s No.2 Washed	500-600	1650	
39	Dodecane		Grootegeeluk Washed	500-600	1000	
40	Dodecane		G/s No.2 Washed	500-600	1650	1000rpm-coal add
41	Dodecane		G/s No.2 Washed	500-600	1650	1 C water
42	Pegasol 3745 240-250		G/s No.2 Washed	500-600	1650	Strong agglom.
43	Pegasol 3745 180-190		G/s No.2 Washed	500-600	1650	No agglomeration
44	Pegasol 3745 210-220		G/s No.2 Washed	500-600	1650	Agglomeration
45	Hexyl benzene		G/s No.2 Washed	500-600	1650	
46	Shellsol A		G/s No.2 Washed	500-600	1650	
47	Dodecane		G/s No.2 Washed	500-600	1650	
48	Pegasol 3745 230-240		G/s No.2 Washed	500-600	1650	
49	Dodecane		G/s No.2 Washed	500-600	1650	
50	Hexadecane		G/s No.2 Washed	500-600	1650	
51	Pegasol 3745 240-250		G/s No.2 Washed	500-600	1650	rep.

52	Shellsol K		G/s No.2 Washed		500-600	1650	
53	Pegasol 3745 240-250		G/s No.2 Washed		500-600	1000	1000rpm-coal add
54	Dodecane		G/s No.2 Washed		500-600	1650	300ul strong agg
55	Dodecane		G/s No.2 Washed		500-600	1650	
56	Dodecane	yes	G/s No.2 Washed		500-600	1650	
57	Dodecane	yes	G/s No.2 Washed		500-600	1650	Oil before MIBC
58	Dodecane	yes	G/s No.2 Washed		500-600	1650	MIBC>coal>oil
59	Hexyl benzene	yes	G/s No.2 Washed		500-600	1650	Oil before MIBC
60	Hexyl benzene	yes	G/s No.2 Washed		500-600	1650	
61	Hexyl benzene	yes	G/s No.2 Washed		500-600	1650	MIBC-oil mixed
62	Hexyl benzene	yes	G/s No.2 Washed		500-600	1650	MIBC>coal>oil
63	Pegasol 3745 210-220		G/s No.2 Washed		500-600	1650	
64	Pegasol 3745 210-220	yes	G/s No.2 Washed		500-600	1650	MIBC-oil mixed
65	Pegasol 3745 210-220	yes	G/s No.2 Washed		500-600	1650	MIBC>coal>oil
66	Hexyl benzene		G/s No.2 Unwashed		500-600	1650	
67	Hexyl benzene		G/s No.2 Unwashed		500-600	1650	Oil to pulp
68	Dodecane		G/s No.2 Unwashed		500-600	1650	
69	Dodecane		G/s No.2 Unwashed		500-600	1650	
70	Hexyl benzene		G/s No.2 Unwashed		500-600	1200	
71	Dodecane		G/s No.2 Unwashed		500-600	1200	Oil to pulp
72	Dodecane	yes	G/s No.2 Unwashed		500-600	1650	
73	Hexyl benzene	yes	G/s No.2 Unwashed		500-600	1650	
74	Dodecane	yes	G/s No.2 Unwashed		500-600	1650	
75	Dodecane		G/s No.2 Unwashed		500-600	1650	
76	Dodecane		G/s No.2 -1.4	SG u/w	500-600	1200	
77	Dodecane		G/s No.2 -1.4	SG u/w	500-600	1200	Dodecane aging
78	Hexyl benzene		G/s No.2 -1.4	SG u/w	500-600	1200	
79	Hexyl benzene		G/s No.2 +1.4 -1.6	SG u/w	500-600	1200	
80	Hexyl benzene		G/s No.2 +1.4 -1.6	SG u/w	500-600	1650	
81	Hexyl benzene		G/s No.2 +1.6 -1.8	SG u/w	500-600	1200	
82	Hexyl benzene		G/s No.2 Unwashed		500-600	1200	No ZnCl contam.
83	Hexyl benzene		G/s No.2 +1.8 -2.4	SG u/w	500-600	1200	
84	Shellsol AB		G/s No.2 Unwashed		500-600	1200	
85	Pegasol 3745 240-250		G/s No.2 Unwashed		500-600	1200	
86	Shellsol K		G/s No.2 Unwashed		500-600	1200	
87	Hexyl benzene		G/s No.2 +2.4	SG u/w	500-600	1200	
88	Pegasol 3745 180-190		G/s No.2 Unwashed		500-600	1200	
89	Pegasol 3745 210-220		G/s No.2 Unwashed		500-600	1200	
90	20% hex benz in dod.		G/s No.2 Unwashed		500-600	1200	
91	40% hex benz in dod.		G/s No.2 Unwashed		500-600	1200	
92	Dodecane		G/s No.2 t/underflow		425-600	1200	
93	Hexyl benzene		G/s No.2 t/underflow		425-600	1200	

* Original batch

APPENDIX 3.5

Photographs showing the working of the device used to consolidate and drain water from the coal sample, and to add the coal as a slug to the adsorption vessel.



APPENDIX 4

RESULTS OF STEPHENS' GOODNESS-OF-FIT TESTS FOR SOME OF THE BUBBLE DISTRIBUTIONS.

Description of the experiment and test follows the table. For more details of the procedure refer back to Appendix 2.4.

x_i (μm)	$(x_i - \mu)/\sigma$	Cum. e_i	Cum. p_i	$ \text{Cum. } e_i - \text{Cum. } p_i $
-838			0.0950	0.095
838	-1.190	0.1170	0.1203	0.003
894	-1.078	0.1405	0.1417	0.001
950	-0.966	0.1670	0.1661	0.001
1006	-0.854	0.1966	0.2003	0.004
1062	-0.742	0.2290	0.2445	0.015
1118	-0.630	0.2643	0.2842	0.020
1174	-0.519	0.3019	0.3245	0.023
1230	-0.407	0.3421	0.3626	0.021
1286	-0.295	0.3840	0.4093	0.025
1342	-0.183	0.4274	0.4506	0.023
1398	-0.071	0.4717	0.4980	0.026
1454	0.041	0.5164	0.5329	0.017
1510	0.152	0.5604	0.5716	0.011
1566	0.264	0.6041	0.6184	0.014
1622	0.376	0.6475	0.6654	0.018
1678	0.488	0.6873	0.7045	0.017
1735	0.600	0.7257	0.7451	0.019
1791	0.712	0.7617	0.7826	0.021
1847	0.824	0.7950	0.8191	0.024
1903	0.935	0.8251	0.8556	0.030
1959	1.047	0.8524	0.8834	0.031 *
2015	1.159	0.8768	0.9081	0.031
2071	1.271	0.8982	0.9260	0.028
2127	1.383	0.9167	0.9417	0.025
2183	1.495	0.9326	0.9538	0.021
2239	1.606	0.9458	0.9647	0.019
2295	1.718	0.9571	0.9743	0.017
2351	1.830	0.9664	0.9814	0.015
2407	1.942	0.9739	0.9874	0.014
2463	2.054	0.9800	0.9926	0.013
2519	2.166	0.9848	0.9948	0.010
2575	2.277	0.9886	0.9970	0.008
2631	2.389	0.9915	0.9977	0.006
2687	2.501	0.9938	0.9980	0.004
2743	2.613	0.9955	0.9990	0.003
2799	2.725	0.9968	0.9993	0.002

Reagent : Pegasol 3745 210-220°C cut.

400 μl mixed in 1 litre of water at 1200 rpm for 2 min. Cell filled during a further minute of mixing.

$$\mu = \bar{x} = 1434 \mu\text{m}$$

$$\sigma = s = 501 \mu\text{m}$$

Data intervals : 37

$$* = D' : 0.031$$

Stephens' 5 % critical D'_{37} value : 0.1439

Therefore the null hypothesis for goodness-of-fit is accepted.

Reagent : Hexyl benzene.

200 μl mixed in 1 litre of water for 2 minutes at 1200 rpm. Cell filled during another minute of mixing.

$$\ln \mu_g = \ln \bar{x}_g = \ln (890 \mu\text{m})$$

$$\ln \sigma_g = \ln s_g = \ln (1.190 \mu\text{m})$$

Data intervals : 41

$$* = D' : 0.138$$

Stephens' 5 % critical D'_{41} value : 0.2076

Therefore the null hypothesis for goodness-of-fit is accepted.

(The data for this test are tabulated overleaf)

x_i (μm)	$\ln x_i$	$\frac{(\ln x_i - \ln \mu_g)}{\ln \sigma_g}$	Cum. e_i	Cum. p_i	$ \text{Cum. } e_i - \text{Cum. } p_i $
520	6.255	-3.088	0.0010	0.003	0.002
552	6.314	-2.745	0.0030	0.005	0.002
584	6.370	-2.422	0.0077	0.009	0.001
616	6.423	-2.116	0.0172	0.015	0.003
648	6.474	-1.825	0.0340	0.020	0.014
680	6.522	-1.549	0.0607	0.038	0.023
712	6.568	-1.285	0.0994	0.060	0.040
744	6.611	-1.032	0.1510	0.105	0.046
775	6.653	-0.790	0.2148	0.155	0.060
807	6.694	-0.558	0.2885	0.230	0.058
839	6.733	-0.335	0.3688	0.299	0.070
871	6.770	-0.120	0.4129	0.376	0.037
903	6.806	0.087	0.5347	0.456	0.079
935	6.840	0.287	0.6130	0.518	0.095
967	6.874	0.480	0.6844	0.583	0.101
999	6.906	0.667	0.7477	0.637	0.111
1031	6.938	0.848	0.8017	0.680	0.122
1062	6.968	1.023	0.8468	0.714	0.133
1094	6.998	1.193	0.8836	0.747	0.137
1126	7.027	1.359	0.9129	0.775	0.138 *
1158	7.055	1.520	0.9357	0.799	0.136
1190	7.082	1.676	0.9531	0.816	0.137
1222	7.108	1.828	0.9662	0.839	0.128
1254	7.134	1.977	0.9760	0.853	0.123
1286	7.159	2.121	0.9830	0.864	0.119
1318	7.184	2.263	0.9882	0.883	0.106
1349	7.207	2.400	0.9918	0.895	0.097
1381	7.231	2.535	0.9944	0.901	0.093
1413	7.254	2.666	0.9962	0.911	0.085
1445	7.276	2.795	0.9974	0.922	0.075
1477	7.298	2.920	0.9983	0.931	0.067
1509	7.319	3.043	0.9988	0.940	0.059
1541	7.340	3.164	0.9992	0.955	0.044
1573	7.360	3.282	0.9995	0.964	0.035
1605	7.381	3.397	0.9997	0.970	0.030
1636	7.400	3.511	0.9998	0.974	0.025
1668	7.420	3.622	0.9999	0.980	0.020
1700	7.438	3.731	0.9999	0.984	0.015
1732	7.457	3.838	0.9999	0.989	0.011
1764	7.475	3.943	1.0000	0.991	0.009
1796	7.493	4.046	1.0000	0.993	0.007

APPENDIX 5.1FLOTATION CONCENTRATE REMOVAL PROCEDURE

- 7 seconds Air turned on.

0 Start for flotation kinetics.

Scraping time

5 seconds	]	First concentrate. (No wash water used)
10		
15		
20	]	Second concentrate. (Wash water used on scraper and cell lip).
25		
30		
40	]	Third concentrate. (Wash water used).
50		
1 minute		
10	]	Fourth concentrate. (wash water used).
20		
30		
40		
50		
2 minutes		
15	]	Fifth concentrate. (Wash water used).
30		
45		
3 minutes		
15		
30	]	Sixth concentrate. (Wash water used).
45		
4 minutes		
15		
30		
45		
5 minutes		
15	]	Seventh concentrate. (Wash water used).
30		
45		
6 minutes		
Manual removal of remaining floated coal	]	

APPENDIX 5.2

EXAMPLE OF CALCULATION USED FOR DETERMINING SELECTIVITY PLOTS

Let overall concentrate ash (%) = A
 overall concentrate mass (g) = M

In the concentrate :

mass of ash-free coal = m_1
 mass of intrinsic gangue = m_2
 mass of added gangue = m_3

(The percentage of intrinsic gangue is assumed to equal the ash percentage in the concentrates obtained during tests done in the absence of added gangue, i.e. 14 %)

$$M = m_1 + m_2 + m_3 \quad [1]$$

$$\frac{m_1}{M} = \frac{100 - A}{100} \quad [2]$$

$$\frac{m_2}{m_1 + m_2} = 0.14 \quad [3]$$

From Equation 3,

$$m_2 = \frac{0.14 m_1}{0.86} \quad [4]$$

substitute Equation 4 in Equation 1,

$$\begin{aligned} M &= m_1 + 0.14 m_1 / 0.86 + m_3 \\ m_3 &= M - m_1 / 0.86 \end{aligned} \quad [5]$$

Substitute Equation 2 in Equation 5,

$$\begin{aligned} m_3 &= M - \frac{M (100-A)}{100 \times 0.86} \\ &= M(A - 14)/86 \end{aligned}$$

The masses of ash-free coal, intrinsic gangue (assumed to be 14 %) and added gangue are thus known for both the feed and derived concentrate, allowing the construction of the histograms to portray selectivity.

APPENDIX 5.3

FLOTATION TESTS - SELECTIVITY

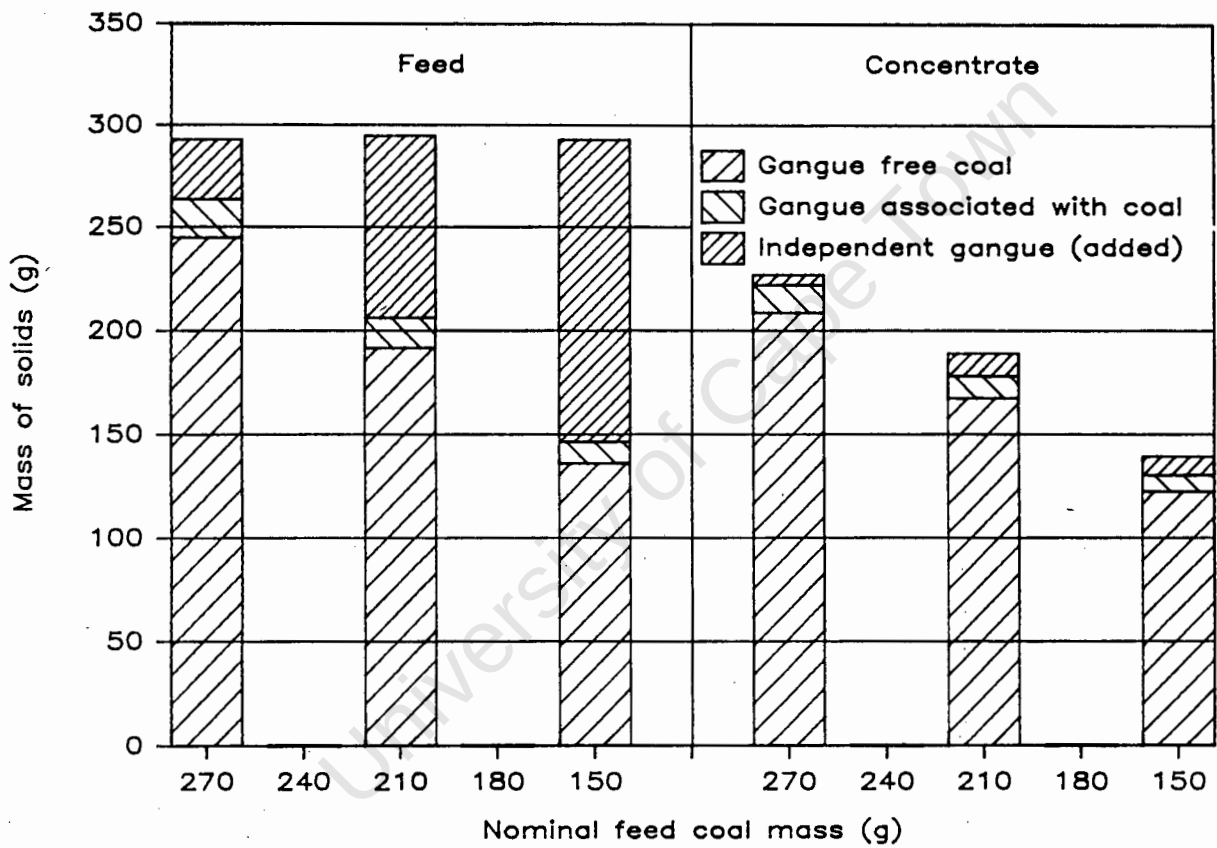


Figure A5.1 : Masses of gangue free coal, gangue associated with coal and independently added quartz in a flotation concentrate compared to their respective masses in the flotation feed. Greenside No.2 seam unwashed coal (-150 μm) and milled quartz added in various proportions to total 300 g (nominally).

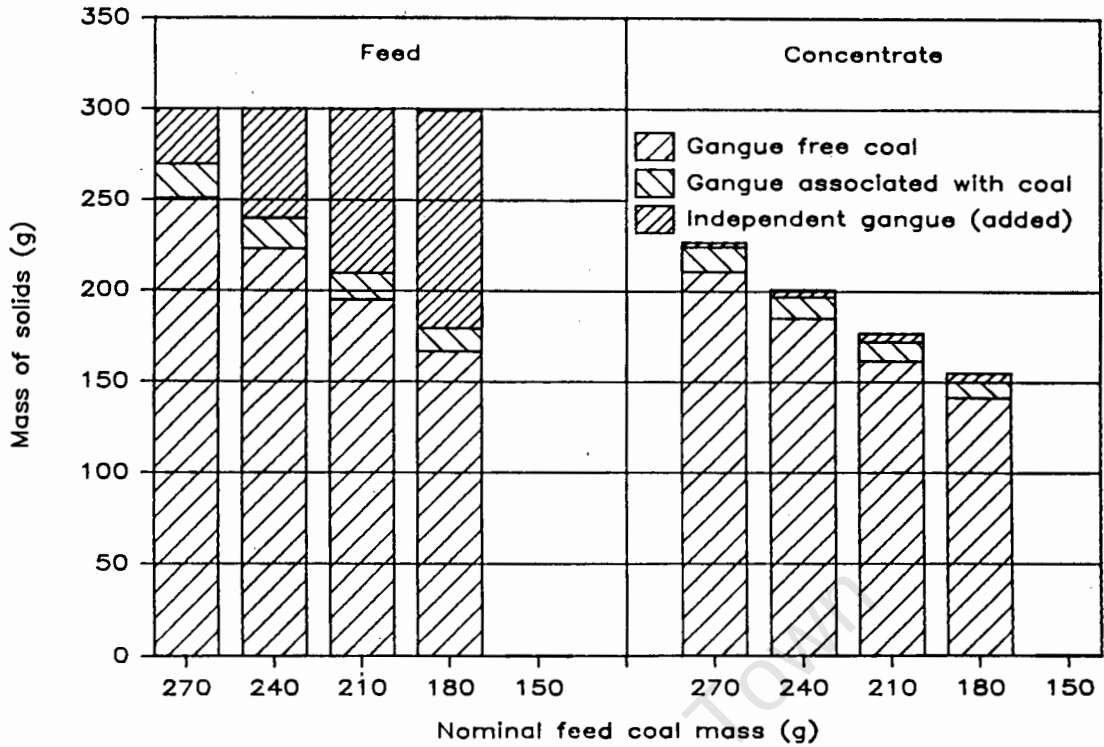


Figure A5.2 : Masses of gangue free coal, gangue associated with coal and independently added quartz in a flotation concentrate compared to their respective masses in the flotation feed. Greenside No.2 seam washed coal ($-150 \mu\text{m}$) and quartz added in various proportions to total 300 g (nominally).

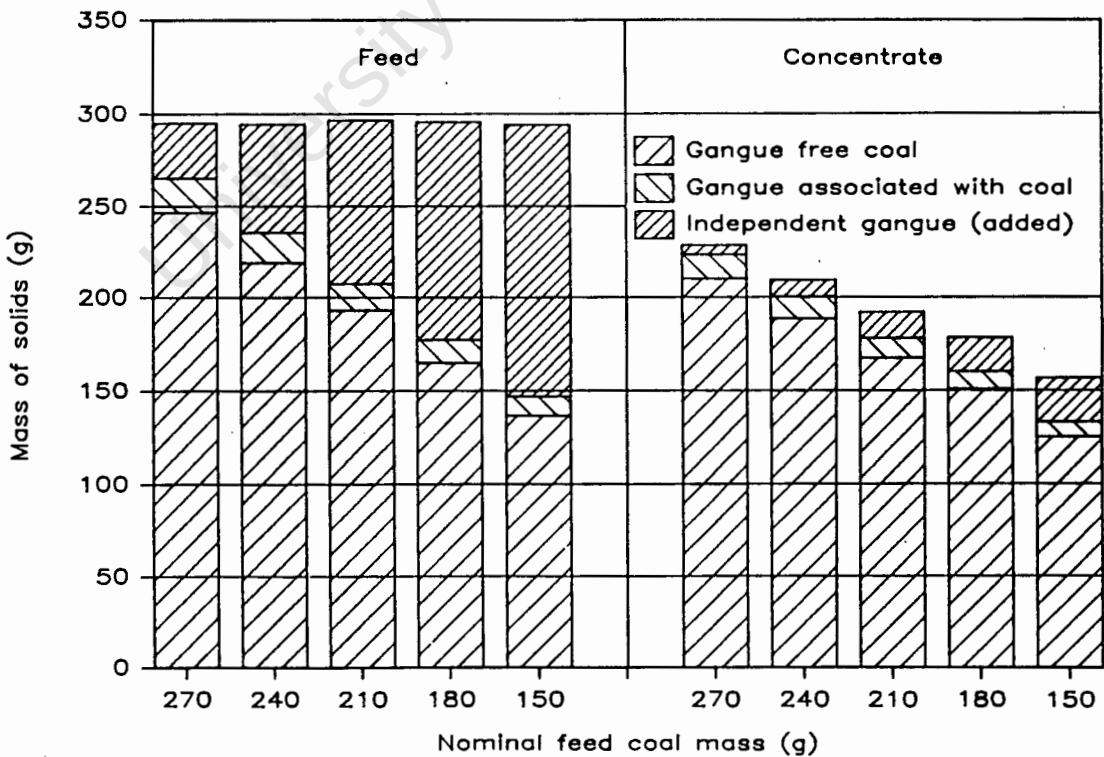


Figure A5.3 : Masses of gangue free coal, gangue associated with coal and independently added kaolin in a flotation concentrate compared to their respective masses in the flotation feed. Greenside No.2 seam washed coal ($-150 \mu\text{m}$) and kaolin (50 % $-2 \mu\text{m}$) added in various proportions to total 300 g (nominally).

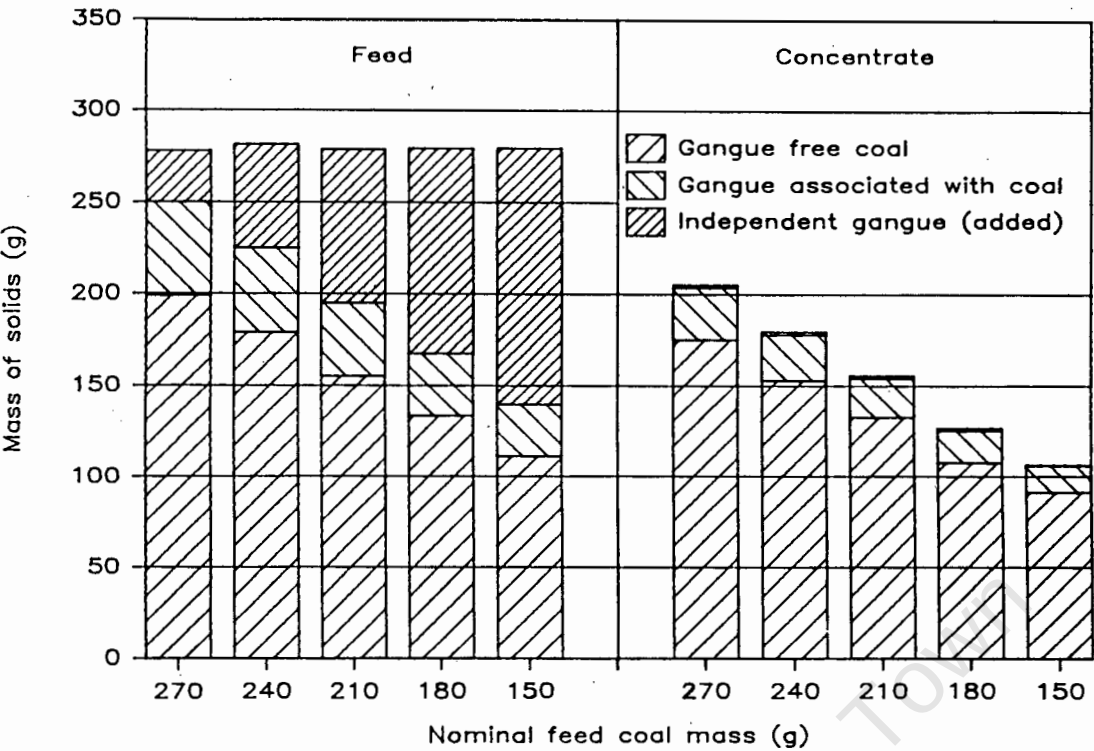


Figure A5.4 : Masses of gangue free coal, gangue associated with coal and independently added kaolin in a flotation concentrate compared to their respective masses in the flotation feed. Greenside No.2 seam thickener underflow coal and kaolin (50 % -2 μ m) added in various proportions to total 300 g (nominally).

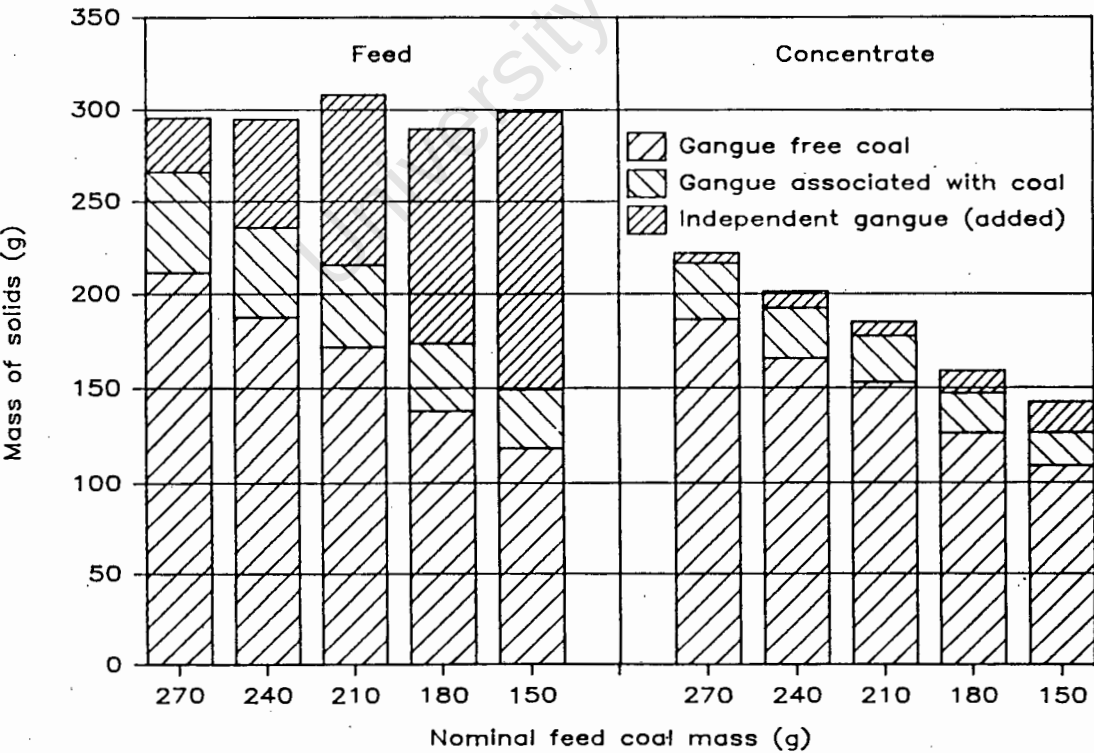
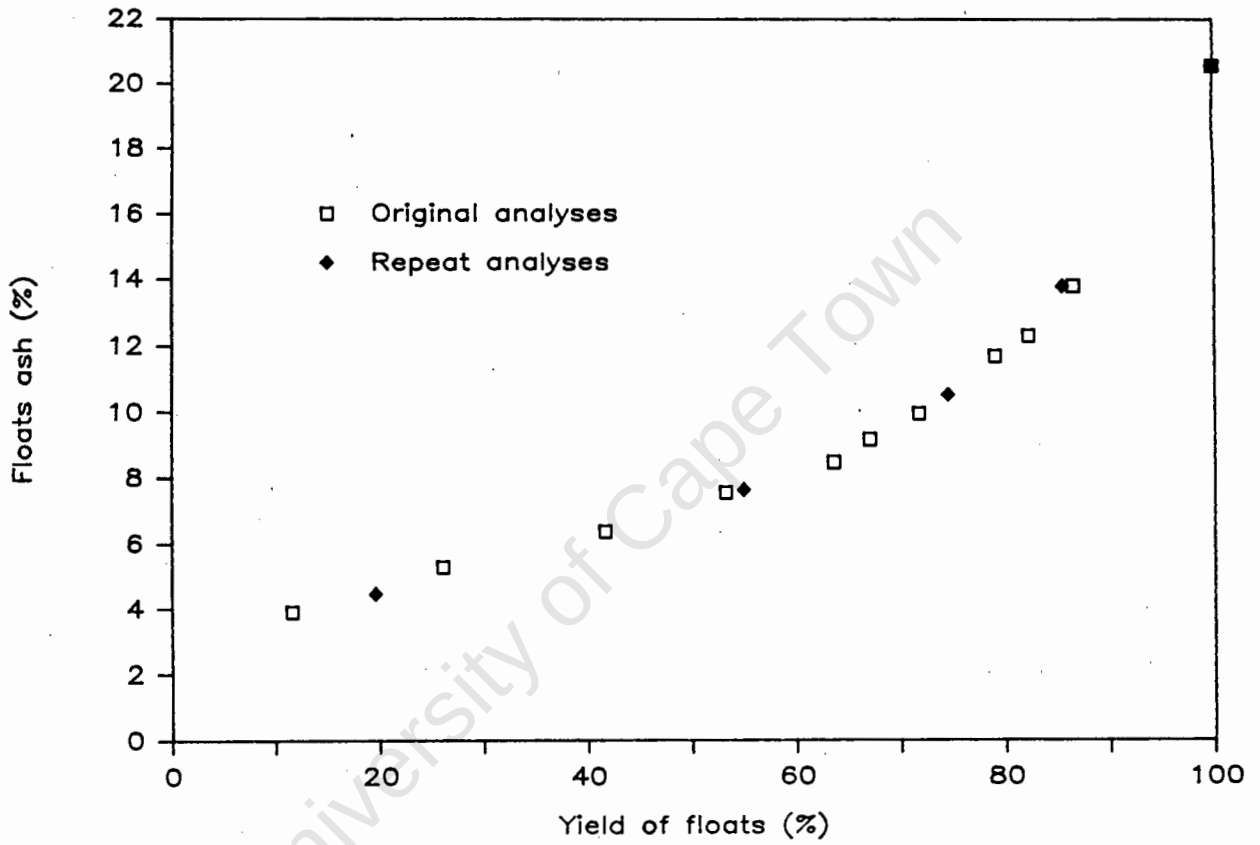


Figure A5.5 : Masses of gangue free coal, gangue associated with coal and independently added quartz in a flotation concentrate compared to their respective masses in the flotation feed. Greenside No.2 seam thickener underflow coal and quartz added in various proportions to total 300 g (nominally).

APPENDIX 5.4FLOAT-SINK TECHNIQUE REPEATABILITY

APPENDIX 5.5

SUMMARY OF RAW RESULTS (UNWASHED COAL SAMPLE)

(For detailed results refer to Data Appendix 4: use the Float ref. no.)

Float ref. no.	Collector oil	Oil dosage (μ l)	MIBC dose (μ l)	Condit proced.	Conc. mass (g)	Conc. ash (%)	Predic ash (%)
71	10% hex benz in dod	400	18	11pm	48.52	11.8	5.9
61	10% hex benz in dod	200	36	11pm	60.79	12.4	6.4
68	10% hex benz in dod	200	54	1pdc	64.45	13.2	6.6
66	10% hex benz in dod	200	54	11pm	82.41	13.1	7.4
64	10% hex benz in dod	400	36	11pm	90.64	14.3	8.0
65	10% hex benz in dod	200	36	11pm/f	109.21	15.0	10.0
69	20% hex benz in dod	200	54	1pdc	73.24	13.8	6.9
62	20% hex benz in dod	200	36	11pm	75.39	13.1	7.0
70	40% hex benz in dod	100	36	11pm	29.46	10.3	4.9
67	40% hex benz in dod	200	54	1pdc	87.07	14.2	7.7
63	40% hex benz in dod	200	36	11pm	91.04	13.9	8.0
13	Dodecane	200	18	1pdc	9.59	9.3	2.8
12	Dodecane	200	18	11pm	13.27	9.6	3.3
56	Dodecane	400	18	hpdc	15.67	10.0	3.6
10	Dodecane	200	18	hpdc	20.45	10.5	4.1
H'	Dodecane	400	18	1pdc	22	10.6	4.2
A'	Dodecane	400	18	1pdc	27.1	11.0	4.7
P	Dodecane	400	18	11pm	33.98	11.2	5.2
55	Dodecane	400	36	1pdc	34.57	11.2	5.3
53	Dodecane	200	36	1pdc	35.36	11.5	5.3
Y	Dodecane	400	18	hpdc	41.86	11.3	5.6
90	Dodecane	200	36	11pm	44.50	10.7	5.8
84	Dodecane	200	36	11pm	45.03	11.2	5.8
86	Dodecane	200	36	11pm	47.81	11.8	5.9
11	Dodecane	200	18	11pm/f	55	12.0	6.2
28	Dodecane	200	36	1pdc	60.2	12.6	6.4
54	Dodecane	200	36	hpdc	74.12	13.1	7.0
U	Dodecane	1000	18	11pm	76.38	12.7	7.1
24	Dodecane	200	36	hpdc	81.56	13.4	7.4
29	Dodecane	400	36	1pdc	88.93	14.1	7.9
Z	Dodecane	400	18	11pm/f	95.5	13.6	8.4
25	Dodecane	400	36	hpdc	97.77	14.1	8.7
23	Dodecane	200	36	11pm/f	112.08	15.1	10.5
2	Hexyl benzene	200	18	11pm/f	21.57	10.5	4.2
20	Hexyl benzene	200	0	hpdc	28.32	10.9	4.8
44	Hexyl benzene	200	18	11pm/f	43.46	11.8	5.7
22	Hexyl benzene	400	0	1pdc	48.91	11.7	6.0
21	Hexyl benzene	400	0	hpdc	54.8	12.2	6.2
5	Hexyl benzene	200	18	11pm	59.16	12.2	6.4
47	Hexyl benzene	200	18	11pm/f	62.48	12.7	6.5
4	Hexyl benzene	200	18	1pdc	72.9	14.2	6.9
43	Hexyl benzene	200	18	1pdc	73.25	14.4	6.9

Float ref. no.	Collector oil	Oil dosage (μ l)	MIBC dose (μ l)	Condit proced.	Conc. mass (g)	Conc. ash (%)	Predic ash (%)
1	Hexyl benzene	200	18	11pm	85.65	13.7	7.6
45	Hexyl benzene	200	18	11pm	95.27	14.6	8.4
42	Hexyl benzene	200	18	hpdc	95.55	15.4	8.4
3	Hexyl benzene	200	18	hpdc	97.92	14.8	8.7
89	Hexyl benzene	200	36	11pm	99.25	14.1	8.8
C'	Hexyl benzene	400	18	lpdc	100.64	14.9	9.0
87	Hexyl benzene	200	36	11pm	102.53	15.0	8.8
26	Hexyl benzene	200	36	11pm/f	103.48	13.6	9.3
46	Hexyl benzene	400	18	11pm/f	108.96	16.3	10.0
D'	Hexyl benzene	400	18	11pm/f	110.24	15.8	10.2
Q	Hexyl benzene	400	18	11pm	112.02	15.8	10.5
B'	Hexyl benzene	400	18	hpdc	113.06	16.3	10.6
30	Hexyl benzene	400	36	lpdc	118.88	16.4	11.6
27	Hexyl benzene	200	36	hpdc	121.31	16.1	12.1
33	Hexyl benzene	400	54	lpdc	126.37	16.6	13.2
V	Hexyl benzene	1000	18	11pm	131.8	16.5	14.5
W	Pegasol 3745 180-190	400	18	11pm	104.64	15.2	9.4
57	Pegasol 3745 190-200	400	18	11pm	81.25	14.6	7.4
T	Pegasol 3745 200-210	400	18	11pm	110.8	14.8	10.3
37	Pegasol 3745 210-220	200	36	lpdc	88.48	14.0	7.8
58	Pegasol 3745 210-220	400	18	11pm	90.18	13.8	8.0
40	Pegasol 3745 210-220	400	36	lpdc	104.5	13.7	9.4
36	Pegasol 3745 210-220	200	36	hpdc	107.84	14.7	9.9
35	Pegasol 3745 210-220	200	36	11pm	109.21	14.2	10.0
39	Pegasol 3745 210-220	400	36	11pm	122.94	16.2	12.5
34	Pegasol 3745 210-220	200	36	11pm/f	123.55	16.3	12.6
59	Pegasol 3745 220-230	400	18	11pm	93.02	13.6	8.2
60	Pegasol 3745 230-240	400	18	11pm	79.63	12.8	7.3
X	Pegasol 3745 240-250	400	18	11pm	94.91	13.5	8.4
81	Pegasol 3745 240-250	200	36	11pm	100.98	13.8	9.0
80	Pegasol 3745 240-250	400	36	11pm	120.09	15.8	11.9
18	Shellsol AB	200	0	hpdc	5.6	8.6	2.2
7	Shellsol AB	200	18	11pm/f	24.63	10.3	4.5
6	Shellsol AB	200	18	11pm	29.18	10.4	4.8
8	Shellsol AB	200	18	hpdc	57.81	11.4	6.3
19	Shellsol AB	200	0	lpdc	64.16	13.7	6.6
16	Shellsol AB	400	0	hpdc	101.63	15.5	9.1
9	Shellsol AB	200	18	lpdc	105.97	15.2	9.6
17	Shellsol AB	400	0	lpdc	110.59	15.9	10.2
E'	Shellsol AB	400	18	11pm/f	112.88	15.9	10.6
F'	Shellsol AB	400	18	hpdc	116.36	15.9	11.2
R	Shellsol AB	400	18	11pm	117.52	15.6	11.4
G'	Shellsol AB	400	18	lpdc	121.15	15.8	12.1
14	Shellsol K	200	18	11pm	10.27	9.1	2.9
S	Shellsol K	400	18	11pm	36.68	11.3	5.3
15	Shellsol K	200	18	11pm/f	65.34	12.2	6.6

$$\text{Predicted ash} = 1.2327 + 0.18394(\text{mass}) - 0.0024711(\text{mass})^2 + 0.00001397(\text{mass})^3$$

Water recovery (g)	1st conc mass (g)	1st con ash (%)	Predic 1st ash (%)	1st conc H ₂ O rec. (g)	1st conc rate (g/s)	Comments
	54.46	13.9	6.2		3.631	
123.29	66.02	14.9	6.6	78.88	4.401	
123.84	68.99	15.8	6.7	83.91	4.599	
	68.35	15.3	6.7		4.557	
131.85	64.13	14.2	6.6	77.77	4.275	1600-800-1200 rpm
	42.92	16.0	5.7		2.861	
104.70	74.74	15.6	7.0	88.69	4.981	800-800-1200 rpm
159.12	55.12	12.8	6.2	86.98	3.675	
172.18	83.04	16.1	7.5	134.26	5.536	
	81.06	15.7	7.3		5.404	
	82.44	15.9	7.4		5.496	
	80.55	16.8	7.3		5.370	
167.72	68.62	16.4	6.7	84.98	4.575	
173.99	85.43	16.3	7.6	111.17	5.695	
205.93	70.57	16.7	6.8	91.13	4.705	
	72.1	16.4	6.9		4.807	
	85.07	15.2	7.6		5.671	
102	61	14.9	6.4	66.7	4.067	
	81.05	14.7	7.3		5.403	
102.02	62.8	14.4	6.5	68.8	4.187	
108.97	56.55	13.9	6.3	60.15	3.770	
132.4	73.96	15.4	7.0	88.86	4.931	
130.51	77.67	14.8	7.2	88.63	5.178	
143.79	78.27	14.3	7.2	91.73	5.218	
178.66	93.47	16.1	8.2	124.13	6.231	
197.85	101.84	16.0	9.1	165.16	6.789	
109.6	51.59	13.4	6.1	56.72	3.439	
105.28	38.44	12.7	5.4	45.37	2.563	
	43.8	12.9	5.7		2.920	
121.71	58.49	13.4	6.3	66.01	3.899	
162.96	80.42	15.4	7.3	103.08	5.361	
12.65	1.59	8.6	1.5	6.01	0.106	
58.48	8.45	10.0	2.6	28.15	0.563	
63.27	9.88	9.9	2.8	31.52	0.659	
84.83	25.45	11.1	4.5	44.95	1.697	
76.35	44.65	14.5	5.8	48.25	2.977	
157.42	85.39	15.8	7.6	136.51	5.693	
132.11	76.43	15.6	7.1	91.37	5.095	
155.33	86.72	16.3	7.7	112.68	5.781	
	91.92	16.1	8.1		6.128	
	87.88	16.1	7.8		5.859	
	95.12	15.7	8.4		6.341	
	88.43	15.9	7.8		5.895	
23.16	2.5	9.4	1.7	6.7	0.167	
	21.02	12.0	4.1		1.401	
96.14	53.41	12.2	6.1	80.19	3.561	

APPENDIX 6

PAPER PUBLISHED ON THE TECHNIQUE FOR STUDYING OIL ADSORPTION

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A technique to study the adsorption of oily collectors onto coal and gangue minerals

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Summary A technique has been developed to study the adsorption of paraffinic i.e. alkane (or other hydrocarbon oil) collectors onto coal and gangue mineral surfaces under dynamic conditions. The oily collector is present as the dispersed phase of a dilute oil-in-water dispersion. Solid particles are added to this dispersion and agitated to give a system analogous to that found in flotation cells prior to aeration, i.e. during conditioning.

The technique enables study of the overall or apparent kinetics involved in the collision and effective adsorption of collector droplets onto coal or mineral particles.

Results obtained show that adsorption is very rapid and tenacious, even under turbulent conditions. The hydrocarbon collectors are selective. Adsorption onto gangue (undesirable minerals) is limited and decreasing adsorption is evident as coal fractions become increasingly dense, i.e. as their gangue (ash) content increases. Commercial kerosene (Shellsol K) behaved in a similar way to the pure alkane collector with similar boiling point (dodecane).

INTRODUCTION

There are two reasons for developing a technique to study the adsorption of oily collectors onto coal and gangue minerals. One is to provide additional means of evaluating the potential of oily hydrocarbons as coal collectors, additional to those of contact angle measurement. The other is to throw light on the first step in the sequence of events occurring during flotation of coal with oily collectors, by determining adsorption rates and selectivity.

Because of the turbulent conditions in a flotation cell, a strong, stable adsorption of the collector is one prerequisite for effective flotation. This assumes that the bubble-particle aggregate is not sufficiently stable to permit flotation without a collector, i.e. that the particle is not sufficiently hydrophobic. Obviously strong adsorption will not necessarily imply a good mass recovery if the chemical has no collecting ability.

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Additionally, strong adsorption does not necessarily imply beneficiation which is, after all, the objective of the process. The collector must also be selective.

Selectivity is determined during the adsorption step. If the oily collector droplets cannot distinguish between a coal-rich surface as opposed to one dominated by gangue, or are able to spread over such surfaces from adjacent coal surfaces, then there is no point in attempting beneficiation by floating with these collectors.

Contact angle

Contact angle measurements are widely used in predicting the potential of reagents as flotation collectors. Contact angle measurements are made under static conditions and do not take into account the turbulent conditions in a flotation cell. For instance, they give only a limited idea of the strength of the solid-collector adsorption bond. Špetl and Dědek (1966) pointed out that contact angle measurements (advancing, receding or stationary) merely represent the final phase of the adhesion process. In their review, Finch and Smith (1979) concurred with this opinion, pointing out that contact angle is a consequence of successful attachment, and is therefore dependent on the success of the steps occurring prior to contact.

The success of a particle—droplet encounter will depend on the paths, relative velocities and masses of the particle and the droplet, as well as on the length of their time of contact. Contact time must be longer than the 'induction' time required for the thinning and rupture of the hydrate layers surrounding the particle and retreat of the water film, thus allowing initial contact. Sufficient time must also be available for some spontaneous spreading of the droplet on the particle (i.e. for an increase in contact angle) to ensure tenacious adhesion (Finch & Smith, 1979).

These are factors which cannot be taken into account when measuring contact angles. In addition, contact angle measurements are subjective and vary from operator to operator. This problem is compounded by the heterogeneous nature of coal surfaces, as contact angle measurements are limited to a single droplet which obviously only occupies a small part of the surface.

In developing the present technique, the main aim was to allow the adsorption process to be studied under dynamic conditions and with a completely representative surface, i.e. for the pulp as a whole.

Macroscopic versus microscopic cell kinetics

In laboratory batch flotation experiments macroscopic cell kinetics are normally studied, i.e. cell kinetics are inferred from the observed rate of concentrate production. However, without an intimate knowledge of the individual steps occurring in the flotation cell, it is difficult to say which particular step(s) is (are) responsible for the flotation performance exhibited, and which step is rate-limiting or rate-controlling. Such knowledge is essential for modelling purposes.

Despite the simplicity of the macrokinetic approach, it has been suggested by Flint (1973) that it is impossible to predict flotation performance accurately at conditions other than at which the macrokinetic parameters (e.g. rate constants) were obtained. Flint submitted that accurate prediction can only be achieved from a thorough knowledge of the microkinetics and ultimately of the surface chemistry.

Flint (1973) presented a diagram which depicts the various material transport paths involved in a flotation process. This is reproduced below (Fig. 1) with a modification to indicate the collector droplet–solid particle encounter step which constitutes the first part of the overall sequence of events occurring in the process when insoluble collectors are used.

Flint (1973) maintained that flotation models were hampered by ignorance of the collection and detachment processes occurring in the pulp. This is still largely the case. Semi-empirical models are still the most commonly used for modelling all stages in the sequence of events occurring duration flotation (McMichael 1985).

The development of the present technique is aimed at quantifying the process in which collector droplets adsorb onto the surfaces of particles of different types and sizes, under different physical and chemical conditions. This will ultimately shed more light on the microscopic cell kinetics, and contribute to a better understanding of the dynamics of measured flotation performance.

THE TECHNIQUE

Introduction

A suitable method had to be found in order to study the collector droplet adsorption onto coal particles. Initially a method similar to that developed by Haung and Miller

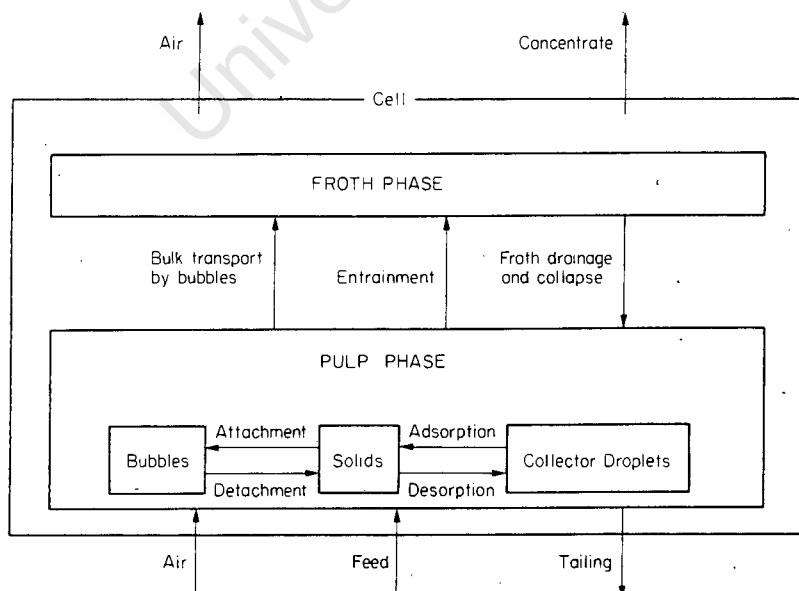


Figure 1. Material transport paths in flotation.

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(1978) was considered. They developed a procedure to study the kinetics of the xanthate-pyrite reaction using a stirred batch reactor containing the ore pulp and a xanthate collector. A fritted glass sparger was used to sample the pulp and after further filtration the xanthate concentration was determined by UV spectrophotometry.

It was anticipated that a similar procedure would permit study of the adsorption reaction of coal and water-immiscible hydrocarbon collectors in terms of both kinetics and the ultimate adsorption levels attained. Kinetic investigations of these coal-collector reactions have not been reported, though Smitham and Firth (1982) have studied the final adsorption levels.

Method development

In attempting to apply a similar procedure to the coal-hydrocarbon collector reaction, it became apparent that the chemical constitution of these collectors and their immiscibility with water would present several problems. These were:

- (1) Difficulty in separating a representative sample of the water-oil dispersion from the pulp solids, and doing this rapidly enough to quench the reaction and so enable the adsorption to be studied;
- (2) the absence of functional groups and/or multiple bonds in the collector molecules selected, thereby limiting chemical analytical techniques;
- (3) the presence of two liquid phases (as an unstable oil-in-water dispersion) in samples and the need to prepare these for chemical analysis;
- (4) and the low concentrations of collector. For instance an initial collector dosage of 2000 g per ton of coal (S. G. of 1.35) in a 5% (m/m) solids pulp corresponds to about 105 ppm of collector (mass basis). The concentration drops rapidly from this level as adsorption ensues.

Overcoming problems

To take a sample of pulp liquid, solid particles had to be significantly larger than collector droplets so that separation of the two on a size basis was possible. This is one limitation of the technique. Droplet size analyses of the dispersions were made using a Coulter counter (Model TA II) and the minimum solid size determined from these. Figure 2 shows a typical size distribution. In every cm^3 of pulp liquid there are hundreds of thousands of small collector droplets. Droplet numbers decrease rapidly with increasing size but most of the collector volume (mass) is concentrated in the upper size ranges.

Solids were screened into narrow size ranges (250 to 300 μm , 500 to 600 μm) because Pooley (1967) and Smitham and Firth (1982) have shown that the macrokinetics displayed after collector addition are dependent on the size distribution of solids in the pulp. It was thought that quantification and comparison of the micro-kinetics measured might also be difficult with a broad size distribution, even if this were accurately known and reproducible.

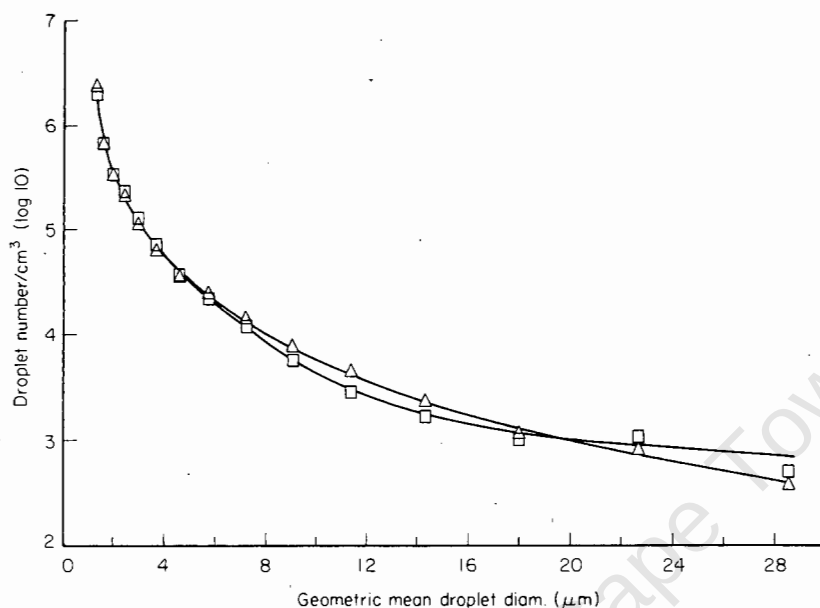


Figure 2. Dispersion size analyses. Conditions: 1 minute dispersion at 1600 r/min^{-1} , 70 mm^3 of dodecane per 0.5 dm^3 distilled water at 292 K . ($\square$) Dodecane; ($\triangle$) Dodecane/MIBC mixture (9:1 m/m).

Sintered glass and stainless steel filters were initially used to take liquid samples from the pulp. However, in addition to any sorption effects severe decreases in collector concentration occurred because the pores in these filters are inconsistent in size and so trapped many large droplets.

Eventually, suitable filters were made by building up clusters of hypodermic needles of selected bores, as in Fig. 3. Multiple needles overcome blocking problems and have been found to give very rapid and excellent separations.

Gas-liquid chromatography (GLC) using a packed column and a flame ionization detector was chosen for determining collector concentration within the pulp samples. Analysis is quantitative, and is based on the measurement of peak heights or areas. An exactly known amount of 'internal standard' (e.g. decane) is added via the CCl_4 used for collector extraction (see below) to enable peak measurements to be related to actual concentration.

GLC requires mm^3 quantities of liquid for analysis. It is thus difficult to obtain a representative dispersion sample especially if any phase separation has occurred which will undoubtedly be the case.

A liquid extraction technique using CCl_4 is used to render the dispersion sample amenable to gas-chromatographic analysis. Homogenizing the samples with a solvent (e.g. ethanol) mutually compatible with both the collector and water, was found to be unsatisfactory because of excessive dilution and incompatibility with the GLC column packing selected. Liquid extraction has an advantage in that the collector concentration can be increased. Fortunately, high boiling point paraffinic collectors are insoluble in water so that partitioning between the water and CCl_4 is not a problem. Extractions using

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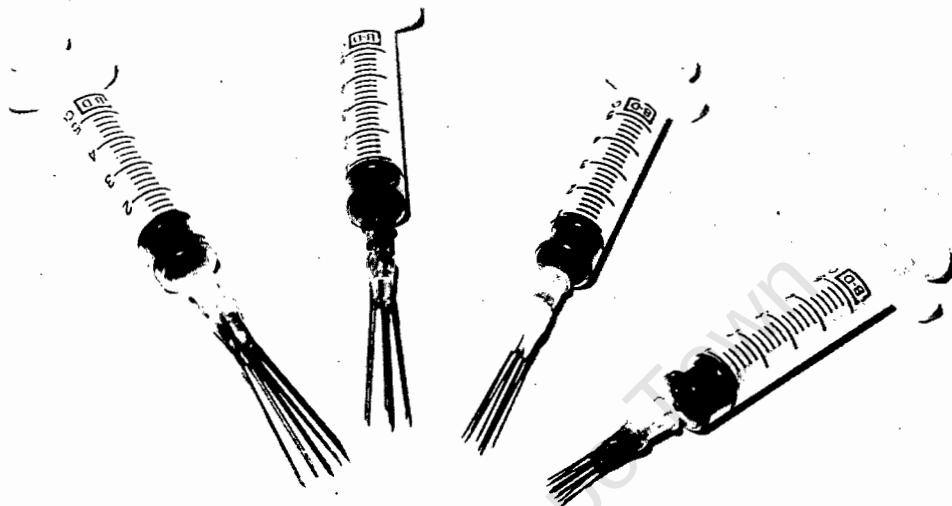


Figure 3. Needle filters on disposable hypodermic syringes. The smaller the needle bore the smaller the minimum solid particle size which can be filtered.

CCl_4 are rapid and complete, i.e. there is insufficient collector (if any) left in the water to permit detection by the extremely sensitive detector.

The method

Sample bottles and syringes with their needle filters were weighed (to 0.1 mg). The collector (with or without a frother) is then added to 0.5 dm³ of water at 298K (or some other controlled temperature) in a baffled stainless steel vessel (cylindrical; 9.5 cm diameter, 12 cm height) and dispersed using a turbine impeller (see Fig. 4). All four baffles are full length and 1 cm in width. The impeller consists of a stainless steel disc 60% of the vessel diameter, with eight blades (1 cm × 0.5 cm) mounted so that the blade extends 0.3 cm beyond the disc periphery.

After 2 min of agitation a sample of the dispersion is withdrawn and solid particles added immediately afterwards as a prewetted slug. The first sample is used to normalize results, as a time-dependent loss of collector from the reactor was discovered. In other words the collector concentration at the time solids are added is not the same as the initial concentration. This loss phenomenon is discussed below. The mass of solids added is adjusted according to the solid specific gravity (S.G.) to ensure similar surface areas. Masses are based on that mass (26.3 g) which gives a 5% (m/m) pulp solids concentration, assuming a solids S. G. of 1.35.

The pulp is sampled directly using the filters devised and 5 cm³ disposable syringes. Small volumes (~2 cm³) are withdrawn to prevent any significant changes of pulp density or concentration within the reactor. Sampling of the pulp is thus on a discrete basis. The



Figure 4. Experimental apparatus. Stainless steel vessel and turbine impeller; waterbath; needle filters; device for adding a wetted slug of solids and micro-syringe for adding reagents.

adsorption is monitored over a 5 min period with samples taken at 10, 20, 30, 45, 60, 90, 180, 240 and 300s after addition of the solid particles.

Syringes containing the dispersion samples are reweighed. CCl_4 containing the internal standard is then drawn into them. The filters are removed and all the syringes capped tightly. The extraction is performed by shaking the syringes on a Heidolph testtube-shaker using an adapter to prevent a syringe making direct contact with the shaker. Syringes are shaken for 1 min after the contents first appear 'milky'. Extractions must be carried out within the sampling syringes because any transfer of dispersion from the syringes to the sample bottles before extraction causes serious error. This is largely a result of collector adsorbing onto the syringe wall.

The syringe contents are now transferred to the preweighed sample bottles which are capped and reweighed. Any CCl_4 lost by evaporation or adsorption by the syringes is then accounted for. The mass of water and of CCl_4 can now be determined. The masses of collector and standard are insignificant and are ignored in these calculations.

Using a micro-syringe $3\text{--}5\text{ mm}^3$ of the CCl_4 layer are withdrawn and injected into the GLC instrument. Detector response is linear with respect to both sample concentration and volume at the levels used in the technique. Standards containing known concentrations of both the collector and the internal standard in CCl_4 are also analysed to determine detector response factors. Knowing these factors, the ratio of collector to standard (from the GLC analysis) and the masses of water and CCl_4 , it is simple to

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calculate the collector concentration in the pulp at the time of the sample. The amount of collector adsorbed is found by difference.

TESTWORK

The method developed has been used in a limited experimental program in order to explore its potential. Runs were carried out with two different coals and a sample of quartz. A paraffinic hydrocarbon (dodecane) and an industrial kerosene (Shellsol K), which is 99.5% aliphatic, were used as collectors. Collector sorption characteristics were investigated for two size range fractions of coal and quartz, and for different density fractions of coal.

Bituminous coal from the Witbank No. 2 seam at Greenside Colliery was received as +6 mm – 12 mm washed coal 'peas'. These were rod milled for a predetermined period to give the maximum yield of the desired size ranges (250–300 μm and 500–600 μm) for the adsorption tests. These size fractions were screened out. A sample of coking coal was obtained from Vryheid Coronation Colliery in Natal. The sample was of feed to flotation plant, and was simply wet screened. The quartz sample was from Industrial Sands near Cape Town. The desired size range was screened out.

A pure component collector was selected for the initial work to facilitate chemical analysis. *n*-Dodecane was chosen because it is recommended as a collector in a standard froth flotation method (Australian Standard 2579.1, 1983) and preliminary work with alkane collectors found dodecane to be the most successful (Harris 1983).

RESULTS AND DISCUSSION

The results presented here are intended to illustrate the potential of the technique. As work is still in progress, conclusions drawn are tentative, but are nonetheless interesting.

Figures 5 to 9 show the rate of disappearance of collector from the pulp after solids addition. This records the actual situation within the pulp. The adsorption rate would be the inverse of this, assuming that collector loss from the vessel has a negligible effect on the rate of collector disappearance from the pulp.

The two curves in Fig. 5 show the difference in adsorption rate of dodecane for the 250–300 μm and 500–600 μm coal particle size ranges of the Greenside No. 2 seam coal. Each run was carried out with a single particle size range. The results are for two duplicate runs for each size range. As may be seen, good repeatability was obtained in duplicate experimental runs. Any difference is that error accumulating within the technique as a whole, i.e. solids preparation, sampling of the pulp, dispersion, preparation and GLC analysis. (Good repeatability was also obtained in the other runs, but Figs 6, 7 and 8 show only the average values obtained from duplicate runs, so as not to clutter the figures with too many points.)

Curves in Fig. 5 also indicate that adsorption is more rapid for the finer particle size range, as would be expected with the four-fold increase in surface area. The particles used in the adsorption tests are relatively large in terms of conventional coal flotation

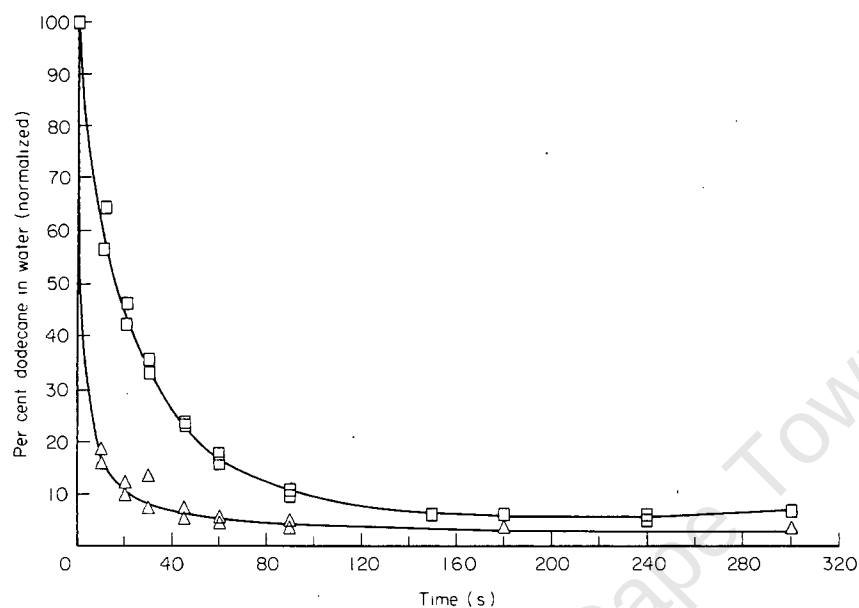


Figure 5. Dodecane sorption. 105 ppm (m/m) dodecane in distilled water. Greenside washed coal in a 5% (m/m) pulp. ($\square$) 500–600 μm ; ($\triangle$) 250–300 μm .

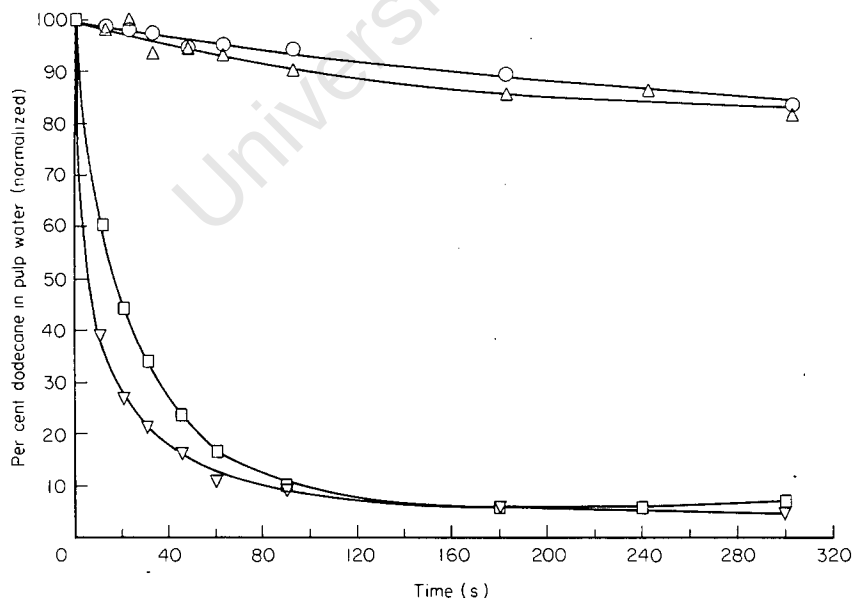


Figure 6. Reagent sorption. 105 ppm (m/m) dodecane in distilled water. Independent Greenside coal and quartz samples both of 500–600 μm particle size range. 5% (m/m) coal pulp. 10% (m/m) quartz pulp. ($\square$) Coal. Dodecane; (∇) Coal. Dodecane/MIBC mix (9:1 m/m); ($\triangle$) Quartz. Dodecane; ($\circ$) Quartz. Dodecane/MIBC mix (9:1 m/m).

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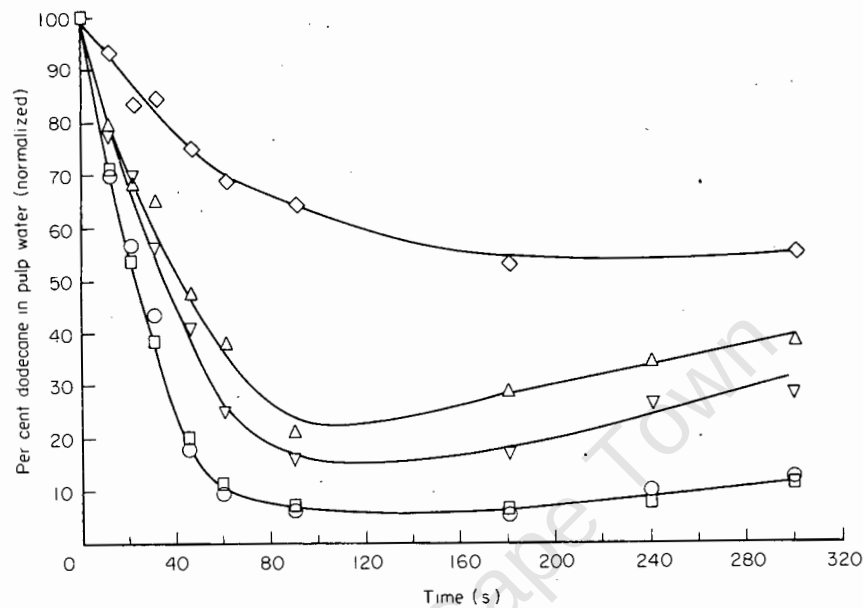


Figure 7. Dodecane sorption. 105 ppm (m/m) dodecane in distilled water. 425–600 μm Vryheid Coronation coal from their feed to flotation. Separated into density fractions. Percentage of solids in the pulp adjusted according to the density of each fraction (for constant surface area). (□) –1.3 S.G.; (○) +1.3 –1.4 S.G.; (▽) +1.4 –1.5 S.G.; (△) +1.5 –1.7 S.G.; (◇) +1.7 S.G.

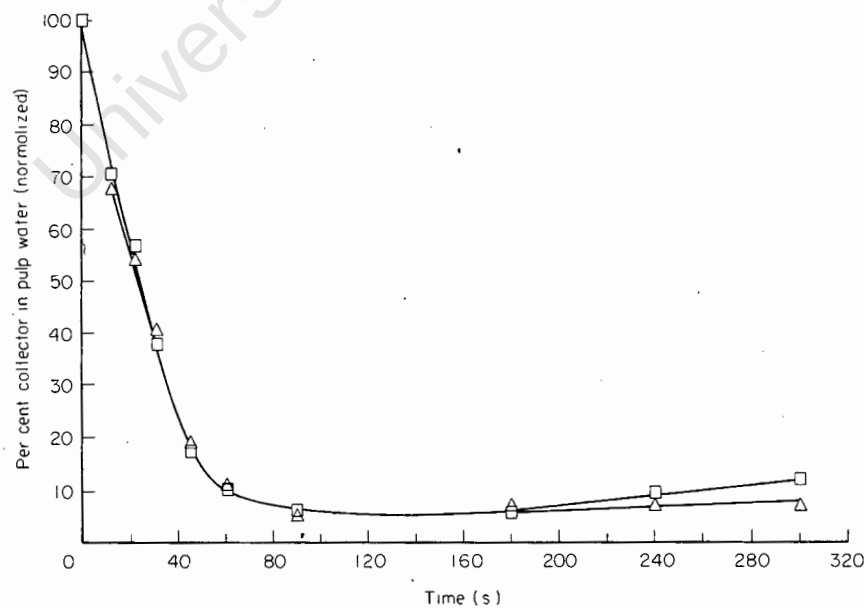


Figure 8. Dodecane and Shellsol 'K' sorption. 105 ppm (m/m) reagent dosage (similar oil densities). +1.3–1.4 S.G. fraction of Vryheid Coronation coal of 425–600 μm , particle size range. (□) Dodecane; (△) Shellsol 'K'.

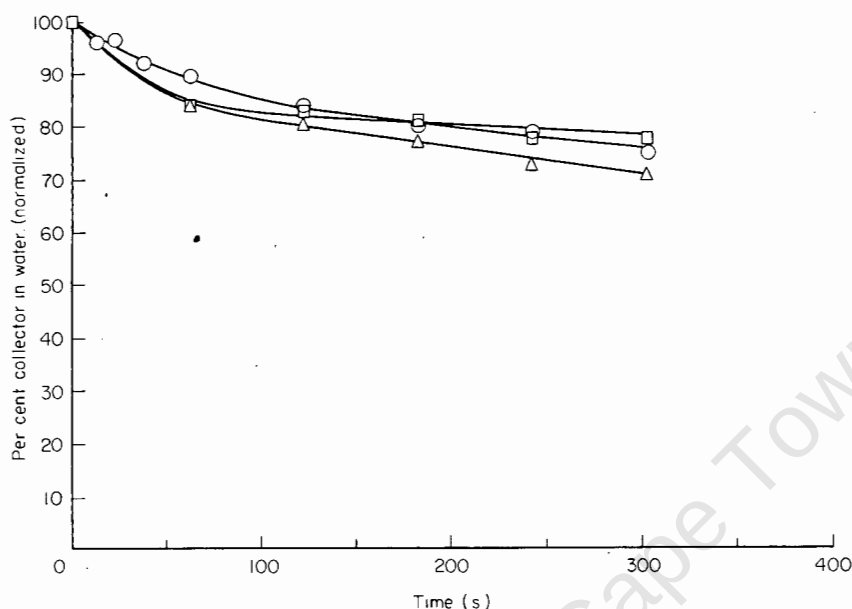


Figure 9. Collector loss from the reactor. 85 mm^3 added to 0.5 dm^3 distilled water at 298K. (Δ) Dodecane; (○) Tetradecane; (□) Hexadecane.

practice, where a significant proportion of very fine (less than $25 \mu\text{m}$) particles is often present. It is likely that the adsorption rate for these finer particles will be much greater still.

It is well known that the feed size distribution has a significant effect on the yield obtainable from single stage flotation of coal (Mishra 1985; Bensley & Nicol 1985). Firth *et al.* (1976) attributed this to finer particles adsorbing a disproportionately high quantity of collector at the expense of the coarser particles, on account of their greater abundance and overall surface area. The increased adsorption rate observed with the finer particle size range in Fig. 5 supports this conclusion and shows how the phenomenon arises.

Figure 6 shows how the addition of MIBC frother affects adsorption of dodecane on coal and quartz particles of the same size fraction. The quartz and coal experiments were carried out separately. MIBC and dodecane were mixed on a 1 to 9 mass basis before dispersion in water. The same amount of dodecane as used in the coal runs was used in the quartz runs. The higher S.G. of quartz required that a proportionately higher mass of quartz be used to obtain overall surface areas similar to those of the coal.

As may be seen, sorption of collector on coal is accelerated by the addition of MIBC but a similar trend is not apparent with quartz. The effect may be due to a decrease in the mean collector droplet size although the surfactant may be promoting adsorption onto the coal surface.

From a comparison of the quartz and coal curves it can be deduced that dodecane would adsorb on coal in preference to quartz even when a surfactant (MIBC) is present, i.e. that dodecane is selective.

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To test selectivity with naturally arising unwashed coals, a sample of feed to flotation was obtained from Vryheid Coronation Colliery. This was sized by wet screening and the desired range (425–600 μm) was separated, dried and then divided into density fractions using ZnCl_2 solutions. These fractions were filtered and then washed continuously with water for two hours to remove residual ZnCl_2 . Adsorption tests were then carried out on each of the fractions.

Results obtained are shown in Fig. 7. It appears that dodecane is able to distinguish between coal rich as opposed to gangue dominated solid particles. Adsorption is more rapid for the lower S.G. fractions and residual collector levels are lower (greater adsorption). For all the density fractions, particle size ranges were the same, i.e. available surface areas were similar. On going from the low to the higher S.G. fractions the quantity of collector remaining in the pulp water levelled off at progressively higher values. This levelling off indicates that all adsorption sites have been occupied. If the collector were not selective or could spread over gangue areas adjacent to coal sorption sites, final adsorption levels attained would be roughly equivalent for all the density fractions as their external surface areas are approximately equal.

The apparent desorption effect, which is especially prevalent with the higher density fractions, is attributable to a break-up of this particular coal at the impeller speed used (1650 rpm). Very fine particles of this friable coal were observed to pass through the filters. Collector adsorbed on these particles is removed from their surfaces during the extraction step thereby increasing the collector concentration within the CCl_4 .

Figure 8 gives an example of the kinetics displayed when an industrial kerosene, Shellsol K, which finds application as a coal collector, was used in place of dodecane. This kerosene behaves in an almost identical manner to dodecane with the density fraction selected (1.3–1.4 S.G.).

Collector mass loss

A phenomenon which has been noted from the start of this testwork is that of the concentration of collector within the reactor decreasing with time even when no solids are present. This may be seen from Fig. 9 which shows the loss of dodecane, tetradecane and hexadecane from the adsorption vessel in separate experiments. This loss is consistent from run to run (average values are shown). Slightly decreased losses noted with the higher boiling point alkanes could be due to their lower vapour pressures but also to differences in viscosity and spreading coefficients.

The loss in each case is very small in terms of mass but is serious at the concentrations used if not taken into account, i.e. if results are normalized with the initial collector concentration value rather than the actual concentration at the moment the solids are added.

An extensive investigation into possible causes found that extraction was complete, sampling reliable and evaporation probably insignificant because of the high boiling points and comparatively short reaction times. Finally, the loss was attributed to the very hydrophobic collectors spreading or 'creeping' up the stainless steel of the reactor walls

in much the same manner as they might spread over a quiescent water surface. This hypothesis was confirmed by arranging a solvent trap, consisting of a groove machined into the top of the reactor and filled with solvent, and noting an increasing concentration of collector in the solvent as time passed (by GLC analysis). However, this accounted for only a small part of the mass lost and it was concluded that the remainder was being adsorbed on the submerged steel walls. This is supported by the rapid initial drop in concentration followed by a much slower loss, probably due to the 'creep'.

Smitham and Firth (1982) in their work on equilibrium or final adsorption levels also encountered a collector imbalance phenomenon and were forced to normalize their results. They used a radiotracer (n -[1- ^{14}C] hexadecane) in kerosene to study the distribution of this insoluble collector on fine ($\sim 500\ \mu\text{m}$) coal particles. They attributed losses to either extraction inefficiency or to variations in the original dosage. Their duplicate experiments showed considerable variation while duplicate extractions for individual experiments were in good agreement. The authors concluded that variation in the initial dosage was the reason for the discrepancies. However, percentages of collector extracted were as low as 47% of the initial dosage and it is hard to imagine a $0.1\ \text{cm}^3$ pipette, which they used for collector addition, being so inaccurate. The present work suggests that the problem may also have been adsorption of collector onto container walls and 'creep'.

Although the phenomenon of mass loss is not very satisfactory, the loss is consistent and adsorption is often very rapid relative to the loss (as may be seen from Figs 5 to 8). It is reasonable to assume that once the initial change in concentration has been accounted for, there is little effect on the kinetics.

Potential of the technique

Initial experiments indicate that the technique which has been developed is a useful tool for investigating the influence of a number of variables on collector sorption. It has shown that the adsorption of oily collectors onto coal and gangue surfaces occurs at a finite rate, which is measurable with good repeatability.

Results to date show that adsorption is dependent on particle size, being more rapid as the particle size range decreases. Adsorption of n -dodecane onto coal is accelerated by the addition of MIBC, while the (poor) adsorption onto quartz is unaffected. Selectivity of the collector is indicated by the rate and extent of adsorption being dependent on the S.G. of the coal, i.e. on its ash content. Adsorption of industrial oily collectors may also be measured with this technique; the adsorption curve of Shellsol K was seen to be identical to that of dodecane.

Work is continuing in order to collect adsorption data for other pure and industrial oily collectors on a variety of coals. The influence of rank, coal type (maceral content) and the degree of coal oxidation is being investigated. In addition the effect of factors such as pH, temperature, degree of agitation, and the presence of frothers or other surfactants on the collector adsorption kinetics will be evaluated. More fundamentally, the influence of the collector droplet size distribution on the adsorption process is being

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investigated, in order to determine whether droplets of any particular size attach in preference to those of other sizes.

Quantifying the adsorption step in these ways would contribute to the understanding of the microkinetics of coal flotation. Furthermore, the present technique, used in conjunction with micro-flotation and froth stability tests, should assist in determining the specific role of oily collectors in the froth flotation of coal.

CONCLUSION

A technique has been developed to study the adsorption of paraffinic collectors onto coal and gangue mineral surfaces under dynamic conditions. The technique is simple and reasonably flexible and could encompass other size ranges and be extended to other hydrocarbons or other water immiscible collectors or mixtures thereof. It requires only small coal samples and is relatively quick and foolproof.

The technique can quantify collector adsorption rates with various coal types, coal constituents and gangue fractions and so determine whether rates are sufficiently slow and differences sufficiently large to enable commercial exploitation.

Differences in selectivity of the collectors towards different substrates can be deduced. If these differences can be correlated with actual flotation performance then the technique developed could be a useful tool in helping to predict or explain flotation performance.

ACKNOWLEDGEMENTS

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REFERENCES

- Australian Standard 2579.1-1983. Standards Association of Australia.
- Bensley, C. N. & Nicol, S. K. (1985) *Coal Preparation* **1**, 189.
- Finch, J. A. & Smith, G. W. (1979) *Minerals Sci. Eng.* **11**, 36.
- Firth, B. A., Swanson, A. R. & Nicol, S. K. (1978) *Proc. Australas. Inst. Min. Metall.* **267**, 49.
- Flint, L. R. (1973) *Min. Sci. Eng.* **5**, 3, 232.
- Harris, M. C. (1983) (unpublished).
- Huang, H. H. & Miller, J. D. (1978) *International Journal of Mineral Processing* **5**, 241.
- McMichael, A. O. (1985) MSc. Thesis, University of Natal, Durban.
- Mishra, S. K. (1985) *Mining Engineering* 1121.
- Pooley, F. D. (1967) *Inst. Min. Metall.* **76**, 282.
- Smitham, J. B. & Firth, B. A. (1982) *Proc. Australas. Inst. Min. Metall.* **No. 283**, 29.
- Spetl, F. & Dédék, F. (1966) *Fifth International Coal Preparation Congress. Section A: Paper 2*, Pittsburgh, p. 25.