ZERO-CONDITIONING TIME CONCEPT IN FLOTATION

by

KEJIAN DING

B.Sc., Northeastern University, China, 1984
M.Sc., Changsha Research Institute of Mining and Metallurgy, China, 1990
M.Sc., The University of Witwatersrand, Johannesburg, South Africa, 2001

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ABSTRACT

In the particle-to-bubble attachment process collector species are needed at the attachment point to render the mineral surface hydrophobic. It is common to assume that such species are transported toward mineral particles via diffusion/mixing and render the mineral surface hydrophobic by adsorption. However, collector species can also be brought to the point of attachment by bubbles carrying the species on their surfaces. That ensures that the collector is at the right time at the point where it is needed to facilitate the attachment of the particle to the bubble.

It is generally accepted that flotation with amines is very rapid and that only a short conditioning time is required in such a cationic flotation. This indicates that the transportation of the collector species toward mineral particles is very favorable when amines are applied. This implies that in such systems the major portion of amine is brought to the mineral surface by bubbles, and that the conventional introduction of such flotation reagents to the pulp via dissolution in the pulp does not constitute the best way of utilizing such reagents.

These ideas were tested in a reverse coal flotation process. In this process a quaternary aliphatic amine, dodecyltrimethyl ammonium chloride (DTAC), was used as a collector to float gangue while depressing coal particles. The process is interesting because low rank/oxidized coals float poorly, and because of the possible utilization of such clean coal products in the form of coal-water slurries. However, to float gangue efficiently the process requires very high dosages of the quaternary amine since adsorption of the amine onto coal is very high. However, if amine is transported with bubbles then it should be possible to carry out the process at "zero conditioning time" that would (i) reduce the amount of the amine adsorbed by coal thus reducing its overall consumption and (ii) improve gangue flotation. The process can be carried out either without any conditioning step prior to flotation, or, more efficiently, with the amine introduced to the flotation system with the stream of bubbles. The experiments confirmed entirely the hypothesized mechanism in which amine is mainly transported by bubbles, and showed that, with the

zero conditioning tests, coal reverse flotation could be successfully carried out at reduced amine consumption.

However, in order to become a viable option the coal reverse flotation process requires a very substantial reduction of the quaternary amine consumption. In search for the ways of reducing the collector dosage in this process the attention was turned to polymers which in potash flotation are utilized as blinders. The batch flotation tests carried out using a mechanical cell confirmed that some polyacrylamides worked very well as blinders in the coal reverse flotation process. At the same time the standard flocculation tests showed that the polyacrylamides acted as total non-selective flocculants. This obvious discrepancy revealed the importance of conditioning in selective flocculation. Reverse flotation with a simultaneous use of polyacrylamide, which significantly reduced consumption of amine collector, can be selective only after sufficient conditioning. It was found that the polyacrylamides with a different degree of anionicity responded differently to conditioning. Only the addition of the polymers with a lower degree of anionicity promoted the flotation of gangue. The flocculation turned out to be significantly more selective after more intense conditioning with polyacrylamide.

Since in reverse flotation coal is not recovered as a hydrophobic froth product but as a hydrophilic concentrate, it is much easier to utilize such a product to produce a coal-water slurry. The rheological measurements indicate that the viscosity reducing chemical additives are not needed when the slurries are prepared from the reverse flotation clean coal product.

Additionally, since coal reverse flotation increases the column carrying capacity because of the reduced yield of froth product, it could minimize the associated problems in the use of flotation columns in coal flotation.

While this thesis deals specifically with coal reverse flotation, these results have much broader implications since amines and polyacrylamides are widely applied in flotation and flocculation.

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A	cross-sectional area of a nitrogen molecule (area)
A_{BET}	specific surface area as determined by the BET method (area per mass)
BET	the method of determination of the specific surface area of solid particles developed by Brunaer, Emmet and Teller.
$C_{Equilibrium}$	equilibrium concentration in solution (mole per volume)
c_i	concentration of compound i in solution (mole per volume)
$C_{Initial}$	initial concentration in solution (mole per volume)
CMC	carboxymethyl cellulose
c.m.c	critical micelle concentration (mole per volume)
CWS	coal water slurry
D	shear rate (time $^{-1}$)
$DTAB$	dodecyltrimethyl ammonium bromide
$DTAC$	dodecyltrimethyl ammonium chloride
$F.C.$	fixed carbon content in coal (mass percent)
G	Gibbs free energy (energy)
g	gravity constant (length per squared time)
h	height of a capillary rise (length)
HMW	high molecular weight (dimensionless)
h_{SOL}	height of a capillary rise for a dilute solution (length)
h_W	height of a capillary rise for water (length)

IR	infrared spectroscopy
LMW	low molecular weight (dimensionless)
M	molecular weight (Daltons)
m	mass of material in adsorption tests (mass)
MIBC	methyl isobutyl carbinol
N	Avogadro number (number of molecules per mole)
ODA	octadecylamine
P	partial pressure of nitrogen (force per surface area)
PAM	polyacrylamide
p_0	saturated vapor pressure of nitrogen (force per surface area)
*PSS*10	polystyrene sulfonate
R	universal gas constant (energy $\times$ mole^{-1} $\times$ temperature^{-1})
r	radius of a capillary (length)
S_{Total}	total surface area (area)
T	absolute (Kelvin) temperature (degrees)
V	volume of pulp in adsorption tests (volume)
V.M.	volatile matter content in coal (mass percent)
X	weight of nitrogen adsorbed (mass)
X_m	weight of nitrogen at a monolayer coverage (mass)
Γ	adsorption density (mole per unit area, or mass per unit area)
Γ_{Ads}	amine adsorption density (mole per unit area)
Γ_{SL}	adsorption density at solid-liquid interface (mole per unit area)

Γ_{SV}	adsorption density at solid-vapor interface (mole per unit area)
γ	surface tension (force per length, or energy per unit area)
γ_{LV}	surface tension at liquid-vapor interface (force per length, or energy per unit area)
γ_{SL}	interfacial tension at solid-liquid interface (force per length, or energy per unit area)
γ_{SV}	interfacial tension at solid-vapor interface (force per length, or energy per unit area)
η_C	Casson viscosity (mass $\times$ time^{-1} $\times$ length^{-1})
η_N	Newtonian viscosity coefficient (mass $\times$ time^{-1} $\times$ length^{-1})
η_{PL}	plastic viscosity (mass $\times$ time^{-1} $\times$ length^{-1})
μ_i	chemical potential of compound i (energy per mole)
μ_i°	standard chemical potential of compound i (energy per mole)
θ	contact angle (degree)
ρ_1	density of a liquid (mass per volume)
ρ_2	density of a gas (mass per volume)
τ	shear stress (force per area)
τ_B	Bingham yield stress (force per area)
τ_C	Casson yield stress (force per area)
τ_{SOL}	adhesion tension of a solution (force per length, or energy per unit area)
τ_W	adhesion tension of water (force per length, or energy per unit area)

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adhesion tension	difference between the solid/gas and solid/liquid interfacial tensions, a measure of work required for dewatering a solid surface
adsorption density	amount of a reagent adsorbed at an interface (mole/g or mole/m^2)
ash	solid residue after burning coal under standardized conditions; the ash is a relative measure of the amount of mineral matter in coal (mass percent)
coagulation	aggregation process based on reducing interparticle repulsion, i.e., by compressing the electrical double layer or by charge neutralization
coal	organic sedimentary rock, composed of macerals intermixed with minerals
coal water slurries	aqueous suspensions containing 50-75% by weight of fine coal, usually cleaned by flotation
concentrate	flotation product that contains valuable component; in this thesis: in the forward flotation this is the froth product and in the reverse flotation this is the product that does not report to the froth
contact angle	angle formed by a drop of liquid (water) resting on the surface of a solid (measured through the liquid)
degree of anionicity	percent of amide groups in polyacrylamide replaced by carboxylic groups (percent)
extraneous ash	the portion of ash that can be separated from coal organic matter by physical means
fines	commonly in coal flotation this is a -0.5 mm size fraction
flotation	process of separation based on differences in the surface properties of mineral particles
flocculation	aggregation process induced by polymer bridging individual solid particles
forward flotation	process of separation in which valuable material (coal in this thesis) is floated and report to the froth product

hydrophilic coal	coal that is wetted by water; water spreads on the surface of such a coal; commonly these are low-rank (or oxidized) coals
hydrophobic coal	coal which is not wetted by water; commonly these are bituminous coals
inherent ash	the portion of ash resulting from the finely disseminated mineral matter that cannot be separated from coal organic matter by physical means
macerals	the smallest distinguishable components of coal organic matter, different macerals vary in physical and chemical properties
metallurgical coal	coal used for making a coke
mineral matter	inorganic compounds associated with coal
oxidation	process in which oxygen adsorbs on and reacts with coal surface
polyacrylamide	synthetic polymer used as a flocculant
raw coal	untreated, usually run-of-mine coal
rheology	the science of deformation or flow of matter,
reject	flotation product that is not recovered, usually gangue
reverse flotation	flotation process in which valuable material (coal in this thesis) is depressed and does not report to the froth product
selective flocculation	process of separation by selectively aggregating very fine particles of different minerals into flocs to enable their effective separation
surface tension	the work required to increase the area of a surface isothermally and reversibly by unit amount (force per unit length or energy per unit area)
shear stress	the force applied to cause flow, parallel to the direction of flow, per unit area
steric stabilization	stabilization against aggregation of particles suspended in a liquid by adsorbed polymer layers
thermal coal	coal used as a fuel for power generation

wettability   the ability of water to spread on the surface of solid; wettable-hydrophilic; non-wettable-hydrophobic

yield   mass percentage of flotation products

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CHAPTER 1   INTRODUCTION

Conditioning with reagents is a very important unit operation in flotation. The intensity of agitation and subsequent dispersion are interrelated and are closely associated with the time required for physical and chemical reactions to take place (Wills, 1992).

Although conditioning prior to flotation is now considered standard practice and is an important factor in decreasing flotation time, it depends on a number of factors such as collector type and pH. Firstly the conditioning depends on the type of a collector (Laskowski and Nyamekye, 1994). The collectors can broadly be classified into ionic and non-ionic. While the former are usually highly soluble in water, the latter, and especially the oily collectors are insoluble in water and require intense conditioning which can only be reduced by prior emulsification of the reagents (Sun et al., 1955; Laskowski, 2001).

While it is convenient to classify collectors into ionic and non-ionic, and assume that the former are easily soluble in water, the closer inspection reveals that this is not necessarily true. The ionic collectors can be further classified into strong and weak electrolytes (Castro, Vurdela and Laskowski, 1986; Vurdela and Laskowski, 1987; Laskowski, 1988, 1989 and 1993; Laskowski, Vurdela and Liu, 1988). The weak electrolyte collectors may be poorly soluble in water. Whenever the collector is poorly soluble in water, it requires longer/more intense conditioning. In such a case the collector is present in the form of colloidal particles in the pulp, which are characterized by slow diffusion, and longer conditioning times are then required to improve flotation. Flotation with fatty acids in acidic solutions depends strongly on the conditioning time and can be very much improved after longer conditioning times, while the results in the alkaline environment do not exhibit significant dependence on conditioning since the adsorption equilibrium is established fairly quickly for an ionized collector (Laskowski and Nyamekye, 1994).

Froth flotation utilizes the differences in physico-chemical surface properties of particles of various minerals. After treatment with reagents, such differences between the minerals within the flotation pulp become apparent and for flotation to take place, an air bubble must attach itself to a hydrophobic particle and lift it to the pulp surface. The

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hydrophobicity results from the adsorption of the collector onto the mineral to be floated. The collector on the mineral particle is then needed for the particle-to-bubble attachment. The collector could also be brought to this process by the bubbles carrying the collector, which kinetically may be much more favourable. The theoretical analysis of a collector adsorption at solid-liquid, solid-gas and liquid-gas interfaces made by de Bruyn et al. (1954) indicates the importance of the adsorption of a collector at the mineral-air interface. Leja and Schulman's penetration theory (1954) shows that bubbles can carry a very sufficient portion of the reagents. Digre and Sandvik (1968) measured the adsorption of amine on quartz through bubble interaction and found that the adsorption density was a few times higher in the presence of bubbles. Somasundaran (1968) and Somasundaran and Fuerstenau (1968) confirmed the significant role of collector adsorption on the bubble surface in determining the bubble-mineral attachment. It is puzzling that all the experimental measurements which showed that the adsorption density at the solid/gas interface is higher than the adsorption density at the solid/liquid interface were carried out with amines (Digre and Sandvik, 1968; Somasundaran, 1968; Ter-Minassian-Saraga, 1975). This correlates rather well with some observations that while flotation with anionic collectors (e.g. fatty acids) is slow and requires intense conditioning at high solids content, flotation with amines is rapid and requires only short conditioning times (Baaron et al.,1962; Zhang et al., 2002). This leads to the conclusion that some special reasons must exist, which explain why amines are so well transported by bubbles. Laskowski et al. (1989) working with weak electrolyte collectors showed through electro-kinetic measurements that these surfactants are strongly adsorbed onto bubbles. Somasundaran (1968) analysed the adsorption of a collector at the mineral/air, mineral/solution and solution/air interfaces through Young's equation and postulated that reducing conditioning time was more favourable for a bubble-particle attachment to occur. He then suggested that the collector could be introduced into the flotation system in the form of aerosol with gas stream as it was demonstrated by Wada et al. (1968) who was able to significantly reduce the consumption of reagents using this technique.

In this thesis, a quaternary amine, dodecyltrimethyl ammonium chloride (DTAC), is selected as a collector for coal reverse flotation. Reverse flotation of coal has been studied by several researchers (Stonestreet and Franzidis, 1988, 1989 and 1992; Pawlik,

2002; Pawlik and Laskowski, 2003a and 2003b). The tests showed that coal reverse flotation is possible but a huge amount of collector (over 6 kg/t) is needed in the process.

In order to reduce the DTAC consumption, a new technique, which is referred to as the zero-conditioning time process, has been tested in this thesis. This involves addition of DTAC directly into the flotation cell without any conditioning. It has been found that the zero-conditioning time method allows significant reduction in the consumption of the collector. With the addition of a suitable polymer, A100 polyacrylamide, and properly selected conditioning conditions, the consumption of DTAC in the zero-conditioning time flotation experiments is further significantly reduced.

Polymers used as flocculants in mineral processing circuits promote settling, aid in filtration of fine suspensions, and are used in solid/liquid separation unit operations in which a so-called total flocculation occurs. The hydrodynamic conditions in the conditioning stage preceding flocculation (total flocculation) have been extensively studied and procedures which describe how such tests should be carried out are now widely accepted (Hogg, 1999).

Selective flocculation was developed to selectively separate very fine particles of different minerals that are much too fine to be treated by other methods. Yarar and Kitchener (1970), in their fundamental paper on selective flocculation, formulated general principles governing the process. The most important two principles involve initial full dispersion of the pulp, and selective adsorption of the chosen flocculant only on those minerals that are to be flocculated. These recommendations also include gentle stirring of the settled flocs to release the entrapped particles and to consolidate the flocculated materials. As pointed out by Hogg (1999), when a polymer flocculant is added to a suspension these macromolecules are initially adsorbed on external floc surfaces, and the adsorption and flocculation are simultaneously coupled processes with breakage and reformation of the flocs occurring continuously. The addition of a high molecular weight flocculant to stable dispersions leads to the development of bimodal size distributions consisting of dispersed primary particles and some relatively large flocs.

Since fine particles are difficult to float it would be logical to aggregate them into larger particles which, provided that the adsorbed polymer does not interfere with subsequent adsorption of the collector, could then be recovered by flotation. Usoni et al.

(1968) were perhaps the first to study such a use of flocculants in the flotation process. In their flocculation tests, a given amount of a flocculant solution was added to a suspension of a finely ground mineral and the system was then gently agitated. Since hydrodynamic conditions in the mechanical flotation cell are very different, their flotation tests with flocculants were carried in a small pneumatic cell. It is now well established that flocculation tests are best carried out by adding a flocculant solution to a vigorously agitated suspension. However, agitation should be discontinued immediately after the reagent addition to avoid the breakage of the flocs. According to Hogg (1999), flocculants are not very effective for treating stable dispersions. If stable suspensions are treated with a flocculant some flocculation is observed but unless very high polymer dosage is used, large quantities of dispersed primary particles remain. Since the stability/coagulation ranges of physico-chemical conditions for different minerals may vary, the flocculation process of individual mineral components in a mixed suspension may be different and should respond differently to conditioning.

Selective flocculation-flotation is employed in the processing of potash ores. In the flotation of potash ores, long-chain primary amines are used to float sylvite from halite. However, sylvinite ores also contain insoluble minerals (clays, dolomite, anhydrite, etc.) which appear in the pulp as slimes. Since the surface area of such fine particles is huge, they abstract large quantities of the amine and make the process both expensive and not very selective. In the selective flocculation-flotation process used in potash flotation (Brogoitti and Howald, 1974; Chan et al., 1982; Cormode, 1985; Perucca and Cormode, 1999), polyacrylamide flocculants are used to selectively flocculate the slimes which are then floated off with secondary amines. As a result of flocculation, the surface area of the flocculated slimes decreases and since polyacrylamides apparently do not interfere with the action of the secondary amine collector, the flocs are then successfully removed from the system by flotation. The consumption of amine in this process is likely reduced because of the decreased surface area of the flocculated slimes.

In the reverse flotation of coal, quaternary amines are used as a collector to float gangue particles. It was found that while the process was technically possible it required large quantities of amine. It is quite likely that the large amine consumption results from the fine size of the treated particles. The amine consumption can then be reduced by

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flocculation of the fines in the reverse coal flotation process. But only selective flocculation can aid flotation and so the process also requires development of a selective flocculation procedure.

It is generally accepted that selective flocculation depends on the selective adsorption of a flocculant on the surfaces of the minerals to be flocculated. But polymer adsorption and flocculation are simultaneously coupled processes, and it was found that under intense conditioning formation of smaller separate flocs of coal and gangue dominates over formation of large non-selective flocs. Column flotation tests confirmed that the separation depends on the conditioning with polyacrylamide. The amine consumption is reduced due to the aggregation of fines.

The application of the zero-conditioning time concept along with the use of high molecular weight polymers in reverse coal flotation turned out to be quite successful. Since amines and polyacrylamides are widely used in flotation, it is quite likely that the major conclusions of this thesis could also find broad applications in other areas.

CHAPTER 2   OBJECTIVES

2.1 Research objectives

A lot of experimental evidence is available to indicate that amines carried by bubbles have a better chance to make particles floatable. The main objective of this thesis is to experimentally verify the concept of zero-conditioning time flotation through reverse coal flotation along with the use of a polyacrylamide. The objectives also include the development of a reverse flotation process for a low rank hydrophilic coal.

2.2 Research strategy

1. To determine the floatability of pure calcite and dolomite with amine:

In reverse coal flotation, amine is used as a collector to float gangue minerals. The flotation of pure calcite and dolomite is first tested to investigate the floatability of gangue minerals with amine.

2. To verify the zero-conditioning time concept through reverse coal flotation:

The conventional reverse flotation (collector is conditioned) of a mixture of subbituminous coal and gangue minerals is carried out, followed by cleaning of the subbituminous coal to develop a reverse flotation process. In the reverse flotation of the subbituminous coal, both conventional and zero-conditioning (collector is not conditioned) reverse flotation methods are tested. The zero-conditioning time flotation process is verified and optimized along with the use of a polyacrylamide to reduce further the collector consumption in reverse coal flotation.

3. To show the effect of polyacrylamides on reverse coal flotation:

The effect of various polyacrylamides with a different degree of anionicity and molecular weight on the zero conditioning method of reverse coal flotation is assessed. The most effective polyacrylamides are selected through flotation tests. The flocculation tests are carried out to investigate the effect of those flocculants on the behavior of the tested suspension of bituminous coal. Since total flocculation does not favour selective flotation, the ways of using polyacrylamides are studied to promote selective flocculation.

4. To assess the adsorption of amine on coal and silica:

Adsorption of amine on raw coal, clean coal and silica is investigated. The adsorption at solid-liquid and solid-liquid-gas phases is carried out to study whether bubbles can bring more amine to the mineral surface. The effect of polyacrylamides on amine adsorption is also examined.

5. To characterize the rheology of coal-water slurries:

The rheological properties of coal-water slurries prepared from the clean coal products of forward and reverse flotation are studied to find out the possible advantages of using reverse flotation in the seam-to-steam strategy of fine coal utilization.

6. To measure the column carrying capacity:

In the reverse coal flotation, the yield of froth product is reduced and this should increase the column carrying capacity. The experiments are carried out to measure the column carrying capacity in the forward and reverse flotation tests.

CHAPTER 3   LITERATURE REVIEW

3.1   Application of thermodynamics in flotation: zero-conditioning time concept

3.1.1 Floatability of minerals

Flotation is a process for separating valuable minerals from gangue based on the differences in their surface physico-chemical properties. The majority of naturally occurring minerals are hydrophilic, but even the hydrophilic minerals can be made hydrophobic by adsorption of suitable collectors. When the particles are agitated in water and air bubbles are introduced into the pulp, the hydrophobic particles adhere to bubbles and the bubble-particle aggregates then rise to the surface of the pulp and can be removed as a froth product. The process can only be applied to relatively fine particles; if they are too large the adhesion force between the particle and bubble will be smaller than the gravity force and the bubble will detach from the particle.

In flotation, the valuable mineral is usually transferred to the froth, leaving the gangue in the pulp. This is direct forward flotation as opposed to reverse flotation in which the gangue reports to a froth product.

The air-bubbles can only stick to the mineral particles if they can displace water from the mineral surface and this can only happen if the mineral is to some extent hydrophobic. Having reached the surface, the air bubbles can only continue to support the mineral particles if they can form a stable froth, otherwise they will burst and the mineral particles will drop back to pulp. To achieve these conditions it is usually necessary to use several flotation reagents.

There are three major groups of flotation reagents: collectors, modifiers and frothers. Collectors adsorb on mineral surfaces, rendering them hydrophobic and facilitating bubble-solid attachment. Frothers help maintain a reasonably stable froth. Modifiers are used to control the flotation process. They either activate or depress collector adsorption and hence mineral attachment to air bubbles and are also used to control the pH of the flotation system and particle aggregation.

The flotation system is a three-phase system and consists of solid, liquid and gas. At equilibrium the contact angle at three-phase contact is given by Young's equation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta \qquad\qquad (3.1)$$

where γ_{SV}, γ_{SL} and γ_{LV} are the interfacial tensions or surface free energies of solid-air, solid-water and water-air interfaces, respectively. θ is the contact angle between the mineral surface and the bubble through the aqueous phase as shown in Figure 3.1. The success of flotation depends upon the creation of such a finite contact angle at the three-phase contact: mineral-water-air. If the mineral is completely wetted by the water phase, the contact angle is zero and bubbles cannot attach to the mineral. However, when the contact angle is finite, the surface free energy of the system, water-air-mineral particle, diminishes when such particles attach to the bubbles.

Considering a bubble attached to the mineral surface in solution, the change of the surface free energy of the system after the attachment is given by:

$$\Delta G = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV}) \qquad\qquad (3.2)$$

By combining Equation 3.2 with Equation 3.1 one obtains:

$$\Delta G = \gamma_{LV} (\cos\theta - 1) \qquad\qquad (3.3)$$

It can be seen from Equation 3.3 that for a completely hydrophilic surface ($\theta = 0$) ΔG is zero. Therefore, the probability of the bubble-particle attachment is zero. Increasing contact angle results in a ΔG being more negative. The greater the contact angle the greater is the probability that the particle will attach to bubble. With a few exceptions, almost all minerals are completely wetted by water. Thus, the art of flotation relies on adding collectors to water to selectively create a finite contact angle with the mineral to be floated without affecting the wettability of other minerals.

In Young's equation, the surface tension of the liquid (γ_{LV}) can easily be determined, but the two surface tensions of the solid (γ_{SV} and γ_{SL}) cannot be measured directly. However, this equation is still very useful. By carrying out contact angle

measurements it is possible to establish how $\gamma_{SV} - \gamma_{SL}$ varies with the addition of solutes to the liquid phase. Also, Equation 3.1 affords a convenient starting point for calculating energy changes involved in the process of bubble-particle attachment. If the surface tension of the liquid (γ_{LV}) is considered constant, an increase in $\gamma_{SV} - \gamma_{SL}$ will tend to decrease the contact angle. A decrease in $\gamma_{SV} - \gamma_{SL}$ corresponds to an increase of the contact angle. In cases where $\gamma_{SV} - \gamma_{SL} > \gamma_{LV}$ the contact angle is zero. It will only reach finite values when $\gamma_{SV} - \gamma_{SL}$ is smaller than γ_{LV}. Thus, on the basis of Young's equation and contact angle measurements alone, it can be learned how flotation reagents affect the difference ($\gamma_{SV} - \gamma_{SL}$).

3.1.2 Adsorption and adhesion tension

According to thermodynamics, a process can spontaneously occur if the free energy of the system decreases. Thus, following free energy changes, thermodynamics can be used to analyze the probability of various flotation sub-processes.

The thermodynamics can be applied to analyze such molecular interactions at interfaces. De Bruyn et al. (1954) used Young's and Gibbs' equations to analyze the effect of flotation reagents on the contact angle.

A quantitative relationship between the surface tension or interfacial tension and the adsorption occurring at a surface or an interface is given by the Gibbs equation. At constant temperature and pressure, it gives:

$$d\gamma = -\sum_i \Gamma_i d\mu_i \qquad (3.4)$$

where $d\gamma$ is the change in surface tension accompanying a change in chemical potential $d\mu_i$ of the component i of the system, and Γ_i is the number of moles of component i per unit area of surface.

In dilute solutions, the chemical potential of a solute is given by the expression:

$$\mu_i = \mu_i^0 + RT \ln c_i \qquad (3.5)$$

where c_i is the concentration of component i in the bulk solution. When Equation 3.4 is combined with Equation 3.5, it becomes:

$$\Gamma = -\frac{1}{RT}\frac{d\gamma}{d\ln c} = -\frac{1}{2.3RT}\frac{d\gamma}{d\log c} \qquad (3.6)$$

Having $\dfrac{d\gamma}{d\log c}$ determined from the experiments, adsorption Γ can be calculated.

Flotation systems usually contain such a large number of components that writing down the complete Gibbs equation for them, though not impossible, would be tedious. Fortunately, in most cases what happens during simultaneous changes of all the chemical potentials is not of interest, but rather the effects produced by the addition of a single substance (collector, activator or depressant) to the system. In a dilute solution, the addition of a small amount of substance A to the system can be considered to change only the chemical potential of this component and that of the solvent. The chemical potentials of all the other components remain unchanged. Furthermore, the mineral is present as a separate phase and has, therefore, a constant chemical potential. When chemical reactions between the added substance and one or more of the other components occur, more complete forms of the Gibbs equation have to be considered.

In all cases of flotation, the collector is positively adsorbed to the mineral. This means that Γ_i (Equation 3.6) is a positive quantity and the concentration of the collector on the mineral surface is higher than that in the solution. Consequently, according to Equation 3.4, the addition of a collector lowers the interfacial tension between mineral and solution. According to Equation 3.1 and Figure 3.1, the decrease of γ_{SL} would lower the contact angle. Experiments, however, show an increase in the contact angle when a collector is used. The experimental observation cannot be explained by an increase in the surface tension of γ_{LV}, which, if affected, decreases slightly on addition of the collector.

The conclusion is apparent that in the collector system considered here, increase in the contact angle has to be explained by a decrease of the mineral-air surface tension (γ_{SV}), a decrease which has to be larger than the decrease in γ_{SL}. The decrease in the mineral-air surface tension (γ_{SV}) is evidently brought about by adsorption of the collector to that surface. If the mineral-air interface is in equilibrium with the solution, the chemical potential of the collector should be the same at the mineral-air and mineral-solution interface. A larger change in γ_{SV} than in γ_{SL} then demands a higher adsorption density of the collector at the solid-air interface.

The principal value of applying the Gibbs adsorption equation to the flotation system is that the results point directly to the need for experimental work in several hitherto neglected areas of the surface chemistry of flotation. Above all, the relations developed by combining the Gibbs' equation and the Young's equation show that more attention should be given to the mineral-air interfaces. This raises the question whether by studying adsorption only at solid/liquid interfaces the process can be adequately described.

Leja and Schulman (1954) demonstrated that the reagents used as frothers are effective only when there is a suitable degree of molecular interactions between collector and frother molecules. They showed that frothers adsorb onto mineral particles if these particles are first contacted with collectors. These findings led to the development of the particle-to-bubble dynamic attachment theory, also known as the Leja-Schulman penetration theory. Figure 3.2 shows the distribution of collector and frother molecules at interfaces and in bulk solution under flotation conditions (when an air bubble and a particle approach each other). As soon as the air bubble contacts the solid surface, Figure 3.3, the collector-frother molecules at the air-water interface can penetrate the diffused monolayer at the solid, and adsorb strongly onto the solid surface, thus greatly increasing local surface concentration and local hydrophobic character of the surface. As Leja (1956/57, 1957) pointed out, in most cases of flotation collectors both ionized and molecular forms appear at the same time in the solution. While the ionized form may preferentially adsorb onto solid, the molecular form may preferentially accumulate on the surface of bubbles. In such a case, the situation is identical to the one with a collector and frother. Leja and Schulman's penetration theory tells us a very important but somewhat neglected mechanism of

adsorption: the species of flotation reagents can be brought to mineral surfaces by bubbles carrying these species.

Adsorption at a solid/liquid interface can be easily measured using the reagent concentration difference before and after conditioning. Adsorption at a liquid/gas interface can also be calculated by applying Gibbs equation since the surface tension at liquid/gas interface can be conveniently measured. An estimate of reagent adsorption at solid/gas interface can be obtained from the adhesion tension (τ) measurements and the use of Young's equation.

Adhesion tension, τ, a measure of force required for dewatering the solid surface, is given by the equation:

$$\tau = \gamma_{SV} - \gamma_{SL} = \gamma_{LV}\cos\theta \qquad (3.7)$$

By differentiating both sides of Equation 3.7 one gets:

$$d\tau = d(\gamma_{SV} - \gamma_{SL}) \qquad (3.8)$$

Application of the Gibbs equation (Equation 3.6) to solid/gas and solid/liquid interfaces, respectively, gives the adsorption densities at those interfaces expressed as:

$$\Gamma_{SV} = -\frac{d\gamma_{SV}}{RTd\ln c} \qquad (3.9)$$

$$\Gamma_{SL} = -\frac{d\gamma_{SL}}{RTd\ln c} \qquad (3.10)$$

By combing Equations 3.9 and 3.10, one gets:

$$\Gamma_{SV} - \Gamma_{SL} = -\frac{1}{RT}\left(\frac{d(\gamma_{SV} - \gamma_{SL})}{d\ln c}\right) \qquad (3.11)$$

By combining Equations 3.8 and 3.11:

$$\Gamma_{SV} - \Gamma_{SL} = -\frac{1}{RT}\left(\frac{d\tau}{d\ln c}\right) \qquad (3.12)$$

Equation 3.12 can be used to calculate the adsorption density at solid/gas interfaces (Γ_{SV}). To estimate Γ_{SV}, the relation between adhesion tension (τ) and solute concentration(c) needs to be determined.

Somasundaran (1968) used the capillary rise method to estimate the adhesion tension (τ):

$$\tau = \gamma_{SV} - \gamma_{SL} = \gamma_{LV}\cos\theta = \frac{1}{2}grh(\rho_1 - \rho_2) \qquad (3.13)$$

where g is the gravity constant, r is the radius of the capillary, h is the capillary rise, and $\rho_1 - \rho_2$ is the difference in density of the liquid and gas medium. From Equation 3.13, at constant r for liquids of similar density, adhesion tension is proportional to the capillary rise. Thus, using water as a standard, for dilute collector solution, the adhesion tension of the solution (τ_{SOL}) is given by:

$$\tau_{SOL} = \frac{h_{SOL}}{h_W} \times \tau_W \qquad (3.14)$$

For water on glass θ is zero, and τ_W is 72 dynes per cm. With these values, and knowing the capillary rise for water and dilute collector solution, the adhesion tension of the solution can be calculated using Equation 3.14.

Somasundaran (1968) measured the adhesion tensions at four different dodecylammonium acetate concentrations while varying pH. The results are shown in Figure 3.4. It can be seen that these curves exhibited a sharp decline around pH 8 as the solution was made alkaline and showed the greater surface activity of neutral molecules in

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the presence of their ions. As the pH of the ammonium acetate solution was increased, the adhesion tension decreased and a further increase in pH resulted in an increase in adhesion tensions. A decrease in adhesion tension is a result of higher adsorption density of surfactant molecules at the solid/gas interface rather than at the solid/liquid interface. The adhesion tension is affected by pH because a change in pH results in a change in the ratio of neutral molecules to their ions which preferably adsorb onto the different interfaces. A decrease of the wetting tension when pH became more alkaline thus indicated that the molecular amine that appeared over this pH range tended to accumulate at the liquid/gas interface and gave a much higher adsorption density at the solid/gas interface in comparison with adsorption at the solid/liquid interface. This is similar to the results one could see after adding a frother to the flotation system in the Leja-Schulman theory.

Somasundaran (1968) also calculated the adsorption of dodecyl-ammonium acetate at the glass-gas interface and this was compared with the adsorption of dodecyl-ammonium acetate at the liquid-gas and solid-liquid interfaces. The results are shown in Figure 3.5.

Figure 3.5 shows that the adsorption of dodecyl-ammonium acetate at the solid/gas interface is almost the same as the adsorption at the liquid/gas interface. This result is significant since it shows that the bubbles can carry enough collector to the solid/gas interface.

In accordance with Young's equation, the solid becomes hydrophobic only when:

$$\gamma_{SV} - \gamma_{SL} < \gamma_{LV} \qquad\qquad (3.15)$$

To fulfill the condition given by Equation 3.15, γ_{SV} should be kept small and γ_{SL} should be made as large as possible. Since positive adsorption always decreases surface tension, conventional conditioning of mineral particles with a collector prior to flotation only reduces γ_{SL}. Therefore, to keep γ_{SL} as large as possible and reduce γ_{SV}, the collector should be introduced into the flotation system in the form of aerosol with a gas stream. Transfer of the collector to the solid-gas interface is energetically more favourable in the gas-phase adsorption process than in the liquid-phase adsorption process. This thermodynamic principle is behind the concept of the zero conditioning flotation process in

which flotation reagents are not conditioned at all before flotation but rather introduced into the flotation system along with air bubbles.

Digre and Sandvik (1968) experimentally confirmed that bubbles can bring more collectors to the mineral surfaces. They demonstrated in their experiments with hydrochlorides of C_{12}, C_{14} and C_{16} primary amines that adsorption onto quartz more than doubled when the conditioning of a quartz suspension was carried out in the presence of gas bubbles. The results reveal that under the test conditions, an introduction of bubbles increased the amine adsorption on quartz by a factor of 2-3. Digre and Sandvik further claimed that the number of bubbles present and the contact opportunities between bubbles and quartz in the adsorption tests are on a much lower level than in an intensely aerated and agitated flotation cell. Therefore, a far stronger effect in a practical flotation system can be expected.

Digre and Sandvik's results again confirmed that the adsorption density of amines at the liquid-gas interface is much higher than the adsorption density at the solid-liquid interface and that the collector molecules/ions adsorbed at the liquid-gas interface can be carried mostly on the surfaces of gas bubbles. Therefore, a bubble contacting a solid under the above conditions will bring enough collector molecules/ions to the mineral surface to induce flotation. Their results also correlate well with the classical experiment of Blodgett and Langmuir (1937), who demonstrated that an oriented monomolecular calcium palmitate film may easily be transferred from a gas-liquid interface to an amenable solid surface. Ter-Minassian-Saraga (1964) demonstrated that such a transfer takes place from the gas/liquid interface of aqueous solutions of dodecyl-trimethyl-ammonium bromide on to glass slides. Ter-Minassian-Saraga (1975) measured the adsorption of DTAB at the silica-liquid interface and silica-vapor interface and also found that adsorption was higher in the latter case. The importance of adsorption at the liquid/gas interface was demonstrated by Eigeles and Volova (1960) who showed that when depressing and activating compounds adsorb onto bubbles they show a strong effect on flotation.

More recently, Yaminsky and Yaminskaya (1995) investigated the adhesion tension of smooth and homogeneous silica glass surfaces by solution of cetyltrimethylammonium bromide (CTAB) using the Wihelmy plate method. In this method, the adhesion tension was measured using a high stability balance. The balance was moved up and down with a

speed control system incorporated in the apparatus. Measurements were performed in a laminar flow cabinet at a temperature range of 18-21°C. The experimental set-up was partly covered to reduce evaporation. The force (F) on the plate additional to the weight of the plate in air has two additive components, the buoyancy force:

$$F_b = L_x L_y \rho g Z \tag{3.16}$$

and the capillary force:

$$\frac{F - F_b}{L} = \frac{F_c}{L} = \gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL} = \tau \tag{3.17}$$

where L_x, L_y and $L \approx 2L_y$ are the thickness, the width, and the perimeter of the plate respectively, Z is the height of the plate immersed into the solution, and ρ is the density of the liquid (the density of air is neglected). The results are shown in Figure 3.6.

The wetting tension which initially decreased with concentration (because the contact angle increases) goes to a minimum above the point of zero charge (p.z.c.) and then increases up to the critical micelle concentration (cmc). At this point it approaches the value of the surface tension of the solution (reduced as compared to pure water). The contact angle is close to zero above the cmc.

Under equilibrium conditions, the wetting tension equals the difference between the solid/vapor and the solid/liquid interfacial tensions. The difference between the values of adsorption for the two interfaces is calculated by applying the results of wetting tension measurements (as shown in Figure 3.6) to Gibbs equation. The results are shown in Figure 3.7.

The difference between the values of adsorption for two interfaces is positive at a low concentration and negative at a higher concentration (on approaching cmc). In the lower concentration range, adsorption at the silica/air interface is larger than at the silica/water interface. This corresponds to the range of the wetting tension isotherm where the wetting tension decreases with concentration (the contact angle increases). The

adsorption difference (determined by the absolute Γ_{SV} value) is more or less constant going down to a concentration as low as 10^{-6} M. As the wetting tension goes through a minimum and increases on approaching the cmc, the adsorption difference changes sign, becomes negative, and above the cmc its absolute value becomes constant and at least twice as large as the corresponding positive value at low concentrations. Though adsorption of CTAB and similar cationic surfactants at the interface between silica and water at normal pH is low up to the p.z.c., it increases rapidly with concentration at about half the cmc. At cmc Γ_{SL} value is about 2×10^{14} molecules/cm^2 (Yaminsky, 1994). The more than 10-fold increase in adsorption at the solid/liquid interface is due to a "hydrophilic" layer condensed on top of the hydrophobic one by the mechanism of hydrophobic attraction. While the "hydrophobic" adsorption is larger at the solid/vapor interface, the "hydrophilic" layer is condensed only in contact with the aqueous phase. Its formation changes the sign of the adsorption difference and leads to an increase of the wetting tension.

Based on this result, dewetting effects of cationic surfactants on silica receive a new interpretation. A decrease in the wetting tension with increasing amine concentration is not due to an increase in adsorption at the solid/liquid interface (as is usually assumed) but due to the much larger adsorption at the solid/vapor interface. The adsorbed layer at the solid/vapor interface is condensed at very low bulk concentrations of the surfactant in the solution. This adsorption stays constant in concentrations up to the p.z.c. An increase of adsorption at the solid/liquid interface with increasing concentrations contributes to an increase, not a decrease, of wetting tension (this tends to make the surface more hydrophilic). This contribution is, however, negligible on the background of a "hydrophilic" layer condensed on top of the hydrophobic one by the mechanism of hydrophobic attraction. This leads to a subsequent increase in the overall wetting tension at higher concentrations up to the cmc.

All these results agree remarkably well with thermodynamics which undermines the importance of investigating surfactant adsorption at both liquid/gas and solid/gas interfaces. In other words, bubbles are important in the flotation system not only because they lift hydrophobic particles to the froth layer but also because they are the primary

means of transportation of flotation agents to the points of bubble-to-particle attachment in amine flotation (Laskowski, 2005). To improve the probability of particle-to-bubble attachment in flotation, the bubbles should carry as much of flotation reagents as possible to increase adsorption at the solid/gas interface, or the conditioning time should be kept short to reduce the adsorption at the solid/liquid interface since conditioning always results in enhanced surfactant adsorption at the solid/liquid interface. To reduce the conditioning time, surfactants can be injected into the flotation systems along with bubbles to carry the surfactants.

3.1.3 Zero conditioning time concept and its application in flotation

The zero-conditioning time concept in flotation results from the thermodynamic analysis of the particle to bubble attachment in flotation. The idea is to introduce collector molecules/ions directly to the mineral surface via bubbles in order to reduce γ_{sv} as much as possible. This concept seems to be especially important in cationic flotation.

The concept of flotation by gas-phase transport of atomized reagents, such as frother and oily promoters was tested for several systems - coal, tar, copper porphyry ore and lead-zinc sulphide ore. Wada et al. (1968) were probably the first to present experimental results on the aerosol reagent addition. In their experiments, MIBC (Methyl Isobutyl Carbinol) was added as aerosols into a batch mechanical flotation machine (the aerosol generator was not described). The separation results on a lead-zinc sulphide ore were compared with the results of tests carried out in a conventional way, i.e., using liquid phase frother additions. At the optimum separation performance, frother consumption (via aerosol addition) was reported to be only 1/5 of the consumption needed in the conventional tests.

Miller and Misra (1983) carried out coal flotation experiments by gas-phase transport of atomized oil. The experimental results for the thickener underflow from the preparation plant operated by Beaver Creek Coal at Price, Utah, are shown in Figure 3.8. This sample contained 60 wt % below 38 μm material and had an ash content of about 33-38 %. The rate of flotation by gas-phase transport was significantly faster than that for conventional oil addition to the slurry. Moreover, froth formation by atomization was

consistent and uniform, a very desirable feature from a plant operation point of view.

Ultrafine coal flotation by gas phase transport of atomized reagents was conducted by Misra and Anazia (1987). The coal sample used in their tests contained 12.1 % ash and 2.5 % total sulfur. Flotation experiments were performed in a 2-L modified Denver flotation cell at 6 % solids. The atomization of oil droplets was accomplished by an atomizer manufactured by Perkin-Elmer and attached to the flotation cell. In that investigation, No.2 fuel oil was the reagent that was atomized into the flotation cell. The results showed that the recovery of the fine coal increased significantly with the addition of ultrasonically predispersed collector. In 6-min runs, only 45 % coal was recovered with direct collector addition, whereas about 65 % coal was recovered when the collector was ultrasonically emulsified. However, with gas phase atomization of the collector, an increase in coal recovery up to about 70 % was achieved.

Flint et al. (1988) also tested frother addition in the form of aerosol and measured the bubble size. An ultrasonic aerosol generator was employed to add frother solution directly to the gas stream. The results showed that the addition of frother to a flotation column (as aerosol) yielded gas bubbles that were significantly smaller than those produced conventionally; also frother dosage was lower than in the conventional tests.

The effect of atomized conditioning of xanthate and dixanthogen on sulfide ore flotation was studied by Nott (1995). It was found that both the valuable sulfide mineral recovery was increased and the overall selectivity of the valuable sulphide mineral against the gangue sulfide mineral (pyrite) was improved. The atomized conditioning of xanthate and dixanthogen via the air steam resulted in a different mechanism of adsorption of xanthate and dixanthogen onto the sulfide in which xanthate and dixanthogen were brought to the mineral surfaces by bubbles coated with the collectors. This again demonstrated that collectors can be transported to the mineral surfaces by bubbles.

Commercial installations of an aerosol addition apparatus were reported in Australia (Nott et al., 1994; Pokrajcic et al., 2005). The Jameson Cell is used extensively in Australian coal preparation plants in the flotation of fine coal (-0.5 mm). The reagents, typically used in coal flotation are Diesel oil as a collector and MIBC as a frother. The frother is added before the Jameson Cell feed pump to diffuse through the coal slurry. In recent years, it has been found that residual MIBC in the water system can cause frothing

in the pump boxes, pumps, and tanks downstream of the Jameson Cell. The addition of MIBC through the Frothermiser, as described by Pokrajcic et al. (2005), made the use of MIBC more efficient, and improved flotation performance while minimizing downstream effects. The Bowen Basin plant is an example of this option. Following the installation of a Frothermiser in a full scale Jameson cell, thickener tailings' ash content increased by 7 % with a significant MIBC dosage reduction.

3.2   Fine coal utilization and reverse coal flotation

3.2.1 Coal classification and coal characteristics related to coal preparation

Coal is an organic sedimentary rock whose chemical composition changes with coalification - the metamorphic development of coal. Since coalification is synonymous in chemical terms with the progressive enrichment of the coal substance in organically bound carbon, all coals, regardless of their origin or type, can be arranged in an ascending order of carbon content: peat, lignite, subbituminous, high-volatile bituminous, medium-volatile bituminous, low-volatile bituminous, semi-anthracite, anthracite, and graphite.

Coal is very heterogeneous. It contains organic matter which consists of various components with distinct chemical and physical properties referred to as macerals, and inorganic matter mostly in the form of minerals. While coal rank is determined by the thermal history (the temperature and time) which the coal has been exposed to, the macerals are a product of the parent organic materials. The definition of the macerals is based on microscopic examination (Bustin et al. 1983).

The macerals are classified into three groups: vitrinite, exinite and inertinite. They do not occur in isolation but occur in association in various proportions and with variable amounts of mineral matter to give rise to the characteristic banded or layered character of most coals. Macerals are characterized by different chemical compositions and their surface and flotation properties also vary significantly.

Raw coal is upgraded during coal preparation by reducing the content of mineral matter (inorganic impurities). The most common criterion of processing quality is that of ash, which is not removed from coal during beneficiation processes. Instead, particles with a lower inorganic matter content are separated from those with a higher inorganic matter

content. The constituents of ash do not occur in coal naturally but are formed as a result of chemical changes that take place in mineral matter during the combustion process, the ash is sometimes defined as all elements in coal except carbon, hydrogen, nitrogen, oxygen and sulfur.

The terms *extraneous* mineral matter and *inherent* mineral matter were usually used to describe an ash-forming material, separable and nonseparable from coal by physical methods. Coal is heterogeneous at a number of levels. At the first level, a large proportion of mineral matter in coal arises from the inclusion during mining of the roof and floor rock; at the second level, the mineral matter may occur as deposits in cracks, cleats or as vein; at the third level, the mineral matter may be present in the form of very finely disseminated discrete mineral matter particles; and at the forth level, the mineral matter may be present as strongly, chemically bonded elements. Traditionally, in coal preparation processes only the mineral matter at the first and, to some extent, the second levels of heterogeneity is liberated. The rest remains unliberated, and leaves in clean coal and contributes to the inherent mineral matter. Very fine grinding, which also liberates the mineral matter at the third level of heterogeneity, changes the old meaning of terms *inherent* and *extraneous*. The content of the true inherent part of ash-forming material (i.e. the part left in coal after liberating and removing the mineral matter at the first, second, and third levels of heterogeneity) is usually less than 1%.

The most important factor that determines coal cleaning efficiency is the liberation of organic matter from mineral matter, the two main coal constituents. It is obvious that better separation for finer material results from better liberation.

3.2.2 Coal surface wettability

Coal flotation is based on the differences between the surface properties of the carbonaceous matrix and mineral components of coal. It is well known that the interaction of a coal surface with water, referred to as coal wettability, is of primary importance in flotation and therefore the wettability of coals by water has been the subject of very extensive research. Although the relationship between wettability and floatability is not straightforward (Laskowski et al., 1970 and 1991), only those particles of which the

wettability is characterized by a contact angle larger than zero can float, so it is generally assumed that wettability, as expressed by contact angle, is the most fundamental of flotation-related surface properties. Low-rank coals are not very hydrophobic and therefore float poorly. Bituminous coals, if not oxidized, are hydrophobic and are easy to float. Coal surface properties are determined by the hydrocarbon skeleton of coal (related to coal rank), the number and type of oxygen functional groups, and mineral matter impurities. The coal matrix is assumed to be hydrophobic (to a varying degree), and this hydrophobicity is further modified by the presence of hydrophilic functional groups on the coal surface, and by mineral matter impurities which are also hydrophilic. Coal is also porous, which, if pores are filled up with water, may make the coal surface less hydrophobic or, if the pores are filled with air, make the coal more hydrophobic.

Contact angle measurements offer a powerful tool for probing the interfacial interactions between a solid and a liquid. Laskowski (1994) estimated from the Young-Dupré equation that for an ideal (smooth and chemically homogeneous) coal surface the water contact angle should have been 100.5°C. Therefore, any smooth coal surface having a water contact angle of less than 100.5°C contains various hydrophilic areas (polar functional groups, mineral impurities, etc.) on the hydrophobic hydrocarbon matrix.

Brady and Gauger (1940) found that the contact angle values measured on Pennsylvania bituminous coals were larger than that on anthracite, while North Dakota lignites were completely hydrophilic. The results of comprehensive wettability studies on coals from the Donbass (Ukraine) were published by Elyashevitch (1941) while further details were provided by Horsley and Smith (1951). The first complete analysis of the wettability of coals as a function of coal rank was offered by Klassen (1963) in his monograph on coal flotation. When contact angles are plotted as a function of volatile matter content (coal rank), the plots show a maximum at a volatile matter content of about 20%, corresponding to medium - to - low volatile bituminous coals. Both subbituminous and anthracite coals give contact angle lower than those for medium-volatile coals.

Klassen explained low contact angles in the low rank range by the high oxygen content in the coals. The sharp increase in coal aromaticity and increased porosity were suggested as the main reason for the lower hydrophobicity of anthracites.

The wettability of coal surfaces can be changed by the addition of surfactants. More recently Pawlik and Laskowski (2003a) measured the contact angles of bituminous and subbituminous coals in amine solutions (DTAB). The low concentration of DTAB had a negligible effect on the wettability of a bituminous coal. However, the contact angles steadily decreased with increasing DTAB concentration, and finally fell to zero at the cmc. The subbituminous coal was not very hydrophobic in water. As the DTAB concentration was gradually raised, the surface seemed to become more hydrophilic yet exhibited some increased degree of hydrophobicity at a DTAB concentration of two-tenths of the cmc but finally fell to zero at the cmc.

3.2.3 Fine coal utilization and coal-water slurry

The value of coal for utilization is determined by coal rank, impurities and particle size. From the utilization point of view, coals can be broadly classified into three groups: thermal, metallurgical and conversion coals. In some publications a fourth group that involves coals used in making active carbon and electrodes is also included (Osborne, 1988).

Thermal coals are used as fuel either for direct heating or for the production of hot water and steam for power generation. The metallurgical coals are utilized as a raw material to make coke needed in blast-furnace operations and foundries. The term coking refers to a carbonization process where a bituminous coal is heated to drive off the volatile matter and leave a porous solid residue with significantly higher carbon content. Conversion coals are used as feedstock in the production of gaseous and/or liquid fuels derived from coal.

Coal preparation is the stage in coal production at which the run-of-mine coal is made into a cleaner, graded, and consistent product suitable for the market. It includes physical processes that upgrade the quality of coal by regulating its size and reducing the content of mineral matter (expressed as ash, sulfur, etc.). The major unit operations are classification (screening), cleaning (washing, beneficiation), crushing, and solid/liquid separation which also includes dewatering by drying. Coal preparation plants may consists of nothing more than a simple crushing/sizing operation but commonly involve a more

complex circuit cleaning the entire size range of feed coal to reject the majority of impurities associated with run-of-mine coal. While gravity concentration is the dominant cleaning method for coarse and intermediate coal size fractions, flotation is the dominant cleaning method for fine size fractions. However, flotation is practically limited only to coals possessing natural floatability/hydrophobicity (i.e. to bituminous/metallurgical coals). Fine thermal coals are not cleaned and often are discarded as a waste.

The efficiency of gravity separators strongly depends on the size of treated particles and falls off rapidly for sizes finer than 0.5 mm. Flotation also depends on coal size, and its efficiency drops significantly for coarser fractions (-0.5+0.150 mm). These size fractions generally contain the best quality coal and, since the efficiency of gravity methods falls off rapidly for sizes finer than -0.5 mm, and flotation is not very efficient for coal sizes coarser than about 0.15 mm, various flowsheets have been developed that incorporate gravity separation and flotation in the fine coal cleaning circuits.

The final wet coal products must be dewatered commonly by thickening and filtration before they are shipped to the end user. The efficiency of dewatering falls off rapidly as particle size decreases, and may become so low that thermal drying may be required to dewater fine products. Thus, it is not only the separation efficiency which falls off quickly with decreasing particle size, but thickening and filtration efficiency as well. Recent environmental restrictions which require efficient cleaning will inevitably force coal preparation technology into implementing crushing and grinding as a means of liberation before deep cleaning. This will make the dewatering of the fine products even more difficult.

The seam-to-steam strategy offers an entirely different solution for the handling of fine coal (Laskowski, 1999). In this technology, the moist coal is converted into a coal-water slurry (CWS) instead of being dried. Coal water slurries are aqueous suspensions containing 55-70 % by weight of fine coal, usually cleaned by flotation. CWS can be pipelined, stored in tanks, and then directly burned in power generation plants. Since these are mixtures of coal and water, CWS is free from some of the major problems of solid coal. It does not require large handling facilities. Utilization of fine coal in the form of CWS also simplifies the fine coal preparation circuit in that it does not need deep dewatering and drying. On the other hand, chemical additives are required to reduce CWS viscosity and

improve its stability. In existing CWS technologies, a conventional froth flotation process is applied to clean coal before preparing CWS. However, the flotation process has not been optimized for the use of the froth product as a feed to prepare CWS, which consequently requires high amounts of viscosity-reducing additives (Laskowski, 1999).

The characteristics of CWS depend on the coal surface properties and coal particle size distribution. Since CWS must be pumpable, the amount of water is determined by the coal water slurry's viscosity. Generally, the coal content in a CWS is in the range of 55-70 % by weight. Such a high solid content can only be achieved by optimizing coal particle size distribution and by applying viscosity-reducing additives to change the surface properties of the coal particles. In the conventional forward flotation process in which coal is floated, reagents are used to render the coal surface even more hydrophobic and therefore, the particles of coal flotation concentrate are very likely to aggregate. Such an aggregating suspension tends to develop a high yield stress and increased viscosity (Pawlik et al., 2004). While in general, traditional forward coal cleaning has some positive effects on the properties of CWS as it reduces the inorganic impurity content, the presence of flotation reagents in the flotation concentrate makes dispersion of the fine coal more difficult, which indicates that more chemical additives are needed to prepare CWS from the flotation concentrate.

3.2.4 Rheology of coal/water suspensions

Rheology is defined as the science of the deformation of flow of matter, which is most commonly represented by the relationship between shear stress and shear rate, commonly called the flow curve. The typical flow-curves for mineral suspensions are shown in Figure 3.9.

The simplest flow behaviour is exhibited by fluids that obey Newton's Viscous Law. These are referred to as Newtonian fluids and they are characterized by a shear stress that is directly proportional to shear rate. This flow behaviour is shown as flow curve (a) in Figure 3.9 which is a straight line passing through the origin of the shear stress-shear rate plot. The slope of the line is the viscosity which fully characterizes the flow behaviour of Newtonian fluids. Many dilute suspensions exhibit properties of Newtonian fluids.

Fluids or suspensions characterized by the flow curves that deviate from that of a Newtonian fluid are referred to as non-Newtonian. Most mineral suspensions are "non-Newtonian" which implies a non-linear shear stress-shear rate relationship. As a result, most suspensions do not have a single viscosity, rather an "apparent" viscosity that changes with shear rate. The apparent viscosity is defined as the slope of a line passing through the origin that intersects the flow-curve at a specified shear rate and is often used to characterize the rheology of suspensions (Klein, 1992).

In order to describe the flow curves mathematically, several rheological models have been developed. For characterizing the rheology of CWS, the most commonly used models include Newton's Viscosity Law, Bingham Model and Casson Model.

The flow behaviour of Newtonian fluids can be described by Newton's Law of Viscosity.

$$\tau = \eta_N D \tag{3.18}$$

where τ is the shear stress, η_N is the Newtonian coefficient of viscosity, and D is the shear rate.

This equation has been used to describe the rheology of dilute suspensions of non-interacting spheres in Newtonian liquids. However, once a certain critical solids concentration is reached, suspensions exhibit non-Newtonian properties and have to be described using other models.

The Bingham plastic model describes the simplest type of visco-plastic flow. The model characterizes the ideal case in which a complete structure breakdown occurs when the yield stress has been exceeded. Once the yield stress is exceeded a linear relationship exists between the shear stress and shear rate:

$$\tau = \tau_B + \eta_{PL} D \tag{3.19}$$

where τ_B is the Bingham yield stress and η_{PL} is the plastic viscosity.

For most real systems, once the yield stress exceeds some critical value, the

suspensions exhibit a non-linear flow behaviour. In this case the model may be adequate for fitting only the very high shear rate data (Nguyen, 1983). However, using this model to predict yield stress can be very inaccurate. The lack of data at low shear rates often results in a high estimate of the true yield stress value when the Bingham model is used. Therefore, the Bingham yield stress should be considered to be a model parameter rather than a true yield value. The Bingham model is widely used because of its simplicity. The equation is based on observations made with paint and clay suspensions.

The Casson model is a simple two parameter model that has a physical basis and is derived from structural arguments. It is proposed that the particles form chain-like aggregates, the dimensions of which control the viscosity. Under conditions of flow, disruptive stress develops, which is a function of shear rate and particle aggregate size. The disruptive stresses are responsible for the break up of these aggregates such that for a particular shear rate there is a mean aggregate size. The formation of the aggregate is the result of net interparticle attraction forces. The contribution of these aggregates to the viscosity depends on their shape and orientation. It is assumed that the aggregates form chains that can be treated as cylindrical rods. The contributions of hydrodynamic effects involving these rods to the energy dissipation was used to develop the Casson model (Casson, 1959).

$$\tau = \left(\tau_C^{1/2} + (\eta_C D)^{1/2} \right)^2 \qquad\qquad (3.20)$$

Where τ_C is the Casson yield stress, and η_C is the Casson viscosity at high shear rates. Since the Casson yield stress is the intercept with the shear stress axis, and the Casson viscosity is the slope of the flow curve at high shear rates, the coefficients are easy to determine.

The rheological behaviour of mineral suspensions is governed by a balance of four factors: Brownian diffusion of particles, hydrodynamic and physical interactions and interparticle forces (Tadros, 1996). The interparticle forces includes attractive (van der Waals and hydrophobic) and repulsive forces (electrostatic, steric and hydration). Specific contributions of the component factors generally depend on particle size and solids

concentration. For coarse particles, hydrodynamic and physical interaction effects contribute most, while Brownian diffusion and interparticle forces primarily affect the rheology of very fine colloidal dispersion.

Mineral suspensions vary in composition often containing particles with size ranging from colloidal to very coarse (500 µm) and solids contents from dilute to concentrated. Rheological properties become significant in the case of concentrated suspensions (Tadros, 1996).

Rheology modifiers can be conveniently classified as organic or inorganic (Pawlik, 2005). The former include various polymers and surfactants. Chemical additives can be used to modify the rheological properties of concentrated mineral suspensions. These additives adsorb onto the particle surfaces and modify inter-particle interaction. At high solid contents, decreasing aggregation results in a lower yield stress and apparent viscosity. For some applications the objective is to increase the yield stress by inducing aggregation in order to prevent particle settling. In this case coagulants or flocculants may be added.

A coal-water slurry must meet certain rheological requirements in order to be efficiently pipelined and stored. Firstly, the viscosity and the yield stress should be low, and secondly, the settling of solids has to be minimal (Pommier et al., 1984; Papachristodoulou and Trass, 1987). The first objective is achieved by using a suitable dispersant, normally a low molecular weight polymer, that adsorbs on coal surfaces and disperses the particles electrostatically and/or sterically. The settling stability of a coal-water-slurry can be improved by adding another chemical additive, usually a high molecular weight polymer. Such a polymer forms some kind of weak networking that prevents particles from settling thus slightly increasing the viscosity and the yield stress of the slurry and keeping the particles in suspension. Apparently the action of the dispersant opposes the action of the settling stability modifier, so the final product is usually a trade-off between low viscosity and good stability.

A coal-water-slurry is a highly concentrated coal suspension. Its rheological properties are strongly affected by coal particles' surface properties. Pawlik and Laskowski (1998) showed that for bituminous, highly hydrophobic coal suspensions the yield stress was practically independent of pH suggesting that the hydrophobic forces fully control the response of the system. After coal oxidation the yield stress not only decreased but also

showed a dependence on pH. This change in response suggests that for the more hydrophilic material the hydrophobic forces disappear allowing electrostatic repulsion to markedly contribute to the total interaction.

In conventional forward flotation in which coal is floated, the addition of flotation collectors increases the hydrophobicity of coals. A suspension prepared from such a clean coal concentrate tends to aggregate and this increases the dosage of chemical additives needed to control the rheology. In the case of hydrophilic low rank coals, making them hydrophobic by adding flotation reagents and then rendering them hydrophilic again for coal-water-slurry preparation does not seem to be the right practice.

3.2.5 Reverse coal flotation

As discussed above, there is a basic conflict between the objectives of coal cleaning by flotation and the objectives of coal utilization in the form of CWS. Also, traditional flotation reagents are not compatible with the additives required in the preparation of CWS. Poor floatability of low-rank thermal/oxidized coals on one hand, and the incompatibility of common flotation reagents with the CWS technology on the other, call for an entirely different fine coal cleaning processes. Obviously, a reverse coal flotation process in which clean coal is made hydrophilic constitutes an interesting solution.

The coal reverse flotation process in which coal is depressed and gangue is floated can reduce the yield of the froth product from about 50-70 % range down to about 30-50 % range, thus relaxing the carrying capacity limitation of flotation columns and allowing broader application of the columns to clean fine coal. Since only fine clean coal can be utilized to prepare CWS and since flotation collectors are obviously not compatible with the viscosity reducing additives in CWS preparation, a new reverse coal flotation process may eliminate the very weak conventional flotation-CWS preparation link in the existing seam-to-steam technology.

While flotation is currently applied to process hydrophobic metallurgical coals, it is not often applied to treat thermal coals. Old tailing ponds contain huge reserves of oxidized fine coal which may also be difficult to recover using traditional coal flotation method. The application of reverse coal flotation could result in the utilization of such materials.

Only a few papers have been written on reverse coal flotation. Eveson (1961) patented a flotation process in which shale from a bituminous coal was floated while the coal was depressed with the use of quaternary amines. A reverse flotation process was also tested to desulfurize a coal flotation concentrate (Miller, 1975; Miller and Deurbrouck, 1982; Miller, Liu and Chang, 1984). This process, however, separates coal from sulfides of a traditional bulk flotation concentrate.

Stonestreet and Franzidis (1988, 1989 and 1992) were the first to study more fully reverse coal flotation. In their tests, equal amount of silica and washed coal (7 % ash) was mixed as a feed. A reject ash recovery of 92 % was achieved from the feed coal with an ash content of 54 %. The ash content of the product stream (the combustible material that does not report to the flotation froth) was 12 %, but 27 % of coal went to the reject stream (the material that reports to the flotation froth) indicating that the depression of coal was less successful. Further tests showed that stage additions of amines slightly improved the quality of the concentrate.

Pawlik and Laskowski (2003a and 2003b) also examined the reverse flotation of raw coal/silica mixture. They found that high dosages of amine (about 10 kg/t) were needed to initiate reverse flotation. The selectivity dropped dramatically for the less hydrophobic, low rank/oxidized coals.

3.3   Amines in flotation

3.3.1   Structure of amines and their solubility

Amines are cationic surfactants. Primary amines with 8 to 22 carbons, secondary amines, and quaternary amines are the most commercially important amine collectors.

In quaternary amine salts three of the four radicals attached to the carbon atom are usually simple methyl (CH_3-) groups while the fourth one can be as long as C_{20}. Those types of ammonium salts are known as alkyltrimethyl ammonium halides. The structure of DTAC (Dodecyltrimethyl Ammonium Chloride) used in this research is shown in Figure 3.10. While primary, secondary and tertiary amines are weak electrolytes, quaternary amine salts are strong electrolytes.

Quaternary amines are strong electrolytes and ionize in water regardless of pH. The solubility of quaternary amines such as DTAC and DTAB are much higher than that of primary amines. While the solubility of n-decyl amine (C_{10}) is only 5×10^{-4} mol/L, the solubility of DTAC can be as high as 2.2 mol/L (Shapiro, 1968).

3.3.2 Adsorption of anionic and cationic surfactants onto coal

Surfactants can adsorb onto mineral surfaces and change the surface charge and the hydrophobic/hydrophilic character of the surface. The adsorption mechanism of a surfactant onto mineral surfaces involves a number of factors such as the surface charge, the hydrophobicity of the surface, the concentration of the surfactant, the surfactant type, the pH (since this in most cases affects ionization of the surfactant), and electrical charge of the mineral.

To understand the adsorption behavior of a surfactant onto a solid, it is important to distinguish between the solids with hydrophobic surfaces and those with hydrophilic surfaces.

On a hydrophobic surface, the hydrocarbon chain of a surfactant can displace water from the surface and the adsorption tends to begin with the hydrocarbon chain lying horizontally on the surface to make maximum contact. As the surfactant concentration increases, the adsorbed hydrocarbon chains begin to interact laterally with one another and this makes the adsorption stronger. At high concentrations of surfactant, the chains tend to stand vertically with the head groups facing aqueous phase in order to accommodate a higher adsorption density.

On a hydrophilic surface, the surfactant adsorbs with the head group against the surface, attracted by electrostatic forces (or chemical interactions). If the surface charge is high, the number of adsorbed surfactant molecules may be so great that they are close enough together to encourage other surfactant molecules to adsorb into the spaces between them and interact laterally. The apparent sign of the surface charge may then change (Hunter, 1993).

A good example of adsorption of an anionic surfactant onto positively charged hydrophilic solid was presented by Wakamastsu and Fuerstenau (1973). They studied the

adsorption of sodium dodecyl sulfonate (anionic collector) onto hydrophilic alumina, positively charged at pH 7.2. They showed that the adsorption isotherm can be divided into three regions. At low concentrations, adsorption of dodecyl sulfonate ions occurs by an ion exchange mechanism with the adsorbed counter-ions. The shape of the isotherm in this region is of the low-affinity type; only electrical interactions are responsible for the adsorption. In this region the zeta potential is almost constant. In the second region, the adsorbed ions begin to associate, with adsorption increasing significantly due to enhanced adsorption energy. The third region is reached when the zeta potential sign reverses. At concentrations higher than this, the electrostatic interaction opposes the specific adsorption effects, resulting in a decrease in the slope of the adsorption isotherm.

The effect of adsorption of a cationic surfactant (Dodecyltrimethyl Ammonium Bromide, DTAB) on the homogeneous hydrophobic surface (octadecane) and on the hydrophilic surface (quartz) is shown in Figure 3.11 (Elton, 1957; after Pawlik, 2002). In the presence of the cationic surfactant (DTAB) the hydrophobic surface of octadecane becomes hydrophilic. This indicates reverse orientation of the DTAB ions at the solid/liquid interface with the cationic head groups facing the aqueous phase. In this case the hydrophobic interaction between the hydrocarbon chain and the hydrophobic surface is stronger than the electrostatic interaction between the cationic surfactant and (possibly) negatively charged solid surface. In the paper by Fuerstenau (2002), it was shown that the adsorption of dodecylamine on the hydrophobic surface of talc particles reduces the value of the contact angle. For the hydrophilic silica surface, in the presence of a cationic surfactant (DTAB), hydrophobicity increases, but the contact angle is quickly reduced to zero when the concentration of DTAB approaches the cmc.

Coal particles assume negative electrical charge in most practical situations. A good adsorption of cationic surfactants is thus expected. According to Latiff Ayub et al. (1985a and 1985 b), quaternary amines can interact with heterogeneous coal surfaces through both electrostatic and hydrophobic interactions. They determined that even below the i.e.p. of the coal, the cationic surfactants were still able to change the zeta potential towards more positive values. Such a result is consistent with adsorption taking place through hydrophobic attraction. The outwards-oriented charged groups strongly increase the positive charge of the coal surface. On the other hand, as pH is gradually increased above

the i.e.p. towards more alkaline values, the amine adsorption density also increases indicating that when the coal surface is negatively charged, adsorption occurs mainly due to electrostatic attraction. They also found that the adsorption isotherms did not exhibit any characteristic regions. Figure 3.12 (Latiff Ayub et al. 1985a and 1985b) shows the adsorption isotherms of various cationic surfactants onto a low-ash high volatile bituminous coal. The shape of the adsorption isotherms indicates that the surfactant-surfactant interactions do not influence surfactant adsorption on the coal in the same way as on hydrophilic mineral surfaces. This may suggest that the surfactant molecules adsorbing onto the coal surface assume flat orientation because of the hydrophobic interactions between the hydrophobic surface and the surfactant's hydrocarbon chain.

Pawlik and Laskowski (2003a) investigated the hydrophobicity of different coals in the presence of DTAB. The results of contact angle measurements agree very well with these conclusions as shown in Figure 3.13. While the surface of quartz becomes very hydrophobic when the DTAB concentration is increased, the surface of a hydrophobic coal becomes less hydrophobic in the presence of DTAB. In the case of a sub-bituminous coal, which originally is only weekly hydrophobic, the contact angle decreases further in the presence of DTAB. This indicates that it is possible to use quaternary amine in a reverse flotation of coal.

Pawlik and Laskowski (2003a and 2003b) also studied the fundamentals of adsorption of dodecyltrimethyl ammonium bromide (DTAB) on bituminous, oxidized bituminous, and subbituminous coals, as well as on silica. They found that the adsorption density of DTAB on hydrophilic oxidized and subbituminous coals is much higher than on a bituminous coal and silica. The much higher adsorption of DTAB on the hydrophilic/oxidized coals implies higher DTAB consumption in reverse coal flotation. The flotation results demonstrated that the separation of silica from coal by reverse flotation is a kinetic process in which silica floats first followed by coal. The selective recovery of silica was possible only in a very narrow range of amine dosages and the amount of amine needed for best selectivity was a function of coal rank. Research showed that the amine cannot be simultaneously used as a coal depressant and silica collector. DTAB is unable to depress the flotation of a hydrophobic coal. Although the contact angle measurements show that the bituminous coal surface becomes gradually less hydrophobic

in the presence of the amine, the resulting reduction in hydrophobicity is not sufficient to depress coal flotation over a wide range of the amine dosages. Only near the critical micelle concentration of the amine, can the adsorbing micelles finally render the coal surface hydrophilic. At lower concentrations, the role of the amine in the flotation of bituminous coal appears to be simply that of a frother. Therefore, bituminous coals require a depressant during reverse flotation to improve the separation efficiency.

Adsorption measurements (Pawlik and Laskowski, 2003a and 2003b) showed that the adsorption of DTAB on a hydrophobic coal surface took place through hydrophobic interactions between the hydrocarbon chains of these compounds and the hydrophobic coal surfaces. The adsorption density of DTAB on a hydrophilic oxidized coal was much higher than on a bituminous coal. The results indicated that the adsorption mechanism involved some strong interactions between the cationic head group of the surfactant and the negatively charged oxygen groups on the coal surface. Despite the apparent head-to-surface orientation, the adsorbed DTAB molecules did not render the surface hydrophobic; this probably resulted from the fairly chaotic orientation of DTAB molecules on the heterogeneous surface of oxidized coal. The results also showed that DTAB preferentially adsorbed on the coal in a low rank coal/silica mixture, leaving no free amine to activate silica. Due to the mechanism of amine adsorption on such coals, the appearance of residual amine for the activation of silica takes place when the coal is already weakly hydrophobic. Since both the coal and silica could separately float under these conditions, it was the more hydrophobic component that selectively floated from a mixture. However, at a too-high amine concentration frothing was too intense, coal became even more floatable, and the selectivity of reverse flotation dropped dramatically. This implies again that a depressant is needed in the reverse flotation of coal.

3.3.3   The use of amines in flotation

Amine flotation is very rapid and only short conditioning is required (Baaron et al., 1962; Zhang et al., 2002). This is an advantage which permits less flotation cell capacity to process a given tonnage of ore. The average reagent requirement, much less than with fatty acids, is about 95 g/t of amine with extremes of 4.5 g/t to 450 g/t.

Amine flotation is simple and it can be conducted at neutral pH without conditioning; only slimes could cause a significant deteriorating effect. A review of amine collectors was given by Gefvert (1988). The paper presented some rule-of-the-thumb selection criteria for amine collectors, according to particle size, water chemistry, and water temperature. The major conclusions included the following: 1) for very coarse feed, a primary amine or long-chained condensates are more suitable; while ether amines or diamines work better for finer particles because of their better selectivity; 2) pH is not important as long as it is below 10, while increasing water hardness decreases the effectiveness of cationic flotation due to increased competition for the negative sites on the mineral particle; 3) anions reduce the floating power of some cationic collectors, because they react with the ionized amine to form insoluble salts, but condensates seem to be less likely to react with anions than either primary or ether amines.

Hanna (1975) compared two types of quaternary amine salts with two primary amine salts, in terms of their adsorption and flotation performance in separating silica from phosphate, and found that quaternary amine salts were more effective.

The development of modified polymers as phosphate depressants in the amine flotation of silica was disclosed by Nagaraj and others (1987). The addition of this modifier at a dosage of 5-20 g/t of feed resulted in a significant increase in phosphate recovery. Other phosphate depressants in silica flotation were also investigated by a number of researchers (Allen, 1982; Snow, 1988; Wiegel, 1999; Klimpel, 1999).

Zhang et al. (2002) investigated six types of amines in terms of their selectivity for the flotation of silica in the processing of phosphate ores, and obtained the following ranking from the most selective to the least selective amine: quaternary > primary = tertiary = condensate > ether > secondary. Amines as gangue collectors in reverse coal flotation were also reported as reviewed earlier (Stonestreet et al. 1989, 1990 and 1992; Pawlik and Laskowski, 2003a and 2003 b).

Long-chain primary amines are widely used to float sylvite from halite in the flotation of potash ores as discussed in Chapter 1. A polyacrylamide was used to selectively flocculate slimes in order to reduce the amine consumption and increase the selectivity in the process. This aspect will be further discussed.

3.4   Use of water glass in flotation

Water glass is a sodium silicate solution. It is often used as a depressant in anionic flotation. Fuerstenau et al. (1968) studied the effectiveness of varieties of water glasses on calcite flotation. They showed that with increasing ratio of SiO_2 to Na_2O the effectiveness of depressing calcite increases.

Mercade (1981) investigated the depressing effect of water glass and modified water glasses on anionic flotation of calcite. An anionic collector, oleic acid, was used in the tests. The results showed that the flotation of calcite was depressed in the following order: sodium silicate<cobalt silicate hydrosols<nickel silicate hydrosols<aluminum-silicate hydrosols<acidified sodium silicate< ferrous silicate hydrosols<copper silicate hydrosols<chromium silicate hydrosols.

Fuerstenau and Fitzgerald (1986) tested aluminum silicate hydrosols as dispersants in the flotation of porphyry, oxide copper and scheelite ores. The water glass was modified by reacting it with Al^{3+}, and was found to enhance flotation recovery.

Yang (1978) examined modified sodium silicates and developed a dispersant obtained by reacting Na_2SiO_3 with Fe $(NO_3)_3 \cdot 9H_2O$ and H_2SO_4 at a ratio of 5:1:1.

DiFeo et al. (1999) studied the effect of acidified water glass on sphalerite-silica interaction. Zeta-potential measurements revealed that acidified water glass made both sphalerite and silica surfaces more negatively charged, and its use improved the dispersion of the system. Acidified water glass was prepared by first diluting sodium silicate solution with water at pH 11.15, and then by adding sulfuric acid to lower the pH down to 8.2.

The hydrolysis products of sodium silicate contain a number of monomeric, polymeric and colloidal species. According to Gong et al. (1992 and 1993) the flotation active depressing species in silicate solution are polymeric silicate species and small colloidal silica particles. They studied the selective flotation of apatite from iron oxides. Sodium silicate was used as a selective depressant for iron oxides. The flotation pH, the modulus (ratio of SiO_2 to Na_2O) of sodium silicate, the pH and the standing time of the stock solution of sodium silicate as well as the presence of polyvalent metal ions in the silicate solution all affected polymerization of sodium silicate and selectivity with which the iron oxides were depressed.

Since water glass depresses the flotation of calcite and dolomite with anionic collectors, it should promote the flotation when cationic collectors such as amines are used.

3.5 Use of polyacrylamide in flocculation and flotation

3.5.1 Degree of anionicity

Polyacrylamide (PAM) is a synthetic polymer which is water-soluble due to hydrogen bonding. This hydrogen bonding is also essential in the adsorption of PAM onto mineral surfaces. PAM is normally a non-ionic polymer, although by replacing its amide groups ($-CONH_2$) with carboxylic groups ($-COOH$) through hydrolysis it may become anionic. The extent of this replacement is referred to as "the degree of anionicity" (a completely hydrolysed polyacrylamide has a degree of anionicity of 100 %, so it is really a polyacrylic acid). It is known that PAMs with some degree of anionicity (10-30 %) are more efficient flocculants for many applications (Xu and Cymerman, 1999).

Polyacrylamide is a white, granular solid. Its molecular structure is given in Figure 3.14 (a). "Anionic" polyacrylamide, shown in Figure 3.14 (b), has some of the amide groups along the chain replaced by carboxyl groups. Since -COOH groups disassociate in alkaline solution, anionic PAM assumes a negative charge in an alkaline environment. The vast majority of commercial polyacrylamide flocculants are partially hydrolyzed polyacrylamides (or they are copolymers of polyacrylamides and polyacrylic acid). As a result of slow hydrolysis even "non-ionic" polyacrylamides contain some anionic (carboxylic) groups.

In practice, there are two methods to determine the PAM's degree of anionicity: an infrared spectroscopic method, and Kjeldahl's method for analysis of organic nitrogen.

Rogers and Poling (1978) developed a relatively fast infrared (IR) method for determining PAM's degree of anionicity. In this method, a droplet of flocculant solution (about 2.2 mL solution) is first frozen on a 25×25 mm AgCl infrared window, then evaporated under vacuum (freeze-dried). The fine, fibrous structure which remains after freeze-drying is matted against the window by a few second's exposure to steam. After drying in air, the flat, uniform film of solid on the AgCl window is used in an infrared

analysis. In practice, infra-red spectroscopy has a limited quantitative accuracy. However, it has been found that the ratio of intensity of the two adjacent bands within any one spectrum remains constant from one spectrum to the next. Variation of this ratio indicates that the nature of the flocculant has changed. Rogers and Poling indicated that the ratio of the intensity of the 1450-cm^{-1} peak to that of the 1410-cm^{-1} band represents the ratio of anionic -COOH group to the total number of monomers in the spectrum of polyacrylamides. If the ratio is different, it means that the polyacrylamides have different degrees of anionicity. Other intensity-ratios could also be used. A graph of the correlation between the band-intensity ratios and degrees of anionic character can be obtained by measuring the band intensities for pure polyacrylamide samples for which their degrees of anionicity are known. The degree of the anionic character of an unknown flocculant can then be obtained by comparing its infra-red spectrum with the data on the graph.

Kjeldahl's method of nitrogen analysis can also be used to determine the PAM's degree of anionicity. This method consists of three steps. The sample is first digested in concentrated sulfuric acid to convert the amine nitrogen to ammonium ions. The ammonium ions are then converted into ammonia gas that is trapped in acidic solution. Finally, the amount of the ammonia that has been trapped is determined by titration. By comparing with the calibration curve, the degree of anionicity of an unknown flocculant can be determined. This method is quite time-consuming.

3.5.2 Polymer flocculation and adsorption kinetics

Fine particles in a dispersed system can be aggregated into larger structures by various mechanisms. Aggregation processes based on reducing interparticle repulsion (i.e. by compressing the electrical double layer or by charge neutralization) are defined as coagulation and the aggregates are called coagula. If aggregation is induced by polymer bridging action, the process is known as flocculation and the aggregates are referred to as flocs.

Polymers are widely used as flocculants in mineral processing and other applications. They promote settling and aid in filtration of fine-particle suspensions for product recovery and waste treatment. While the basic mechanisms by which polymer

flocculants act are reasonably well understood, the complexity of the process and the extensive interactions among the process variables leave many questions that have yet to be answered satisfactorily (Hogg, 1999).

It is generally accepted that practical applications of polymer flocculants involve the formation of physical linkages between particles (the so-called molecular bridging mechanism) (Michaels, 1954; Linke and Booth, 1959; Smellie and La Mer, 1958; Healy and La Mer, 1962). The usual result is that the polymer sticks to certain points on the mineral surfaces, but for much of its length it is able to trail out into the solvent. Some segments attach to the surfaces as trains separated from one another by loops which extend into the solution and end in a tail at either end of the polymer chain, as Figure 3.15 shows. In the case of relatively low molecular weight polyelectrolytes, the linkages involve electrostatic interactions between charged particle surfaces and patches of adsorbed, oppositely charged, polymer (the charge-patch mechanism) (Gregory, 1973). High molecular weight polymers seem to perform a variety of functions and may serve more as binding agents, opposing floc breakage, than actual promoters of floc growth (Ray and Hogg, 1988).

Adsorption of a polymer is generally necessary for flocculation to occur. However, it is important to recognize that adsorption and flocculation are not separate, sequential processes, but occur simultaneously and may, in fact, be indistinguishable from one another. The key to successful flocculation is to bring polymer molecules and solid particles together in such a way as to maximize particle-particle linkages. Adsorption of polymers on isolated particles does not, in itself, lead to flocculation. Similarly, particle-particle contact in the absence of a polymer linkage produces only limits floc growth.

The polymers used in flocculation are commonly classified into two broad types: coagulants, which are usually highly charged, cationic polyelectrolytes with molecular weight in the 50,000 to 1,000,000 Daltons range, and flocculants, which have substantially higher molecular weight (up to 20 million Daltons) and are usually non-ionic or partially anionic.

The effectiveness of these polymers in destablizing and flocculating fine-particle dispersions depends strongly on the charge on the particles and their relative state of dispersion. Under the proper conditions of particle and polymer charge, coagulants can be

very effective in destabilizing dispersions, though the flocs produced tend to be quite small, especially in agitated systems. Because a great majority of particles encountered in mineral processing and water treatment systems are negatively charged, commercially available polymer coagulants are predominantly cationic. A relatively low molecular weight is appropriate for these applications by providing the large number of individual molecules necessary for highly dispersed particle systems.

High molecular weight flocculants are not very effective for treating stable dispersions. They generally produce some flocculation but, unless very high polymer dosage is used, large quantities of dispersed primary particles remain. On the other hand, these polymers are extremely effective in building large flocs in systems which have already been destabilized by coagulant addition (polymer or inorganic salt) or reduction of the surface potential. Charge conditions appear not to be critical with respect to whether or not flocculation occurs, but are very important in determining the solubility of the reagent and the conformation of molecules in solution or at particles surfaces. Anionic flocculants tend to produce somewhat larger flocs than non-ionic polymers.

The physical conditions that exist when polymers are added to a fine-particle suspension can have a profound effect on the ensuing process, especially when high molecular weight flocculants are added to destabilized suspensions (Hogg et al., 1993). For chemically identical systems, different mixing/polymer addition conditions can lead to floc sizes and settling rates that vary by a factor of ten or more (Keys and Hogg, 1979; Hogg et al., 1987). The general rule for such applications appears to be that the flocculant should be added to a vigorously agitated suspension but the agitation should be discontinued immediately following the reagent addition. In a batch system, rapid addition over a short period of time produces large flocs while slow addition of the same quantity of polymer over a more prolonged period produces smaller flocs. However, the latter appear to be less susceptible to degradation during subsequent handling. Continuous flocculation processes seem to show a generally similar pattern of behavior (Suharyono and Hogg, 1996). However, the effects of the physical conditions appear to be somewhat less pronounced than in the batch process.

Flocculation performance is also affected by the concentration of the polymer

solution added. Hogg et al. (1993) observed about a two-fold increase in the initial limiting settling rate at the same polymer dosage when the concentration of the stock solution was reduced from about 900 mg/L to about 90 mg/L. The effect may be due to improved mixing or more favourable polymer conformation in the dilute solution.

It is generally agreed that the action of polymeric coagulants and flocculants involves adsorption. Adsorption of non-anionic polymers on mineral surfaces is usually considered to occur through hydrogen bonding while polyelectrolytes may adsorb through a combination of charge effects and hydrogen bonding. The role of charge interactions is most pronounced for low molecular weight coagulants. Ray and Hogg (1989) showed that there was essentially no adsorption of cationic polymer on alumina at pH 4 (where the particles are positively charged), some adsorption at the point of zero charge (pH 9) and substantial adsorption on the negatively charged particles at pH 11. A non-anionic polymer, on the other hand, was found to adsorb over the entire pH range, albeit most strongly on the positively charges particles at pH 4.

Polymer adsorption involves the attachments of individual molecular segments to the solid surface. Since the attachment of a single segment represents adsorption of the molecule, it follows that the likelihood of the adsorption increases with molecular weight. If, as a first approximation, the adsorption /desorption of a single segment is considered as an equilibrium process, the interaction can be represented by equilibrium:

$$\text{Segment in Solution} \Leftrightarrow \text{Adsorbed Segment}$$
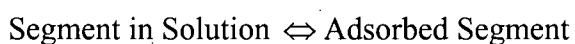
with an equilibrium constant K which represents the relative number of segments that are attached to the surface (adsorbed segment). For a typical polyacrylamide flocculant with a molecular weight of about 15 million Daltons, each segment weight is about 70 Daltons meaning that each macromolecule consists of over 200,000 segments. Thus, even for very weak adsorption (e.g $K=10^{-5}$), the average molecule would have about 2 attached segments and would therefore be adsorbed. As a consequence, high molecular weight polymers tend to adsorb indiscriminately at solid surfaces even in the presence of electrostatic repulsive forces.

Ray and Hogg (1989) also observed an inverse correlation between adsorption and

flocculation. The most effective flocculation, at the least required dosage, occurs close to the point of zero charge where adsorption is generally at a minimum. This apparent paradox arises because of the simultaneous occurrence of the adsorption and flocculation processes. At the point of zero charge, particles are already coagulated to some extent so the surface area available for adsorption is reduced relative to that of the dispersed primary particles. The addition of a polymer causes further flocculation and further reduction in the available surface area. Thus, only a small amount of polymer is needed to provide sufficient coverage of the external surface for bridging to occur. In the case of thoroughly dispersed particles at pH 4 or 11, the total surface area is available and substantially greater amounts of polymers can be adsorbed and, indeed, are required to attain the surface coverage necessary for bridging flocculation. The inverse correlation is also observed when the physical conditions (rate of polymer addition, agitation intensity, etc.) are changed. Conditions that lead to effective flocculation at low polymer dosage invariably correspond to relatively low dosage levels of adsorption.

It is clear from the inverse relationship between adsorption and flocculation that, for systems subject to flocculation, polymer adsorption is a non-equilibrium process. It follows that the kinetics of the processes are important, especially the relative frequencies of polymer-particle attachment and particle-particle collision. Hogg (1999) showed that both processes involve collisions between species dispersed in liquid and that both respond in similar fashion to external forces due to agitation. It was also demonstrated that in most practical systems, adsorption is essentially instantaneous so that the rate of adsorption is effectively controlled by the rate at which fresh polymer is introduced into the system. This finding is consistent with observations that the rate of floc growth during continuous polymer addition is directly proportional to the rate of polymer addition (Hogg et al., 1987).

Based on the analysis of polymer adsorption kinetics, Hogg (1999) showed that, in a polydisperse suspension, the larger particles receive more polymer (per particle) than the finer material, especially under more intense agitation. This has important implications when polymers are added to stable fine particle dispersions. The fine, primary particles receive little polymer and tend to remain in the dispersed state. On the other hand, any small flocs formed as a result of non-uniformity during polymer addition receive

proportionately more polymer which promotes further growth. The overall result is the development of a bimodal particle/floc size distribution consisting of some large flocs as well as dispersed primary particles (Hogg, 1999). As the polymer dosage is increased, the residual primary particles are slowly incorporated into the flocs leading eventually to good flocculation but with high polymer dosage requirements (Rattanakawin, 1998).

The preferential adsorption on the larger particles can be especially critical for high molecular weight polymers, due to the relatively small number of molecules per unit mass of polymer. Hogg (1999) showed that for higher molecular weights ($>10^6$ Daltons) the submicron particles receive, on the average, significantly less than one molecule per particle which is clearly insufficient to promote flocculation. Increased agitation has little effect; if anything, it exacerbates the problem.

It should be recognized that the particle size/polymer molecular weight effect predicted by the adsorption kinetics model is not related to particle-polymer interaction forces or other chemical effects, provided the polymer does adsorb. Polymer type is of little direct consequence in this respect (Hogg, 1999). Rattanakawin (1998) showed that anionic and non-ionic flocculants show very similar behaviour when added to stable dispersions of alumina particles at pH 5. For effective flocculation of such systems, particles should be precoagulated by pH control and/or the addition of salts or low molecular weight polymer coagulants prior to flocculant addition.

It is clear from the above that flocculants should be used only in systems that have somehow been pre-coagulated (destabilized). Under such conditions they can be extremely effective in producing large flocs and clear supernatants. The adsorption kinetics model can also provide insight into the design and control of flocculation under these conditions.

When a fine particle dispersion is coagulated, by charge or coagulant addition, under agitated conditions, the result is the formation of small flocs which typically have a relatively narrow size distribution and, depending on agitation intensity, a median size in the region of around 10 μm (Rattanakawin, 1998). Obviously, this represents a dynamic equilibrium with flocs being broken and reformed at equal rates. When a polymer flocculant is added, it is reasonable to propose that polymer molecules are initially adsorbed on external surfaces and that breakage and reformation of flocs cause the polymer to be redistributed from the surface to the interior of the flocs. There is a rapid

increase in the amount of polymer at the floc surface, when the polymer is first introduced into the system. This stage is followed by a decrease as the polymer is redistributed into the floc interior. Whereas for instantaneous addition, the amount of polymer at the surface falls rapidly to a very small value, continuous addition always provides a significant external surface coverage.

Assuming that an increased coverage of the external surface leads to enhanced floc growth, this indicates the benefit of continuous polymer addition rather than instantaneous addition followed by a period of mixing. It also helps explain some other experimental observations. Specifically, it was shown (Hogg et al., 1987 and 1993) that increasing the rate of continuous polymer addition at the same total dosage not only increased the floc growth rate but also increased the maximum size to which the flocs grew. Another experimental observation is that flocs produced by rapid polymer addition are more susceptible to degradation in subsequent handling than those obtained at low addition rates (Hogg et al., 1987). This finding can also be explained using the kinetics model. At higher rates of polymer addition, more of the polymer resides at the floc surface and, consequently, less is incorporated into the floc interior. If the polymer also functions as a binding agent, it is to be expected that such flocs would have a lower mechanical strength. Unfortunately, adsorption is only one step in this complex process. The relationship between polymer adsorption and flocculation efficiency is still far from clear. Smellie and La Mer (1958) and Healy and La Mer (1962) proposed a simple model which has subsequently been modified by others (Hogg, 1984; Moudgil et al., 1987). None of these have been directly validated by experiment; nor are there general empirical relationships. The development of flocs is ultimately limited by floc breakage. While there were many published studies on this topic, general relationships between floc breakage and floc size, agitation intensity, polymer type and content, etc., have yet to be developed.

3.5.3   Selective flocculation and flotation

Selective flocculation is achieved by selectively aggregating certain kinds of fine mineral particles into flocs to enable their effective separation from others. The process utilizes the differences in the physical-chemical properties of the various fine mineral

components in the mixed system and is based on the preferential adsorption of a flocculant on the particular minerals to be flocculated. This leaves the remainder of the particles in suspension.

Yarar and Kitchener (1970), in their fundamental paper on selective flocculation, outlined the general principles of selective flocculation. Those principles included:

(1)   The mixed pulp must initially be in a dispersed condition so that all the particles are essentially in a separate state.

(2)   Selective flocculation is based on the selective adsorption of the polymer on the different minerals. This occurs because flocculants consist of macromolecular substances which can bind particles together by bridging the gap between them. The polymer must therefore be highly extended, when in solution, and attached by adsorption to the surface of the mineral grains, but selectivity in flocculation can arise only from preferential adsorption, which in turn, depends on differences in surface chemistry.

(3)   The surface properties of minerals in mixtures may be different from those of the separate minerals. Products of dissolution or hydrolysis (or both) derived from one mineral may be taken up by the other. For example, calcite is sufficiently soluble to influence the pH of the suspending medium and, hence, to affect the surface charge of co-mixed quartz.

(4)   Modifying agents can be employed to control the properties of the minerals or the flocculants, or both. Their action may lead to activation or inhibition of flocculation.

(5)   As the solids content of a mixed slurry is increased, an increasing proportion of the component not intended to flocculate is flocculated. This indicates that the grade of the flocculated fraction can be improved by starting with a lower solids content.

(6)   For a given combination of minerals there is an upper limit of the solids content and of the ratio of the components that can be successfully treated with a given set of reagents.

(7)   With a mixture of minerals of very different specific gravity, it is easiest to effect a separation by flocculating the heavier component; a relatively weak flocculant is adequate because of the favourable rate of settling of the flocs. Conversely, if the objective is to flocculate the lighter component, the use of a highly selective flocculant is essential.

(8)   As with total flocculation, efficient selective flocculation requires an initial uniform distribution of the flocculant through the pulp, followed by a period of conditioning at a low rate of shear. Uniform distribution of the flocculant is obtained by a combination of the high rate of stirring and the addition of flocculant in the form of a dilute solution.

(9)   To improve the efficiency of the process, an additional stage can be introduced in which the settled flocs are gently "worked" to release entrapped particles and to consolidate the flocculated material.

Polymeric flocculants have been tested in flotation to improve efficiency and to enhance recovery. Most often the role of the polymeric flocculant is to depress the minerals, while in reality the minerals might be selectively flocculated. The three mechanisms of depression of flotation by polymers are: (a) inhibition of collector adsorption (i.e., blinding the mineral surfaces, thus making the solid surface hydrophilic); (b) formation of large aggregates (flocculation), and (c) complexation of the collector in solution. The distinction between depressing and the flocculating action of polymers lies mainly in the molecular weight of the polymer and its mechanism of action on the mineral surface. In general, polymers having molecular weights of a few hundred thousand or less act as a depressant. On the other hand, use of higher molecular weight polymers (1 million Daltons or more) leads to the bridging and formation of flocs.

A good example of selective flocculation-flotation is the processing of potash ores. Sylvinite, a natural mixture of sylvite (KCl) and halite (NaCl), is the potash ore of greatest economic importance. In Canada sylvinites are processed by flotation. The main problems in such a process are the slimes of insoluble minerals (such as dolomite, illite and chlorite), which, if left untreated, would highly increase collector consumption. Therefore, all potash flotation circuits include a desliming step for eliminating the unwanted fines (slimes) prior to KCl flotation. Two desliming methods are commercially used. Mechanical desliming involves the classification of the feed and rejection of the finest fraction; desliming by flotation involves selective flocculation followed by floating off the slimes. In the process developed at the Agrium plant (Chan et al., 1982) high molecular weight polyacrylamide flocculants are used to selectively flocculate the slimes and then the slime flocs are floated

off with secondary amines, which results in a significant decrease of amine consumption and an improved selectivity.

Arsentiev et al. (1988) also reported the blinding action of polymers in floating selectively sylvite (KCl) from halite (NaCl). In the absence of polymers the recovery of potassium chloride is proportional to octadecylamine (ODA) dosage, and for obtaining 84 % recovery about 1 kg/t amine was required. The recovery of slimes (insoluble residue) did not exceed 25 %. With carboxymethyl cellulose (CMC) addition into the pulp the picture changed. To achieve 84 % recovery, 100 g/t of octadecylamine is sufficient at a carboxymethyl cellulose consumption of 350 g/t. While CMC increased KCl recovery it also decreased the recovery of the water-insoluble slimes, indicating improved selectivity. The results also showed that a polyacrylamide flocculant can enhance rather effectively potassium chloride flotation. CMC probably acted as a blinder by adsorbing onto the surfaces of clay minerals because of its relatively low molecular weight, and the polyacrylamide acted as a flocculant by selectively flocculating clay minerals.

The depressant action of hydrophilic polyacrylamide on coal flotation was confirmed by Moudgil (1983). The coal flotation with MIBC frother was completely depressed with the addition of a nonionic polyacrylamide. This effect was explained by the adsorption of hydrophilic polyacrylamide onto the coal surface, which also rendered the surface hydrophilic. Castro and Laskowski (2002) observed that molybdenite flotation with MIBC frother was completely depressed with the addition of a shear-degraded anionic polyacrylamide.

In summary, the flocculation of fine particle dispersions includes three basic steps: particle destabilization, floc growth and floc breakage. Polymer adsorption is involved in each of these steps. Due to the nature of the overall process, it is unlikely that polymer adsorption ever comes even close to equilibrium. The effectiveness of a polymer in promoting flocculation is therefore determined to a large extent by the kinetics of adsorption on particles and flocs of widely varying size, etc., under the prevailing physical and chemical conditions. Based on the above review of polymers in flocculation and flotation, the following general conclusions can be drawn:

(1) Flocculation of fine particles is affected by both physical and chemical variables.

(2) Low molecular weight polymers adsorb on a particle surface mainly through charge effect, hydrogen bonding and/or even chemical bonding while high molecular weight polyacrylamide flocculants adsorb on particles and cause flocculation through bridge mechanism.

(3) High molecular weight polymers are not effective in destabilizing dispersed particles. Stable dispersions should be pre-coagulated by charge control, or the use of low molecular weight coagulants, prior to flocculant addition.

(4) The addition of high molecular weight polymers to stable dispersions leads to the development of bimodal size distributions consisting of dispersed primary particles and some relatively large flocs. High polymer concentrations can eventually eliminate the fine fraction but only at excessive dosages.

(5) High molecular weight polymers are very effective for producing large flocs in destabilized suspensions.

(6) Continuous polymer additions over the complete mixing period generally provide the best flocculation.

(7) The largest flocs (highest settling rate) are obtained over a limited range of (high) rates of polymer addition (short mixing times). However, such flocs are more prone to degradation than the smaller flocs produced at lower polymer addition rates. Hydrodynamic conditions affect the performance of a flocculant, and its flocculating strength may be lost due to too intense conditioning. However, its depressing ability in flotation is not affected. The floc breakage is obviously affected by conditioning of the suspension.

(8) Selective flocculation is achieved by selective adsorption of a polymer on one mineral but not on another. Efficient selective flocculation requires an initial uniform distribution of the flocculant through the pulp, followed by a period of conditioning at a low rate of shear.

In the reverse flotation of coal, quaternary amines are used as a collector to float gangue materials. Large quantities of amine are required in this process. It is quite likely that these large amine consumptions result from the fine size of the particles. If this is true, the fines could be flocculated prior to flotation in the process similar to one used in selective flocculation-flotation of potash ores. This should lead to a significant reduction of

amine dosage. However, only selective flocculation can promote flotation, and flocculation with high molecular weight polyacrylamides is commonly very unselective. The successful use of polyacrylamides as a blinder in coal reverse flotation will therefore require a development of ways of using polyacrylamides that would promote selectivity.
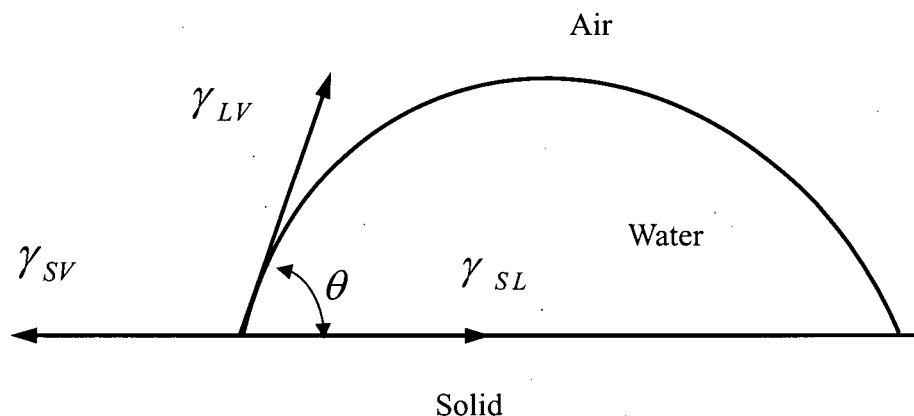
Figure 3.1   Contact angle between bubble and flat surface in an aqueous medium.
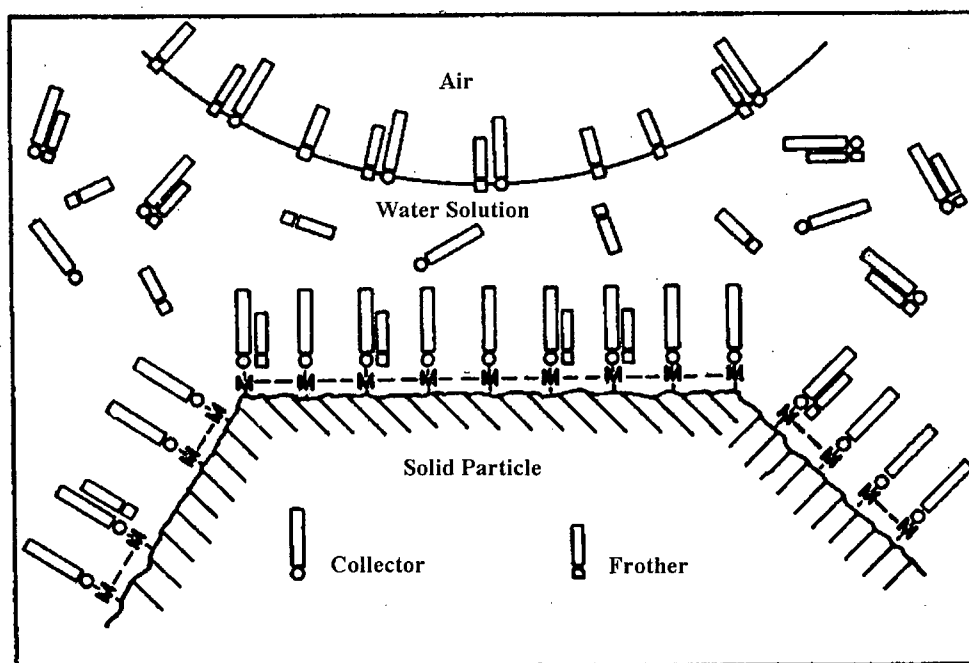
Figure 3.2   Mechanism of bubble attachment: bubble approaching a collector coated solid surface (Leja and Schulman, 1954); © reprinted with permission from *Transactions AIME*, copyright (1954) Society for Mining, Metallurgy, and Exploration.
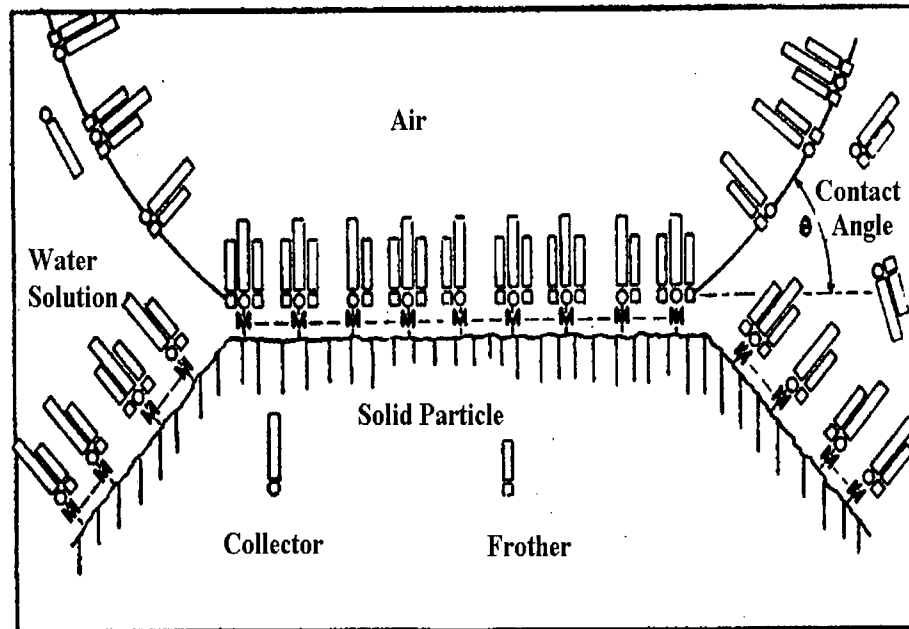
Figure 3.3   Mechanism of bubble attachment: adherence of an air bubble established through the penetration of the monolayer at the solid/liquid interface by the monolayer at the air/liquid interface (Leja and Schulman, 1954); © reprinted with permission from *Transactions AIME*, copyright (1954) Society for Mining, Metallurgy, and Exploration.
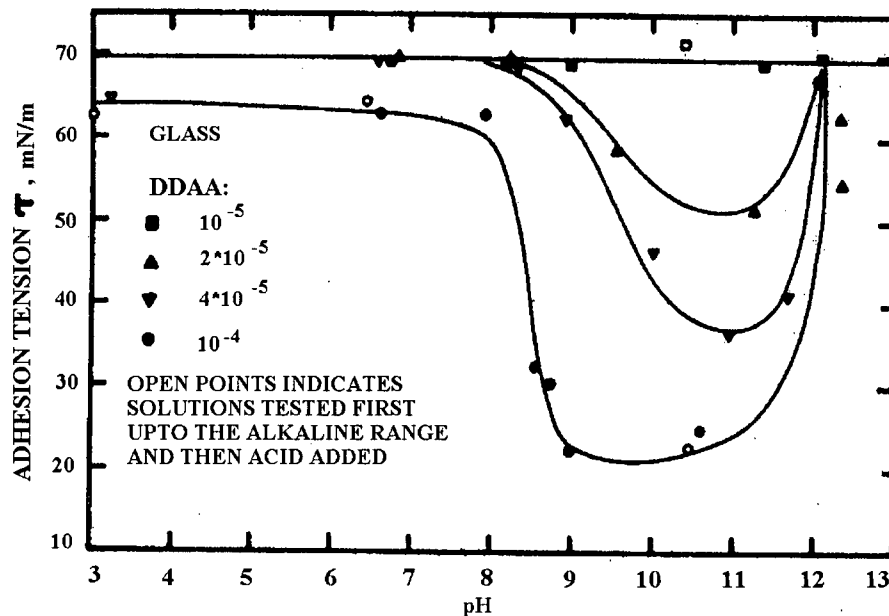
Figure 3.4   Adhesion tension of dodecylammonium acetate solution on glass as a function of pH (Somasundaran, 1968); © reprinted with permission from *Transactions SME*, copyright (1968) Society for Mining, Metallurgy, and Exploration.
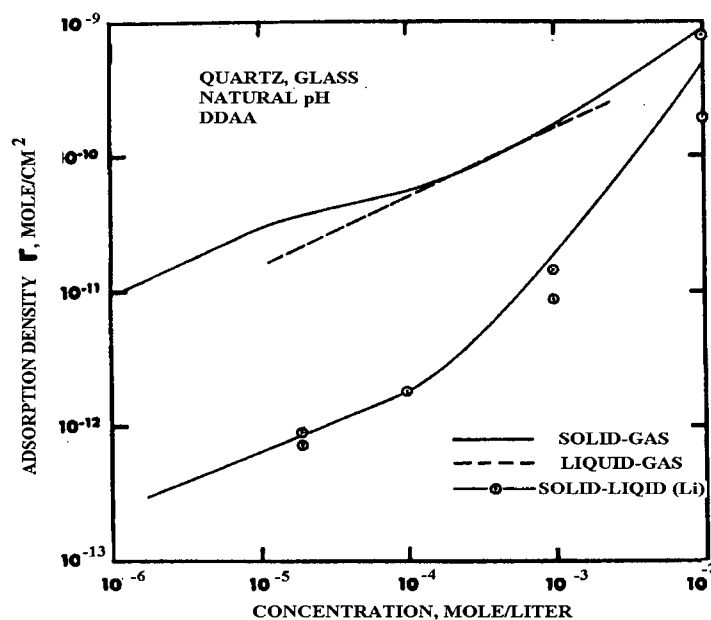
Figure 3.5   Comparison of adsorption of dodecylammonium acetate at different interfaces (Somasundaran, 1968); © reprinted with permission from *Transactions SME*, copyright (1968) Society for Mining, Metallurgy, and Exploration.
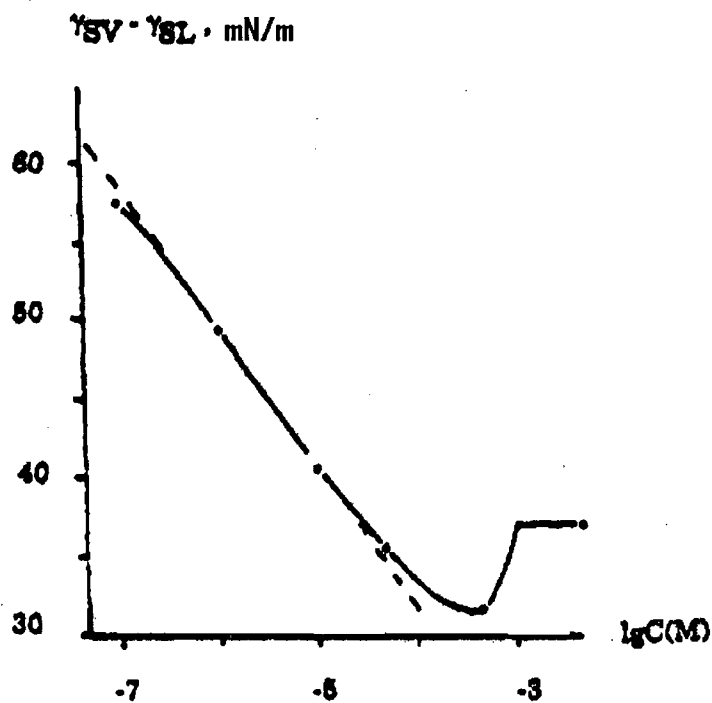
Figure 3.6   Wetting tension isotherm (Yaminsky and Yaminskaya, 1995); © reprinted with permission from *Langmuir*, copyright (1995) American Chemical Society.

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$$\Gamma_{SV} - \Gamma_{SL}, \times 10^{14} \, molecules \, / \, cm^2$$
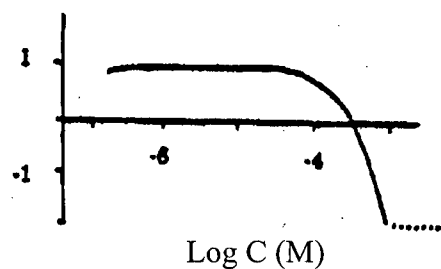
Figure 3.7   Adsorption difference isotherm (Yaminsky and Yaminskaya, 1995);
© reprinted with permission from *Langmuir*, copyright (1995) American Chemical Society.
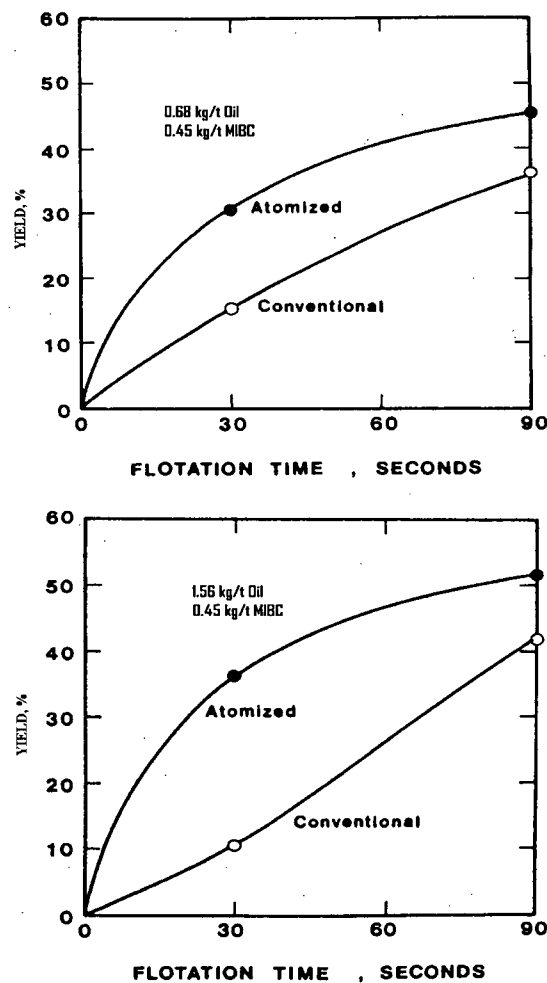
Figure 3.8   Comparison of flotation response for Beaver Creek thickener underflow
(Miller and Misra, 1983); reprinted with permission from the authors.
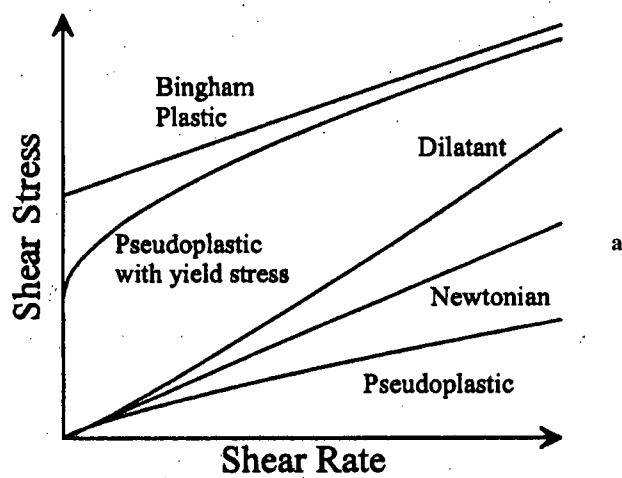
Figure 3.9   Typical flow-curves for mineral suspensions.
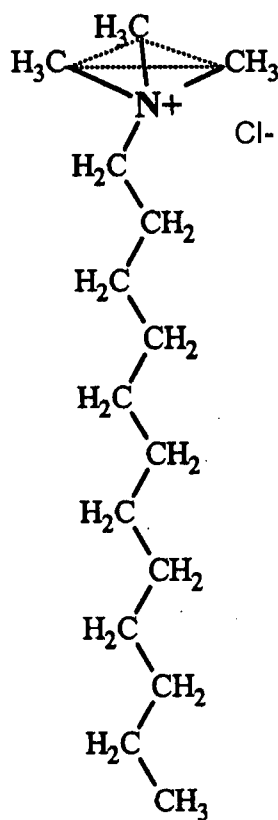
Figure 3.10   Molecular structure of dodecyltrimethyl ammonium chloride ($C_{12}H_{25}N(CH_3)_3Cl$).
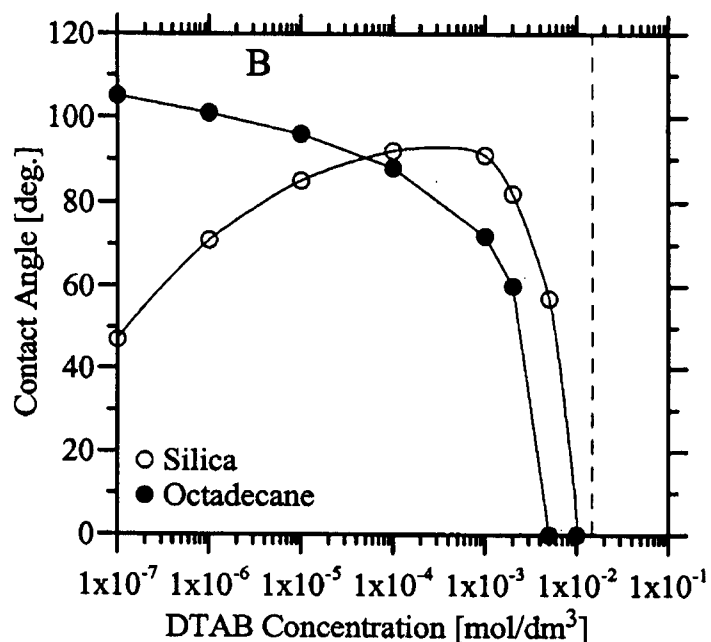
Figure 3.11 Effect of quaternary amine (DTAB) on the wettability of hydrophilic silica and hydrophobic octadecane (Elton, 1957; after Pawlik, 2002); © reprinted with permission from the University of British Columbia, copyright (2002) Pawlik.
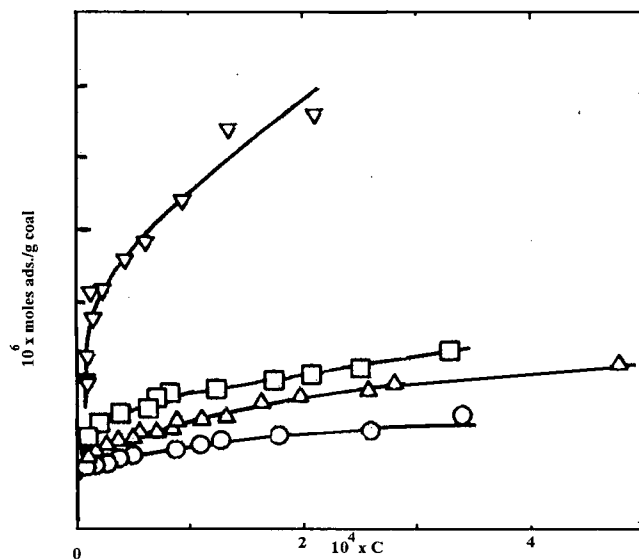
Figure 3.12   Adsorption isotherms of various cationic surfactants on low-ash high volatile bituminous coal; (∇) hexadecyl pyridinium bromide (HPB), ($\square$) tetradecyl pyridinium bromide (TPB), ($\triangle$) dodelcyl pyridinium chloride (DPC) and ($\bigcirc$) dodecyl-trimethyl ammonium bromide (DTAB) on low-ash high volatile bituminous coal (Latif Ayub et al., 1985); © reprinted with permission from *Coal Preparation*, copyright (1985) Taylor & Francis Inc., under licence from Access Copyright, further reproduction prohibited.

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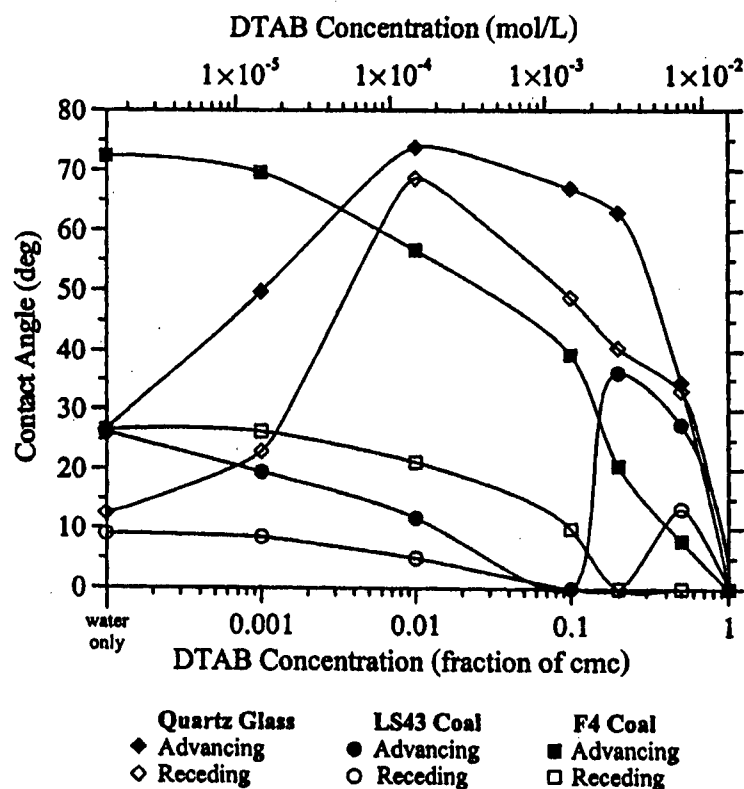
Figure 3.13   Contact angles on LS43 sub-bituminous coal, F4 bituminous coal and quartz plate as a function of DTAB concentration (Pawlik, 2002); © reprinted with permission from the University of British Columbia, copyright (2002) Pawlik.
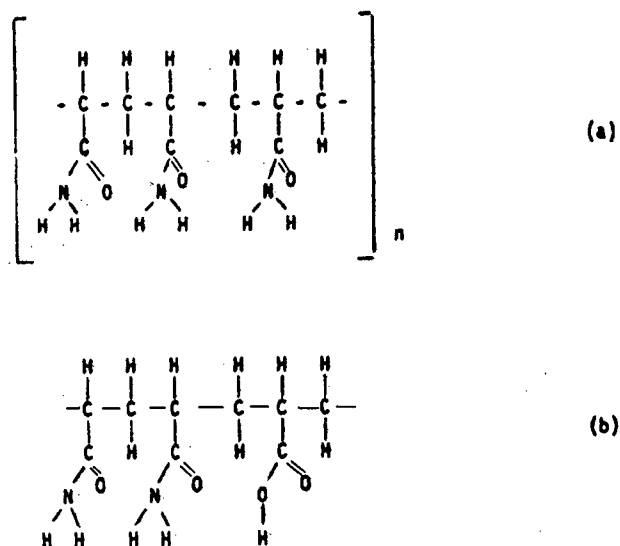
Figure 3.14   Structure of: (a) polyacrylamide and (b) anionic polyacrylamide.
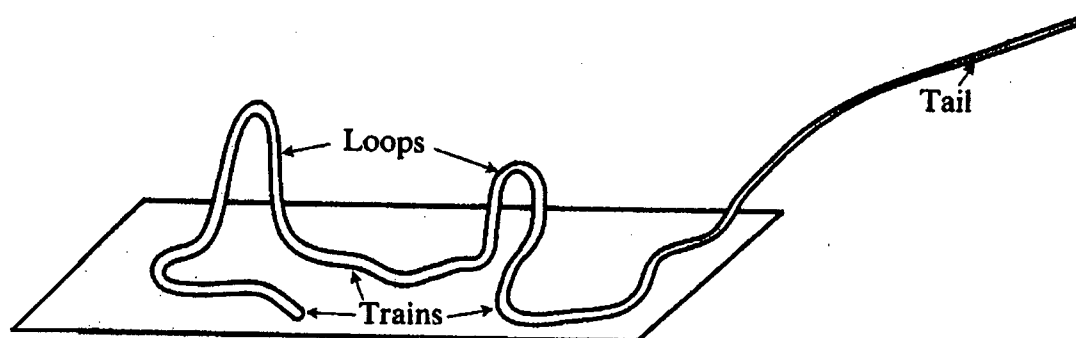
Figure 3.15   Schematic diagram of polymer adsorbed on a surface.

CHAPTER 4   MATERIALS AND METHODS

4.1 Reagents

4.1.1 Dodecyltrimethyl Ammonium Bromide (DTAB) and Dodecyltrimethyl Ammonium Chloride (DTAC)

DTAB was used as a collector in cationic flotation of calcite and dolomite. The reagent-grade DTAB was purchased from Acros Organics. This sample as reported by the manufacturer was 99 % pure. Distilled water was used for the preparation of a 5 % DTAB stock solution. Fresh stock solution was prepared daily.

A technical-grade cationic amine, Arquad 12-50 (which contains about 50 % of DTAC), kindly provided by AKZO NOBEL, was used in the reverse flotation of a mixture of a subbituminous coal and gangue minerals, and in the reverse flotation of the subbituminous coal itself. In the previously published papers on this topic dodecyltrimethyl ammonium bromide (DTAB) was utilized in the reverse coal flotation process (Stonestreet and Franzidis, 1988, 1989 and 1992; Pawlik and Laskowski, 2003a and 2003b). DTAC was used instead of DTAB in this thesis because it is much cheaper and exhibits similar properties. Actually, a total of seven quaternary ammonium salts, all from AKZO NOBEL, were tested in preliminary flotation experiments: Arquad 16-29W, Arquad 16-50, Arquad 12-37W, Ethoquad C/25, Arquad 12-50, Ethoquad C/12, and Ethoquad 18/25. It was found that only Arquad 12-50 and Ethoquad C/12 exhibited similar properties to DTAB in the reverse flotation of coal, and Arquad 12-50 (DTAC) was selected for further tests.

Arquad 12-50 is a solution of DTAC in a propyl alcohol/water mixture. Its composition is given in Table 4.1. As this table shows, the concentration of dodecyltrimethyl ammonium chloride (DTAC) in the sample is 45-55 %. A 2.5 % DTAC stock solution used for this study was made by diluting 50 g of the "as received" reagent to a litre with distilled water.

4.1.2 Dextrin

Dextrin was used as a coal depressant without any purification. The sample was obtained from A.E. Staley Manufacturing Company. The trade name of the sample is Tapioca Dextrin 12 and its molecular weight, as determined by Nyamekye (1993), is 56,000 Daltons. Hot distilled water was used for the preparation of 1 % stock solution.

4.1.3 Water Glass and Modified Water Glasses

Water glass and modified water glasses were used to activate the flotation of calcite and dolomite. Type N water glass, kindly provided by National Silicates Ltd., Canada, has a SiO_2/Na_2O ratio of 3.22 and this solution contains 37.56 % of sodium silicate. The 1.878 % stock solution used for this study was made by diluting 50 g of the "as received" reagent to a liter with distilled water.

Modified water glasses included a series of metal silicate hydrosols and an acidified water glass. The preparation procedures were similar to those employed by Mercade (1981). Metal silicate hydrosols were prepared by adding 1 % solution of a polyvalent metal salt to the 1.878 % solution of water glass at room temperature, while stirring. The stirring was continued for 30 minutes and the product was used 24 hours later. The ratio of polyvalent metal salt solution to sodium silicate was adjusted to keep the metal ion concentration in the metal-sodium silicate mixtures constant at 5.34×10^{-4} mol/L. For example, the ferric silicate hydrosol was prepared by adding 1.1 mL of 1 % solution of $FeCl_3 \cdot 6H_2O$ to 73.9 mL of the 1.878 % solution of water glass. The acidified water glass was made by adding 25 mL of 1 % sulfuric acid solution to 75 ml of the 1.878 % solution of water glass during stirring until the pH of the solution was stabilized at around pH 10.2. The following reagent-grade metal salt hydrates were used to prepare the modified water glasses in this study: ferrous sulfate ($FeSO_4 \cdot 7H_2O$), cobalt sulfate ($CoSO_4 \cdot 7H_2O$), ferric chloride ($FeCl_3 \cdot 6H_2O$), aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$), and cupric sulfate ($CuSO_4 \cdot 5H_2O$).

4.1.4 Tannic Acid

Reagent-grade tannic acid was purchased from Fisher Scientific Company. The addition of tannic acid was found to improve the quality of clean coal in reverse flotation. With the addition of tannic acid the ash content of clean coal decreased by 1-2 %. Tannic acid acted as a dispersant, and the 1 % stock solution was prepared using distilled water.

4.1.5 Polyacrylamides

A number of polyacrylamides with different molecular weight and charge density were used in reverse coal flotation and flocculation experiments. Most of the polymers were provided by Cytec Canada Inc. and the rest were purchased from Polysciences Inc. A 0.2 % stock solution was prepared using distilled water. Properties of all tested polymers are listed in Table 4.2.

The molecular weights of polymers from Cytec Canada Inc. are quoted as low, medium or high, corresponding to the range of 10-20 million Daltons (depending on products from low molecular weight (LMW) through standard to high molecular weight (HMW)).

It should be noted that a completely non-ionic polyacrylamide does not exist because of its residual hydrolysis in solution. The degree of anionicity of non-ionic polyacrylamides from Polysciences Inc. is approximately around 1-2 %.

Other reagents used in this thesis included fuel oil, MIBC frother, HCl and NaOH, and Polystyrene sulfonate (PSS10) dispersant. Fuel oil and MIBC were used as a collector and frother, respectively, in the forward flotation of coal, and HCl and NaOH were used to adjust pH in flotation and flocculation tests.

PSS10 was used as a dispersant in the rheological measurements of coal-water slurries. The PSS10 sample was an anionic polymer with a molecular weight of 14,000 Daltons and was supplied as a 37% aqueous solution by Lion Corp., Japan. It came from a batch that was commercially used in Japan for the preparation of CWS (Pawlik, 2005).

4.2   Minerals and Coal Samples

4.2.1   Calcite, Dolomite and Silica

Quartz, kaolinite and carbonates are common gangue minerals associated with coal. Calcite, dolomite and silica were used to investigate the floatability of those gangue minerals with amine in this thesis.

Calcite was prepared from marble slabs and dolomite from lumps of dolomite ore. Coarse silica (top size about 1 mm) was obtained from Ottawa Silica Company (Illinois, USA). Calcite and dolomite were first crushed and then ground in a rod mill to a desired size. The coarse silica was also reground. The ground materials were then used in flotation. The particle size distributions of calcite, dolomite and silica used in flotation are shown in Table 4.3. A chemical analysis showed that the purity of calcite and dolomite was over 97.5 %, and the silica was 99 % pure according to the supplier.

For adsorption tests, the +74 μm portion was removed and the specific surface areas of the -74 μm fractions of calcite, dolomite and silica, as determined using BET method, were found to be 1.05 m^2/g, 1.52 m^2/g and 1.34 m^2/g, respectively. The particle size distributions of the fine calcite, dolomite and silica samples used in adsorption tests, as determined using Malvern Mastersizer 2000, are shown in Figure 4.1.

4.2.2   Coal

The low rank LS20 coal was selected for this study. This coal was chosen because low rank coals, and coals stored in old tailing ponds, are difficult to beneficiate by flotation. These are thermal coals and they are likely to be utilized in the form of coal-water slurries in the future. The coal was provided by Luscar Sterco Ltd. from the Coal Valley (pit 20) in Alberta. The coal sample was crushed to below 6 mm size in a hammer mill. The crushed sample was further ground to below 0.216 mm using a pulverizer. Its particle size distribution, as determined by screening, is shown in Table 4.4. The specific surface area of this material (BET method) was found to be 6.75 m^2/g. Such a large specific surface area indicates a high content of fines in the sample. This -0.216 mm coal sample was thoroughly mixed and stored in sealed polythene bags for direct use (or further

grinding). The ash content of the sample was 34.6 % and was determined through proximate analysis as shown in Table 4.5. As can be seen from Table 4.4, 53.0 % of the material is under 74 μm and 33.1 % is under 38 μm. The data also reveal that the ash content is higher in fine fractions. The -38 μm fraction had the highest amount of ash content at 52.6 %. Such a large amount of fines could result in higher amine consumption in the reverse coal flotation. The total ash content calculated from the ash content in each size fraction was 35.1 % and quite close to 34.6 % which was obtained analytically from the whole coal sample (Table 4.5).

The mineral composition of LS20 coal is shown in Table 4.6. Quartz, muscovite and kaolinite are the main minerals in this coal. It also contains 5.6 % of calcite and 3.0 % of gypsum.

Inherent ash is the ash content that represents mineral matter which is nonseparable from coal organic matter by physical methods. To determine the inherent ash content of the LS20 coal, the coal was upgraded using a shaking table. After a six-stage concentration it was then determined that the ash content was 10 %. This is consistent with the results obtained from release analysis.

The LS20 coal samples with different size distributions were used throughout this research. They were utilized to carry out flotation experiments, raw and clean coal adsorption tests, and coal flocculation tests. The flotation concentrate was also used to prepare coal-water-slurries for rheological measurements. A description of these different samples is as follows:

- Coal sample for the flotation and adsorption tests: the -0.216 mm LS20 coal was used as a flotation feed throughout the research. This sample was also used to carry out adsorption tests.
- Clean coal sample for the adsorption tests: the clean coal sample was prepared from the -0.216 mm LS20 coal sample. The -0.216 mm LS20 coal sample was concentrated 6 times using a shaking table to avoid any chemical contamination. The concentrate from the shaking table was collected, dried, and then reground to -150 μm for further use.
- Coal sample for the flocculation tests: the -0.216 mm LS20 coal sample was reground to below -45 μm and the product was stored in sealed polythene bags.

- Coal sample for producing flotation concentrates used to prepare coal-water slurries (CWS) in rheological measurements: the concentrates (clean coals) from forward and reverse flotation were used to prepare coal-water slurries. Initially, the coal-water slurries were prepared from the flotation concentrate of the -0.216 mm feed coal sample. It was found that this concentrate was too coarse and settled quickly. This made the rheological measurements very difficult. The -0.216 mm coal sample was then reground to -74 μm and this product was used as a flotation feed to produce concentrates for preparing coal-water slurries. The measurements were carried out at varying solids content.

The particle size distributions of these coal samples, as determined using Mastersizer 2000, are shown in Figure 4.2.

4.3   Experimental and Techniques

4.3.1   Flotation Tests

4.3.1.1 Flotation in a 2 L mechanical cell

The flotation tests included cationic flotation of calcite and dolomite, and reverse coal flotation. In those tests, the feed weight was 200 g, the pulp volume was approximately 2 liters (10 % solids), and the impeller's speed was 1500 rpm, which produced an aeration rate of 2 L/min. The reverse coal flotation experiments included conventional reverse flotation (DTAC collector was conditioned) and zero-conditioning time reverse flotation (DTAC collector was not conditioned).

Cationic flotation of calcite and dolomite: In those tests, pure calcite and dolomite were used and DTAB collector was conditioned. The basic experimental procedure consisted of using a 200 g sample per test, diluted with tap water. Water glass or modified water glass was then added to the slurry, which was agitated for 5 minutes, followed by the addition of DTAB. Agitation continued for another 5 minutes, and the pH was adjusted to a desired level with NaOH or HCl. Frother was not added in these tests. The flotation

process was carried out for 5 minutes, and the froth product and tailings were collected, dried, and weighed. Since pure materials were used, the recoveries were equal to the yield of flotation products.

Conventional reverse flotation of a subbituminous coal/gangue mixture: In those tests, gangue was floated and DTAC collector was conditioned. The flotation feed was prepared by mixing calcite, dolomite and silica with the raw LS20 coal (-0.216 mm) at a ratio of 1:1:1:7. The ash content of the mixture was 48.5 %. Ferric silicate hydrosol was added to the slurry and conditioned for 20 minutes followed by the addition of dextrin and DTAC (each conditioned for 5 minutes). pH was adjusted to a desired level with NaOH or HCl and flotation was performed for 5 minutes. The concentrate (combustible material that did not report to the flotation froth) and the reject (the material that reported to the flotation froth) were collected, dried, and weighed to determine yields of these products. The ash contents of both products were determined following standard procedures.

Conventional reverse flotation of a subbituminous coal: In those tests, gangue was floated and DTAC collector was conditioned. A 200 g coal sample was mixed with tap water and conditioned for 10 minutes to ensure complete wetting of the coal. The reagents were added in the following order: tannic acid, dextrin, polyacrylamide, and DTAC. Each was conditioned for five minutes. Flotation was performed for five minutes after admitting air into the cell. The concentrate and the reject were collected, dried, and weighed; the yields were calculated and the ash contents of the two products were determined following standard procedures.

Zero-conditioning time reverse flotation of a subbituminous coal: The flotation procedures were the same as in the conventional reverse flotation tests except that DTAC was not conditioned with the pulp prior to flotation. DTAC was added in two different ways: either directly or through a sparger. For direct addition, the air valve of the flotation cell was opened prior to the addition of DTAC, and flotation started directly after the addition of DTAC. When the addition was done through a sparger, the DTAC was introduced continuously as aerosols along with compressed air into the flotation cell over the whole period of flotation time. One end of the sparger was immersed into the cell and the other was connected to a 1 L tank attached to a compressed air system (Figure 4.3). The air pressure was about 414 kPa (60 psi). A collector solution of known concentration

was placed inside the tank before each test. The volume change and the injection time of the collector solution in the tank were recorded. The consumption of the collector was then calculated. For direct addition, the flotation began as soon as the collector was added. When sparger was used, the DTAC solution was added continuously during flotation.

The reproducibility was quite good in all batch flotation tests. The yields of products varied within ± 5 % range from repeated experiments.

4.3.1.2 Flotation in an 8 L mechanical cell

Both forward (coal was floated) and zero conditioning time reverse flotation tests were carried out in an 8-liter Denver laboratory cell to produce coal concentrates for the preparation of CWS in order to conduct rheological measurements. In those tests, the feed weight was 1000 g, the pulp volume was approximately 8 liters, and the impeller's speed was 1500 rpm, which produced an aeration rate of 6 L/min.

In preparation of a forward flotation concentrate, an emulsified mixture of 3 kg/t of Diesel oil and 400 g/t of MIBC (5 minutes of conditioning) was used to float the LS20 coal. The flotation was performed for 5 minutes. The ash content of the coal concentrate was 21.3 %. No flotation occurred if only MIBC was used indicating that this coal was not hydrophobic, but there was good flotation with the combined use of the mixture of emulsified Diesel oil and MIBC.

The zero conditioning time technique (direct DTAC addition) was used in the preparation of a reverse flotation concentrate. The reagents were added in the order of tannic acid (1 kg/t, 5 minutes of conditioning), dextrin (1 kg/t, 5 minutes of conditioning), polyacrylamide (400 g/t, 5 minutes of conditioning), and DTAC (2 kg/t, zero conditioning). The flotation was carried out for 5 minutes. The ash content of the concentrate was 23.3 %.

The flotation feed size (LS20 raw coal) was -74 μm.

4.3.1.3 Column flotation

Both forward and conventional reverse column flotation tests of LS20 coal were

carried out to investigate the column carrying capacity. The conventional reverse column flotation tests were also performed to study the effect of conditioning with A100 polyacrylamide on selectivity of coal flotation. The column used in the flotation testwork was constructed at the University of British Columbia. The column was 1.5 m long and had an internal diameter of 53 mm. A schematic diagram of the experimental set-up is shown in Figure 4.4.

Forward column flotation: In the forward column flotation tests, 4.5 kg of LS20 coal (-0.216 mm) was first conditioned with 24.5 L water in a 30 L tank for 10 minutes at 1500 rpm, followed by the addition of 1 L of an aqueous emulsion of MIBC and fuel oil (MIBC 500 g/t, fuel oil 4 kg/t). The solids content of the pulp was 15 %. After 5 minutes of conditioning at 1500 rpm, the pulp was pumped to the column at three different rates: 300 mL/min, 500 mL/min, and 700 mL/min. The operating parameters of the flotation column were as follows:

Froth height: 0.4 m
Collection zone height: 1.1 m
Solids content: 15 %
Feed rate: around 300, 500, 700 mL/min
Wash water rate: 200 mL/min
Air rate: 3.5 L/min

The froth height in the column was controlled manually by adjusting the tails pump rate to maintain a constant pulp/froth interface level. Once the pulp had reached the required level, the tails pump was switched on and the flow rate adjusted so that the pulp/froth interface level remained constant. The column was then allowed to reach steady state over a period of approximately 10 minutes, during which fine adjustments to the tails pump rate were made to maintain a constant pulp level in the column.

For each run, sampling was performed by taking tails and concentrate samples simultaneously over a period of exactly 5 minutes. The samples were dried, processed and sent for ash analysis.

In conventional reverse column flotation tests, 4.5 kg of LS20 coal (-0.216mm)

were conditioned with 23 L water in the 30 L tank for 10 minutes at 1500 rpm, followed by the addition of 500 mL of 0.9 % tannic solution (1 kg/t, 5 minutes conditioning at 1500 rpm) and 500 mL of 0.9 % dextrin solution (1 kg/t, 5 minutes conditioning at 1500 rpm). Then 1000 mL of 0.225 % A100 polyacrylamide solution (500 g/t) were added and conditioned for 5 minutes at a different rate, 400 rpm or 1500 rpm. The feed pump was switched on as 500 mL of 2.475 % DTAC solution (2.75 kg/t) were added into the tank. The final solids content was 15 %. The subsequent operation and sampling procedures were the same as the forward column flotation.

4.3.2 Flocculation Tests

Preparation of flocculant stock solutions: distilled water (1000 mL) was poured into a 1000-mL beaker and stirred with a magnetic stirrer to form a smooth vortex in the center of the beaker. 2 g of polymer powder were slowly sprinkled onto the sides of the vortex. The resulting dispersion was stirred for 12 hours to ensure that all polymer particles were completely dissolved. A homogeneous stock polymer solution of 2 g/L was thus obtained (this solution was also used in flotation tests). The stock solution was diluted to a working concentration of 250 mg/L by adding 1 part of polymer solution to 7 parts of distilled water and stirring for 10 minutes. This solution was used to investigate the effect of un-sheared PAM on the flocculation of coal, and the effect of intense conditioning of the PAM-coal suspension (in a flotation cell) on flocculation of coal.

Preparation of shear degraded flocculant solutions: 1000 mL of polyacrylamide stock solution (250 mg/L) obtained as described earlier were placed in a 1 L flotation cell and subjected to an agitation of 1500 rpm for 30 minutes. The shear degraded solutions were stored and used to study the effect of sheared PAM on the flocculation of coal.

Settling tests: Settling tests were conducted in a 500 mL graduated cylinder. For standard flocculation tests, the suspension was prepared in a 600 mL beaker, in which the polymer solution (unsheared or sheared) was added into a gently agitated coal-water suspension. Settling tests were also carried out after conditioning a polymer-coal suspension at 1500 rpm in a 1 L flotation cell for 5 minutes prior to transfer to the cylinder. In the former case, in order to wet the coal particles, 25 g of coal sample and a

predetermined amount of tap water were conditioned for 10 minutes using a paddle stirrer at 400 rpm in a beaker. The paddle stirrer speed was reduced to 100 rpm before a predetermined amount of the polymer working solution (either unsheared or sheared) was introduced over a period of one minute using a syringe. Once the whole amount of the polymer was added, the agitation was stopped immediately and the pulp (5 % solids content) was quickly transferred into the cylinder. After 4 inversions of the cylinder, a timer was started to record the positions of the interface as a function of time.

In the latter case (in which the coal-polymer suspension was conditioned intensively prior to flocculation), 25 g of coal sample, a predetermined amount of tap water and the unsheared polymer solution (total volume 500 mL, 5 % solids content) were first agitated in a 1-L flotation cell at 1500 rpm for 5 minutes. The conditioned coal-polymer suspension was then quickly transferred into the cylinder to carry out the settling tests. After 4 inversions of the cylinder, a timer was started to record the positions of the interface as a function of time.

In both cases, the top 23 cm layer of the pulp was removed using a pump after 5 minutes of settling. The two products (the top and bottom portions of the suspension) were dried and weighed to calculate the solids content. The ash contents were then determined following the standard procedure described in the following section.

4.3.3 Proximate Analysis and Ash Content Determination

Moisture was determined by heating a 1 g fine coal sample (- 0.216 mm) at 105°C for one hour in an oven providing natural air circulation. After heating, the sample was immediately placed in a desiccator and cooled down to room temperature. The dried sample was weighed quickly to minimize the re-adsorption of moisture from the air. The moisture content was then calculated from the difference in the coal weight before and after heating. Volatile matter was determined after establishing the loss of weight resulting from heating the sample at 950°C for 7 minutes in a platinum crucible without access of air. The ash content was obtained by weighing the residue remaining after burning the pre-weighed coal sample (about 1 g) under 780°C for two hours. Ash content determinations were routinely carried out for all products obtained from flotation and flocculation tests.

The fixed carbon value was determined by subtracting the moisture, volatile matter and ash content from 100 % and expressed on a dry-ash-free basis.

4.3.4 BET Specific Surface Area Determination

A Quantasorb sorption system (Autosorb 1-MP) was used to measure the specific surface area of calcite, dolomite and silica (-0.74 μm) as well as raw coal (-0.216 mm) and clean coal (-0.15 mm, cleaned by a shaking table). In the apparatus, nitrogen was adsorbed from a nitrogen-helium mixture flowing through a powdered sample.

The determination of the surface area is a direct application of the BET (Brunauer-Emmett-Teller) equation in the following form (Brunauer et al., 1938):

$$\frac{1}{X(\frac{P_0}{P})} = \frac{C-1}{X_m C} \times \frac{P}{P_0} + \frac{1}{X_m C} \qquad (4.1)$$

where X is the weight of nitrogen adsorbed at a pressure P (obtained from the desorption peak), P is the partial pressure of adsorbate (nitrogen), P_0 is the saturated vapor pressure of adsorbate, X_m is the weight of adsorbate at a monolayer coverage, C is a constant which is a function of the heat of the adsorbate condensation and the heat of the adsorption.

It can be seen from the BET equation that a plot of $\dfrac{1}{X(\frac{P_0}{P})} \; vs \; \dfrac{P_0}{P}$ is a straight line with the slope S and y-intercept I given by:

$$S = \frac{C-1}{X_m C} \qquad (4.2)$$

$$I = \frac{1}{X_m C} \qquad (4.3)$$

X_m can be calculated from equations 4.2 and 4.3:

$$X_m = \frac{1}{S+I} \qquad\qquad (4.4)$$

The total surface area of the sample, S_{Total}, can be obtained from:

$$S_{Total} = \frac{X_m N A}{M} \qquad\qquad (4.5)$$

where N is the Avogadro number (6.023×10^{23} molecules/mol), A is the cross-sectional area of the adsorbate molecule ($16.2 \times 10^{-20} m^2 / molecule$ for N_2), and M is the molecular weight of the adsorbate (28.01 g/mole for N_2).

The specific surface area of the sample is obtained by dividing the total surface area, S_{Total}, by the weight of the sample. The specific surface areas of the minerals and coal samples used in this thesis are summarized in Table 4.7. The specific surface area of LS20 raw coal is more than 6 times greater than that of the cleaned coal concentrated by a shaking table. Since after the concentration, the large amount of fines in raw coal was removed which greatly reduced the specific surface aera.

4.3.5   DTAB and DTAC Adsorption

Adsorption of DTAB and DTAC onto tested minerals was determined by measuring the residual amine concentration in the filtrate. Amine concentrations were measured using the dye-extraction method (Mukerjee, 1956; Mukerjee and Mukerjee, 1962). A Cary 50 (Varian) UV-VIS spectrophotometer was utilized at 416 nm.

In this procedure, 20 mL of 0.01N hydrochloric acid was mixed with 5 mL of a 1.5 g/L Bromophenol Blue (BPB) solution (in distilled water) and 1 mL of 0.05N HCl, all in a 100 mL volumetric flask. Then, 4 mL of the amine solution was added to the mixture followed by 20 mL of chloroform.

The basis for the method is a reaction between the anionic dye (BPB) and the

cationic surfactant (DTAB/DTAC) to form a water-insoluble dye-amine complex. In the acidic environment, the complex has a 1:1 (BPB: DTAB/DTAC) molar ratio (Mukerjee and Mysels, 1955). The concentration of the BPB stock solution (1.5 g/L =2.17×10^{-3} mol/L) was chosen such that the molar concentration of BPB in the acidified mixture was at least 4 times higher than the highest molar amine concentration (for example DTAB: 180 mg/L = 5.84×10^{-4} mol/L). This excess BPB guaranteed the complete capture of all amine molecules by the dye, as discussed by Mukerjee and Mukerjee (1962).

The water insoluble BPB-amine complex was extracted into the chloroform phase by vigorously shaking the flask for 45 seconds. This time was found to be sufficient to completely transfer the complex into the organic phase. The chloroform-water emulsion was then left for 20 minutes to separate. The chloroform layer turned yellow from the presence of the BPB-amine complex. The acidified aqueous phase (30 mL in total) was removed (the density of chloroform is 1.473 g/mL at 25°C) and the organic phase was withdrawn with a pipette and transferred to a 1 cm quartz cell. The concentration of the complex in the organic phase was spectrophotometrically determined at 416 nm. The amine (DTAB/DTAC) equilibrium concentration was read from a calibration curve (appendix A).

The amount of amine adsorbed was calculated as follows:

$$\Gamma_{Ads} = \frac{(C_{Initial} - C_{Equilibrium})V}{m A_{BET}} \tag{4.6}$$

where Γ_{Ads} is the amount of amine (DTAB/DTAC) adsorbed (mole/m^2), $C_{Initial}$ is the initial amine concentration (mol/L), $C_{Equilibrium}$ is the equilibrium amine concentration (mol/L), A_{BET} is the specific surface area (m^2/g) of the solid, m is the mass of material used in the test (g), and V is the volume of the solution (L).

Since the calibration curve was linear only up to 180 mg/L (Appendix A), more concentrated amine filtrates were diluted. The diluted solutions were then used to determine the original amine concentration in the filtrate, taking into account the dilution factor.

Adsorption of DTAB on calcite and dolomite: The tests included conditioning 5 g of the tested materials (calcite or dolomite) for 20 minutes. This was done with 25 mL of distilled water in 100 mL glass bottles, placed in an Environ shaker at 350 rpm, to ensure complete wetting of the solids. Then 25 mL of DTAB solutions varying in concentration were added to each sample and the mixtures were conditioned for 1 hour which was sufficient to achieve adsorption equilibrium. In the tests with modified water glass, 1 mL of 1.878 % ferric silicate hydrosol was added to the pulp and conditioned for 20 minutes before introducing 24 mL of DTAB solution at a predetermined concentration. After removing the solids by centrifuging, the DTAB concentration in solution was determined to calculate the DTAB adsorption density.

Adsorption of DTAC on LS20 coal, LS20 clean coal and silica: The procedure included conditioning 5 g of the tested sample for 20 minutes with a predetermined amount of distilled water in 100 mL bottles, placed in an Environ shaker at 350 rpm, in order to ensure complete wetting of the solids. Then a predetermined volume of DTAC solution was added to each sample (the total volume of solution was 50 mL) and the mixtures were conditioned over different conditioning times. The mixtures were then quickly filtered and the filtrate was collected to determine the amine concentration. In the tests with PAMs, 8 mL of 250 mg/L PAM solution was added to the mixture and conditioned for 20 minutes before introducing DTAC solution at a predetermined concentration and volume (the total solution volume was 50 mL). After conditioning at different time intervals, the mixture was filtered in a few seconds. It should be noted that a very short conditioning (5 seconds) of DTAC was employed in some of the experiments. In these tests, the mixture was vigorously shaken by hand for 5 seconds and then quickly filtered.

To investigate the effect of air bubbles on the DTAC adsorption on LS20 clean coal and silica, the conditioning was carried out in a 1-L flotation cell with its air valve open. In these tests, a 50 g sample with a predetermined volume of distilled water was agitated for 20 minutes in the cell. Then, a volume of DTAC solution with known concentration was added (total 500 ml) and the pulp was conditioned for different time intervals. The mixture was quickly filtered after conditioning. The adsorption density was measured as a function of DTAC concentrations.

4.3.6   Zeta Potential Measurements

A Zeta Meter (Zeta Meter Inc., New York) with a quartz electrophoretic cell was employed to measure the zeta potential of calcite and dolomite. A small amount of the ground material, usually 0.05 g, was dispersed in 45 mL of 10^{-2} mol/L KCl solution and conditioned at a given pH for 5 minutes. Water glass or ferric silicate hydrosol (5 mL of 3.756 g/L) were added. The conditioned dispersion was allowed to settle for 5 minutes with only the finest portion (the supernatant) used for the measurements. On average, 8 particles were tracked and timed along a calibrated scale under a microscope to calculate the electrophoretic mobility. The Smoluchowski equation was then used to calculate the zeta potential. The reproducibility of the measurement was ± 3 mV as determined from repeated experiments.

4.3.7   Rheological Measurements

The rheological measurements with the suspensions prepared from the forward and reverse flotation concentrates were performed with the use of a Haake Rotovisco RV 20 rotational viscometer. The elongated fixture was chosen as the measuring geometry. The fixture was designed specifically to test settling suspensions. The design of the concentric cylinder has a bob-in-cup, double-gap arrangement with the gap sizes of 2.50 mm and 3.03 mm for inner and outer gaps, respectively (Klein, 1992; Klein et al., 1995).

Coal-water suspensions were prepared from flotation concentrates. The concentrates were filtered and the solid and the filtrate were collected and stored separately. The solid was sealed in a plastic bag and its moisture was determined afterwards. The experiments were conducted as a function of coal solids content. 500 gram portions of concentrate (dry coal basis) were mixed with a given amount of the filtrate in order to obtain slurries with a desired weight percent concentration. Initially the slurries were prepared at the highest possible concentration. After each test they were then diluted with filtrate to lower the solids content. The solids concentration was determined by drying a small sample at 105°C.

The shear rate was programmed using a Haake Rheocontroller RC20. The shear rate was increased from 0 to 250 sec^{-1} over 3.5 minutes.

For each concentrate (forward and reverse), three series of slurries were prepared: in water (filtrate) only, in 0.5 % dispersant (PSS10) solution, and in 1 % dispersant solution. The data were collected and the shear stresses were plotted as a function of shear rates to obtain the flow curves. The apparent viscosities were plotted as a function of coal weight percent content and calculated at 100 sec^{-1}.

4.3.8 Infrared spectroscopy of polyacrylamides

An Infrared spectrum (IR) can be used to identify the functional groups of a polymer. Rogers and Poling (1978) used IR to determine the degree of anionicity of polyacrylamides. The IR spectra of a number of polyacrylamides with different degrees of anionicity were collected and the same procedures described by Rogers and Poling (1978) were followed. The measurements were carried out using a Perkin-Elmer System 2000 FT-IR spectrophotometer.

In infrared spectroscopy, the presence of various functional groups of polyacrylamides is detected by recognizing the characteristic bands and peaks on the infrared spectrum. These infrared spectrum bands are assigned to deformations of chemical bonds in terms of stretches, bond angle bends, oscillations, etc. The qualitative analysis is based on band assignments to functional groups. The infrared (IR) spectra of A100 and A130 polyacrylamides are shown in Figure 4.5 and 4.6.

The dominant features of these two IR spectra are the peaks at around 1668 cm^{-1} and 1565 cm^{-1} wave numbers which are attributed to amide groups (-CONH$_2$) and carboxylic groups (-COOH), respectively. The maximum absorbance peaks appear at 1668 cm^{-1} which indicates the dominant amide groups (-CONH$_2$) in both polyacrylamides (A100 and A130). An increase in the degree of anionicity results in an increased carboxylic group (-COOH) content which corresponds to an increased absorbance peak at around 1565 cm^{-1}, as shown in Figures 4.5 and 4.6. The degree of anionicity for A100 and A130 is 7 % and 33 %, respectively as reported by the manufacturer.

Hydrolysis of a polyacrylamide increases its degree of anionicity. The hydrolysis was carried out by dissolving a polyacrylamide into an alkaline solution and boiling it. Figure 4.7 shows the infrared spectrum of a non-ionic polyacrylamide. The peak at around 1565 cm^{-1} is not detected. After hydrolysis (for two hours), a dominant peak is detected at 1566.69 cm^{-1} (Figure 4.8) showing that carboxylic groups (-COOH) are formed.

The IR spectra of other polyacrylamides are shown in Appendix C.

Table 4.1   Composition of Arquad 12-50 reagent (DTAC).

Name	% by weight
1-Dodecanaminium,N,N,N-trimethyl-chloride	45-55
Isopropyl alcohol	35-45
Water	5-15
Others	0.002-2
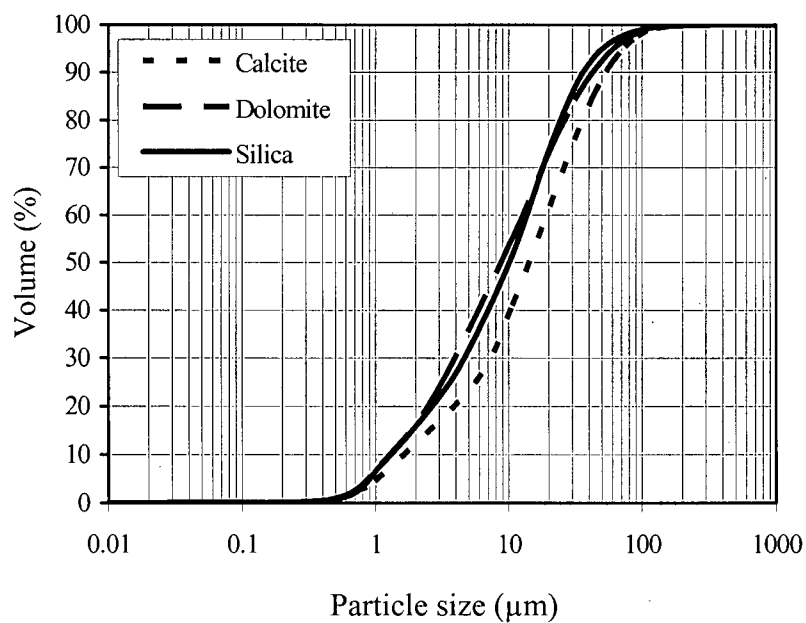
Figure 4.1 Particle size distributions of fine calcite, dolomite and silica (-74 μm).

Table 4.2   Properties of polyacrylamide-based cationic, anionic and non ionic polyacrylamides.

Polymer name	Charge (%)	Molecular weight (Daltons)	Manufacturer
N-100	<2	high	Cytec Inc.
N-300	<1	high	Cytec Inc.
N-300 LMW	<1	medium	Cytec Inc.
A-100	7	high	Cytec Inc.
A-100HMW	7	high	Cytec Inc.
A-110	16	high	Cytec Inc.
A-110 HMW	16	high	Cytec Inc.
A-120 LMW	20	Medium	Cytec Inc.
A-120	20	High	Cytec Inc.
A-120 HMW	20	Very high	Cytec Inc.
A-130 LMW	33	Medium	Cytec Inc.
A-130	33	High	Cytec Inc.
A-130 HMW	33	Very high	Cytec Inc.
A-137	40	high	Cytec Inc.
A-150LMW	50	medium	Cytec Inc.
A-150	50	high	Cytec Inc.
A-150HMW	50	Very high	Cytec Inc.
C-444 (cationic)	20	Medium	Cytec Inc.
C-446 (cationic)	35	Medium	Cytec Inc.
C-491K (cationic)	2	Very high	Cytec Inc.
C-492 (cationic)	10	High	Cytec Inc.
C-494 (cationic)	20	High	Cytec Inc.
C-496 (cationic)	35	High	Cytec Inc.
C-498 (cationic)	55	High	Cytec Inc.
Polyacrylamide 1	10	200,000	Polysciences Inc.
Polyacrylamide 2	70	200,000	Polysciences Inc.
Polyacrylamide 3	40	>10,000,000	Polysciences Inc.
Polyacrylamide 4	Non ionic	10,000	Polysciences Inc.
Polyacrylamide 5	Non ionic	600,000-1,000,000	Polysciences Inc.
Polyacrylamide 6	Non ionic	5,000,000	Polysciences Inc.
Polyacrylamide 7	Non ionic	5,000,000-6,000,000	Polysciences Inc.
Polyacrylamide 8	Non ionic	1,000,000	Polysciences Inc.

Table 4.3   Particle size distributions of calcite, dolomite and silica (for flotation).

Calcite		Dolomite		Silica	
Size (μm)	Yield (%)	Size (μm)	Yield (%)	Size (μm)	Yield (%)
-200+100	6.94	-200+100	7.5	-200+100	5.5
-106+74	3.06	-106+74	4.5	-106+74	8.8
-74	90	-74	88	-74	85.7

Table 4.4   Particle size distribution of LS20 coal (-0.216 mm).

Size(μm)	Yield (%)	Ash (%)
+180	15.6	24.9
-180+149	6.2	23.0
-149+74	25.2	25.5
-74+45	15.6	28.7
-45+38	4.3	34.3
-38	33.1	52.6
Total	100	35.1

Table 4.5   Proximate analysis of LS20 coal.

Moisture (%)	Ash (%)	V.M. (%)	V.M.daf (%)	F.C.daf (%)	Inherent Ash (%)
3.64	34.6	27.5	44.5	55.5	10

Table 4.6   Mineral compositions of LS20 coal

Quarz (%)	Muscovite (%)	Kaolinite (%)	Calcite (%)	Gypsum (%)
42.2	32.3	16.9	5.6	3

Table 4.7   BET specific surface areas of coal and mineral samples.

Material	BET specific area (m^2/g)
Silica (-0.74 µm)	1.34
Calcite (-0.74 µm)	1.05
Dolomite (-0.74 µm)	1.52
LS20 raw coal (-0.216 mm)	6.75
LS20 clean coal (-0.15 mm)	0.98
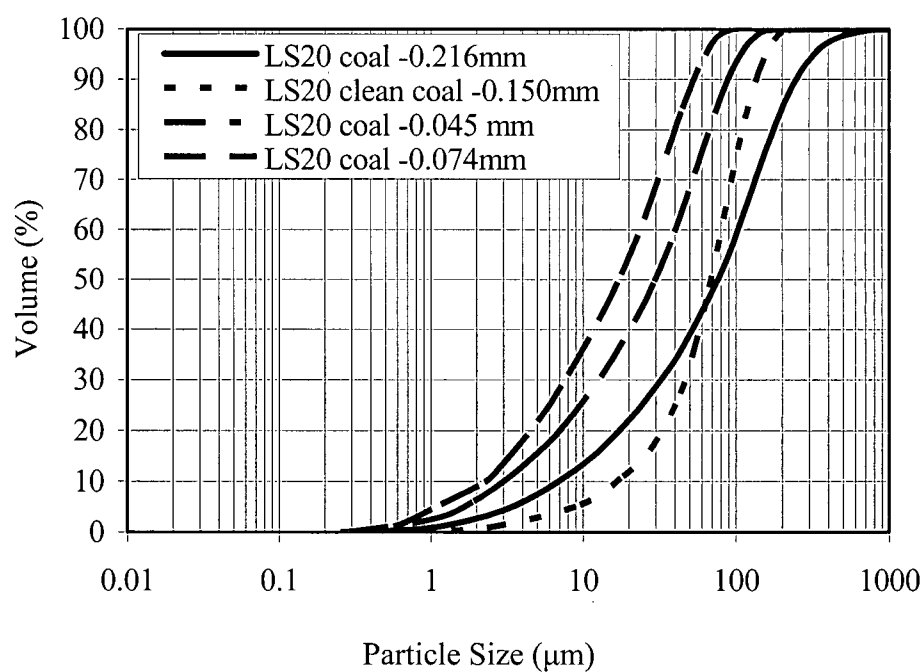
Figure 4.2   Particle size distributions of LS20 coal samples.
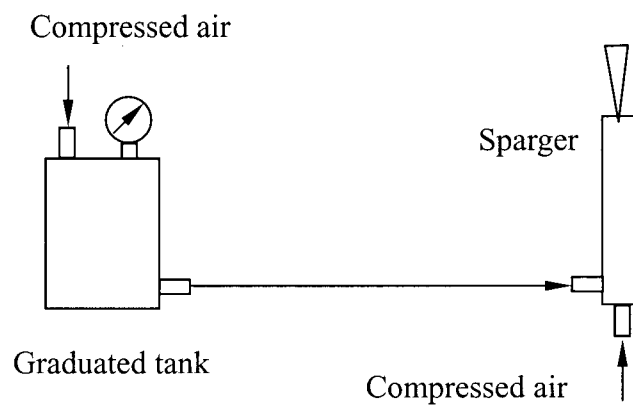
Figure 4.3   Diagram of the aerosols-generating system.
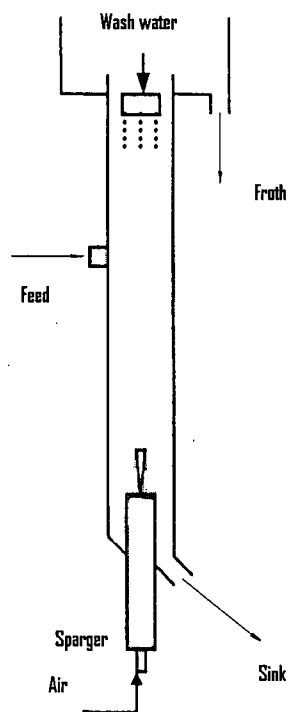
Figure 4.4   Schematic diagram of the experimental set-up of column flotation.
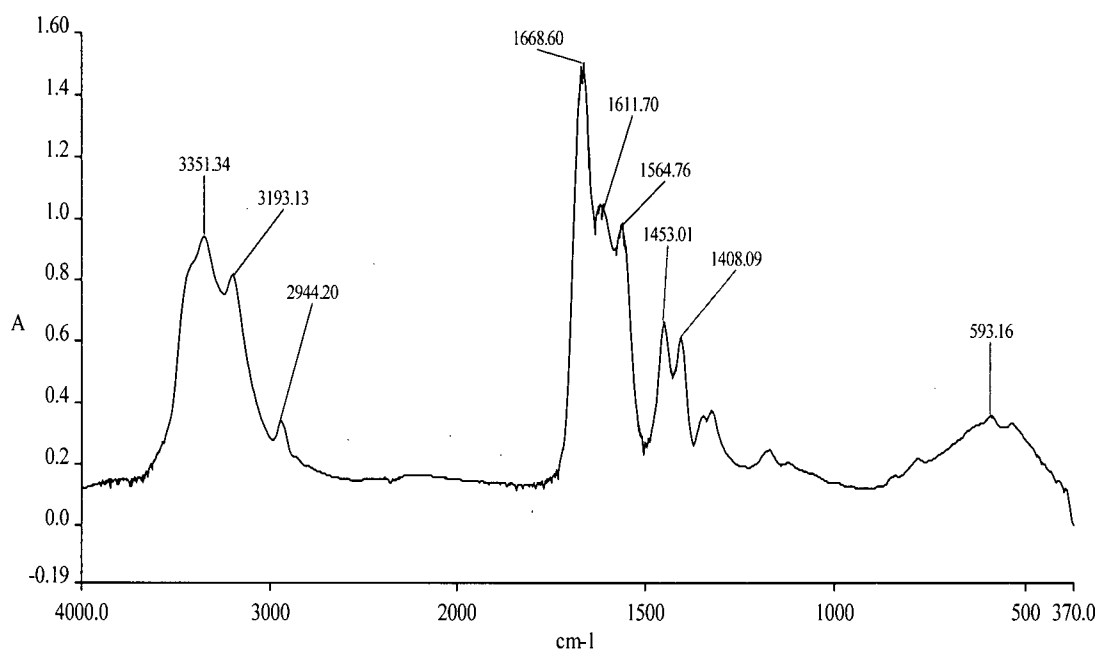
Figure 4.5   Infra-red spectrum of A100 polyacrylamide. Molecular weight 15,000,000 Daltons; degree of anionicity 7 %; solution prepared at natural pH.
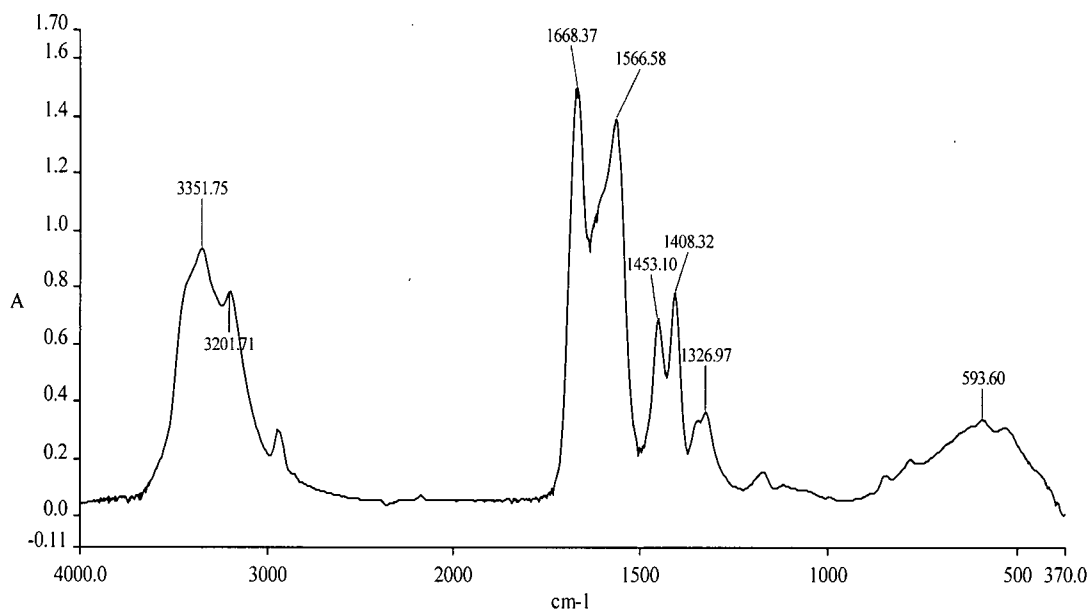
Figure 4.6   Infra-red spectrum of A130 polyacrylamide. Molecular weight 15,000,000 Daltons; degree of anionicity 33 %; solution prepared at natural pH.

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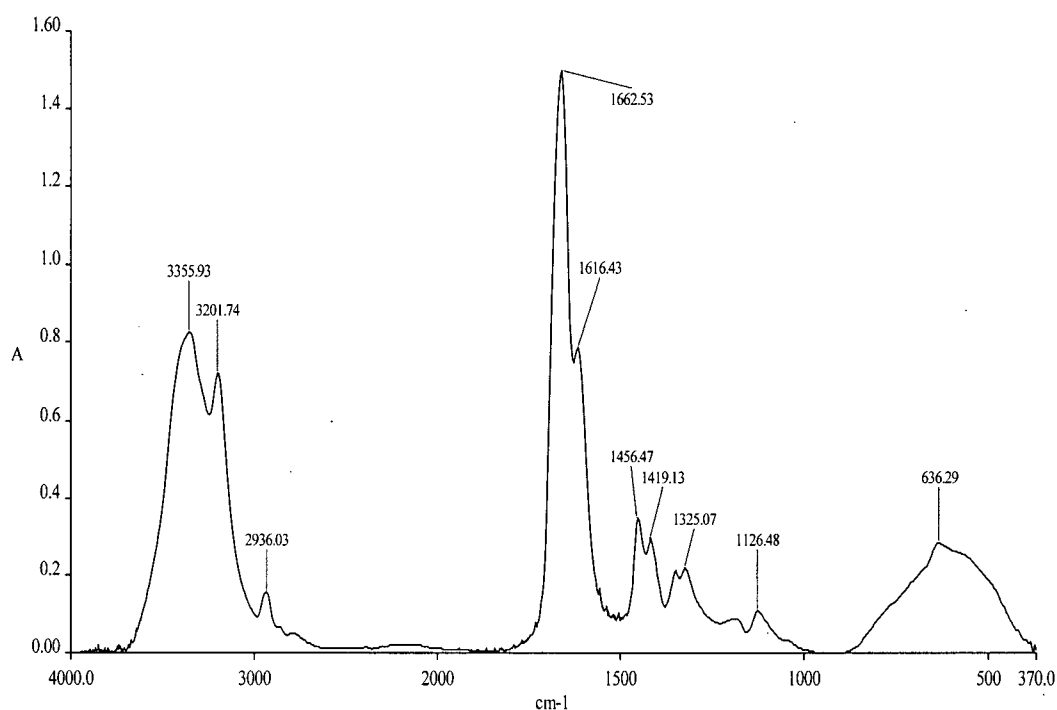
Figure 4.7　　Infra-red spectrum of a non-anionic polyacrylamide. Molecular weight 5,000,000-6,000,000 Daltons; solution prepared at natural pH.
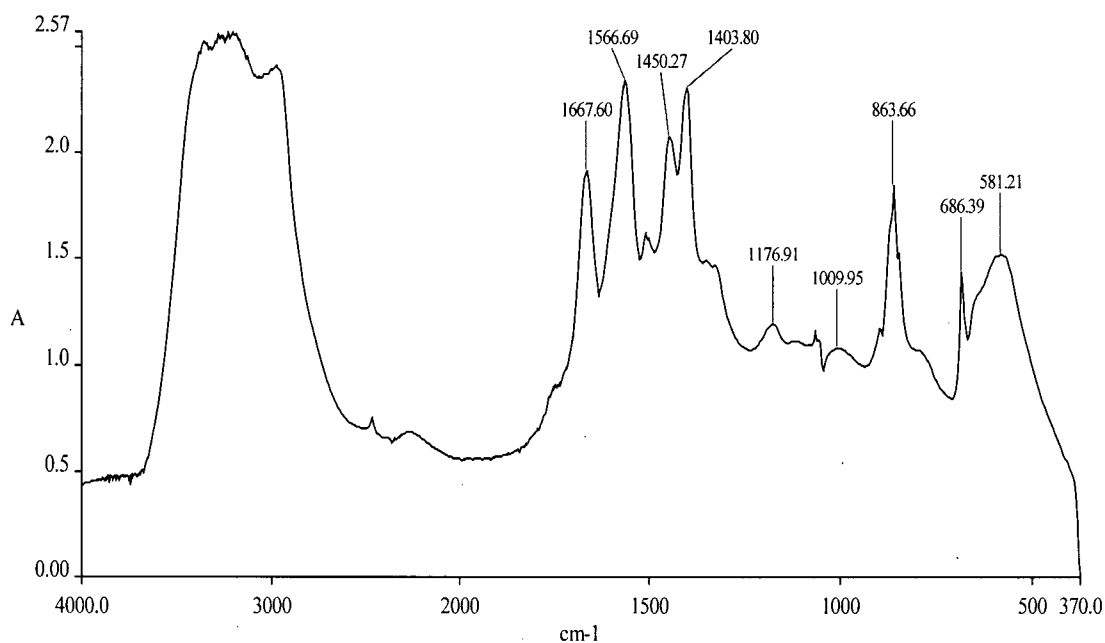
Figure 4.8　　Infra-red spectrum of a non-anionic polyacrylamide after hydrolysis. Molecular weight 5,000,000-6,000,000 Daltons; 0.5 % PAM 25 mL +1 % NaOH 25mL, 2 hours at 100°C.

CHAPTER 5   APPLICATION OF A MODIFIED WATER GLASS IN CATIONIC FLOTATION OF CALCITE AND DOLOMITE

5.1   Introduction

In the reverse flotation of coal, gangue is floated and coal is depressed using amine as a collector. Quartz, muscovite, kaolinite and carbonates are common gangue minerals associated with coal. Quartz floats well with amine. To simplify the process, only pure calcite and dolomite were first used to study the floatability of gangue minerals with amine. Since water glass acts as a depressant in anionic flotation of calcite and dolomite, this agent should promote the cationic flotation of these two minerals. Based on this premise, a cationic collector, dodecyltrimethyl ammonium bromide (DTAB), was used in this study and the effect of water glass, and modified water glasses, on pure calcite and dolomite flotation were first investigated.

Water glass is widely used in flotation as a disperssant/depressant. Commercial water glass is available with ratios of SiO_2 to Na_2O (referred to as modulus) ranging from 1.6 to 3.25. The sample, that is most frequently employed, is type N whose ratio of SiO_2/Na_2O is 3.22. Dispersing/depressing ability of water glass in flotation systems can be improved by reacting sodium silicate with polyvalent metal salts. The depressing properties of different metal hydroxy silicate hydrosols in flotation have been reported by a number of investigators (Belash and Pugina, 1946; Klassen and Mokrousov, 1963; Fuerstenau, Gutierrez and Elgilliani,1968; Yang, 1978; Mercade, 1981; Fuerstenau and Fitzgerald, 1986; Gong et al., 1992,1993; DiFeo et al.,1999).

The cationic flotation of calcite and dolomite was carried out in a 2 L mechanical cell with DTAB collector conditioned for 5 minutes in each test, as described in Section 4.3.1.1, Chapter 4.

5.2 Results and Discussion

The effect of DTAB dosage on the recovery of calcite with and without the addition of ferric silicate hydrosol is shown in Figure 5.1. The recovery of calcite increased with increasing DTAB dosage; the addition of the ferric silicate hydrosol activated the flotation of calcite. In other words, the DTAB consumption was significantly reduced to obtain the same calcite recovery with the addition of the ferric silicate hydrosol. For example, the recovery of calcite was only 68 % at a DTAB consumption of 4 kg/t, but reached 93.5 % when only 2.5 kg/t of DTAB was used in the presence of ferric silicate hydrosol. A similar trend was observed in the flotation of dolomite (Figure 5.2). These results confirmed the assumption that sodium silicate as well as metal silicate hydrosols can promote the cationic flotation of calcite and dolomite.

As indicated in Chapter 4, various metallic cations were reacted with water glass to obtain the modified water glasses. For clarity, in Figures 5.3 and 5.4 only the effect of Na^+ (unmodified water glass), H^+ (acidified water glass) and Fe^{3+} modified water glasses are shown. The efficiency of other metal-activated water glasses was not that different compared to Fe^{3+} modified water glass. The results indicate that the addition of either water glass or modified water glass clearly improves the recoveries of calcite and dolomite. The recoveries of calcite and dolomite increased with increasing dosages of water glass/modified water glass at a constant DTAB dosage. The modified water glasses were more powerful than the natural water glass. 93.9 % of calcite and 98.3 % of dolomite were recovered at a ferric silicate hydrosol consumption of 3.75 kg/t under the tested flotation conditions, comparing to only 46.1 % of calcite and 42 % of dolomite recovered when no ferric silicate hydrosol was added. The only exception was the acidified water glass. This water glass enhanced the flotation of calcite and dolomite more than any other modified samples of water glasses at low dosages, but the activation was hindered at higher dosages. It was found that the addition of high dosages of acidified water glass resulted in the collapse of froth leading to decreased recoveries. The possible reason is that at higher dosages of the acidified water glass the pH of the pulp is lowered and, as Figures 5.9 and 5.11 indicate, the adsorption of DTAB on calcite and dolomite decreases with decreasing pH.

The effect of pH on the flotation of calcite and dolomite mixtures is shown in Figure 5.5. Equal amounts of calcite and dolomite were mixed together to carry out these flotation tests. The results indicate that better recoveries are obtained at higher pH. Over 97.6 % of the mixture is recovered when the pH was higher than 10.

The zeta potential of calcite conditioned with or without water glass is plotted as a function of pH in Figure 5.6. The zeta potential of calcite was positive in the pH range of 7.5-11 with a maximum around pH 9.8, which was roughly in agreement with the measurements made by Liu and Liu (2004). After calcite was conditioned with water glass, or the ferric silicate hydrosol, the zeta potential of calcite became negative.

The zeta potential plotted as a function of pH for dolomite conditioned with or without water glass is shown in Figure 5.7. As can be seen from this figure, the zeta potential of dolomite was positive below pH 11.3. Similar to calcite, the surface of dolomite became strongly negative in the presence of water glass. The results indicate again that the ferric silicate hydrosol is more active than water glass in this process.

Figures 5.8 and 5.9 show the effect of ferric silicate hydrosol on adsorption of DTAB on calcite. As seen from Figure 5.8, the DTAB adsorption density on calcite increases with increasing DTAB concentration; the addition of the ferric silicate hydrosol increased DTAB adsorption even further. Figure 5.9 indicates that the adsorption of DTAB on calcite strongly depends on pH. The DTAB adsorption on calcite increased with increasing pH until a certain point and then began to level off around pH 10-11. The addition of the ferric silicate hydrosol increased DTAB adsorption on calcite at constant DTAB concentration over the entire tested pH range. This is in good agreement with the results of the flotation and zeta potential measurements. Similar results were obtained for dolomite, as Figures 5.10 and 5.11 demonstrate.

The solution system of sodium silicate is complex and contains a variety of polymeric silicate species, monomeric silicate species, and colloidal amorphous silica particles. The degree of the polymerization of silicate depends on pH, and polymeric silicate species have a stronger depressing effect than monomeric and colloidal amorphous species in anionic flotation. The concentration of polymeric species also depends on total SiO_2 concentration. At a relatively high total SiO_2 concentration, the tendency to form polymeric species increases with increasing pH (Gong et al., 1993). This is probably why

better recoveries were obtained at a higher pH range at which higher amine adsorption was measured at mineral surfaces due to an increased concentration of polymeric silicate species.

Fuerstenau et al. (1968) showed that while flotation of calcite with oleic acid $(5 \times 10^{-4}$ M$)$ in the presence of sodium silicate $(5 \times 10^{-4}$ M$)$ was very good, up to pH 6, a complete depression was obtained from pH 7 to 10 with again a good flotation at higher pH values. This was claimed to be consistent with the solubility domain of $SiO(OH)_3^-$. In this thesis the calcite-dolomite mixture floated well in this pH range (pH 7-10) but it was not depressed when pH exceeded 10 (Figure 5.5). This probably can be explained by an increased concentration of polymeric silicate species in the pH range. The electrokinetic experiments indicate that both water glass and the ferric silicate hydrosol extensively adsorb onto calcite and dolomite surfaces since they make the zeta potentials of these minerals more negative. The presence of the silicate hydrosols on the surface of the studied minerals increased adsorption of DTAB onto both minerals (Figures. 5.8 and 5.9) over the entire tested pH range (from 7 to 12), which also correlates nicely with the flotation response (Figure 5.5).

The tests demonstrate without any doubt that water glass, and especially the modified water glass, improves significantly the cationic flotation of both calcite and dolomite. In the processes in which amines are used, for example in the reverse flotation of coal, this may be important. However, it should be noted that the overall DTAB consumptions are still high in the flotation of calcite and dolomite even with the addition of water glass/modified water glass. About 2-2.5 kg/t of DTAB were needed to achieve an over 95 % recovery for both minerals.

5.3   Summary

The electrokinetic measurements revealed that water glass and the modified water glass (ferric silicate hydrosol) adsorb onto both calcite and dolomite. Direct adsorption measurements confirmed that silicate hydrosol adsorption increases the affinity of DTAB towards the surfaces of both tested minerals, and results in an increased DTAB adsorption. This in turn leads to the enhanced cationic flotation of both minerals tested (calcite and

dolomite) when water glass is used. Compared to the effect of the commercial water glass, the modified water glass was found to more efficiently activate the cationic flotation of both minerals tested.

The major conclusion is that water glass/modified water glass can be used to enhance the cationic flotation of calcite and dolomite minerals.
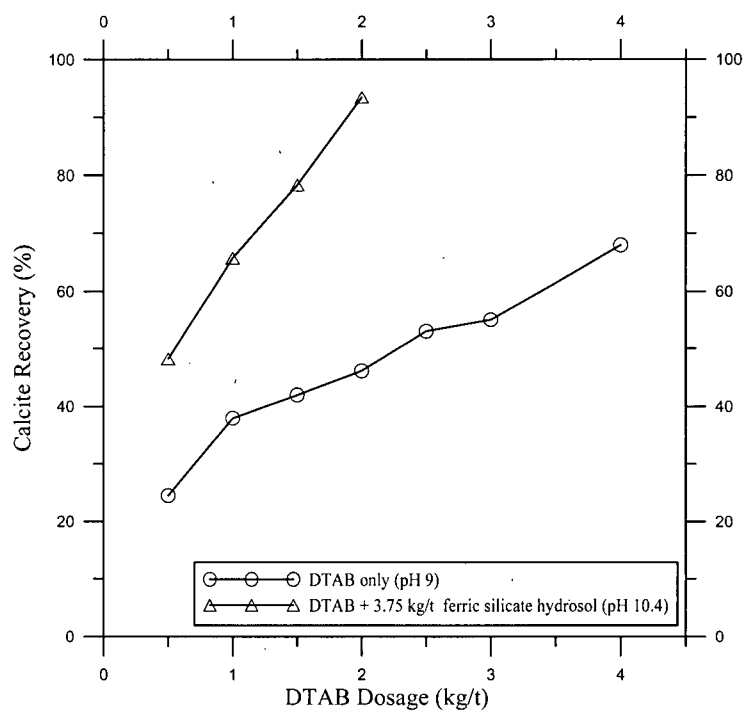
Figure 5.1   Effect of DTAB and ferric silicate hydrosol on calcite flotation (natural pH).
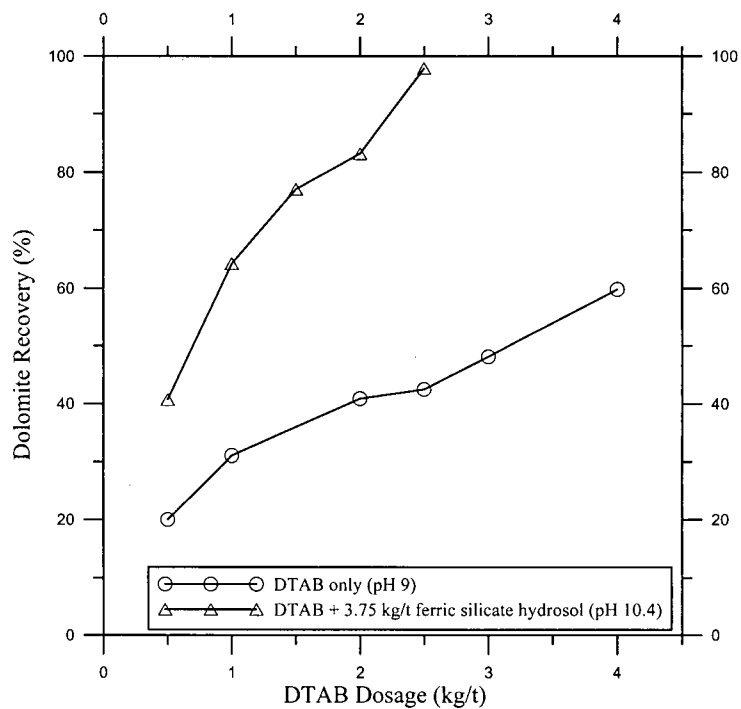
Figure 5.2   Effect of DTAB and ferric silicate hydrosol on dolomite flotation (natural pH).
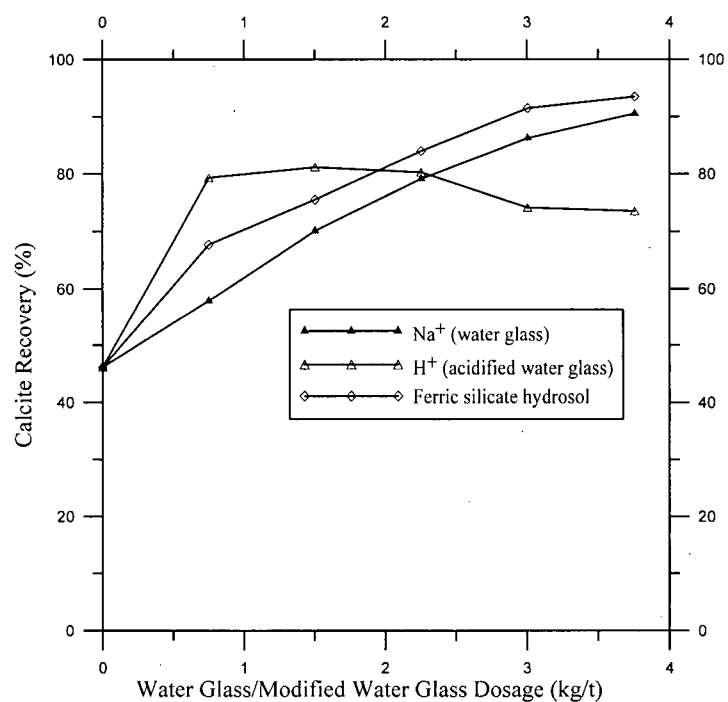
Figure 5.3   Effect of water glass and modified water glasses on calcite flotation (DTAB 2.5kg/t, natural pH)).
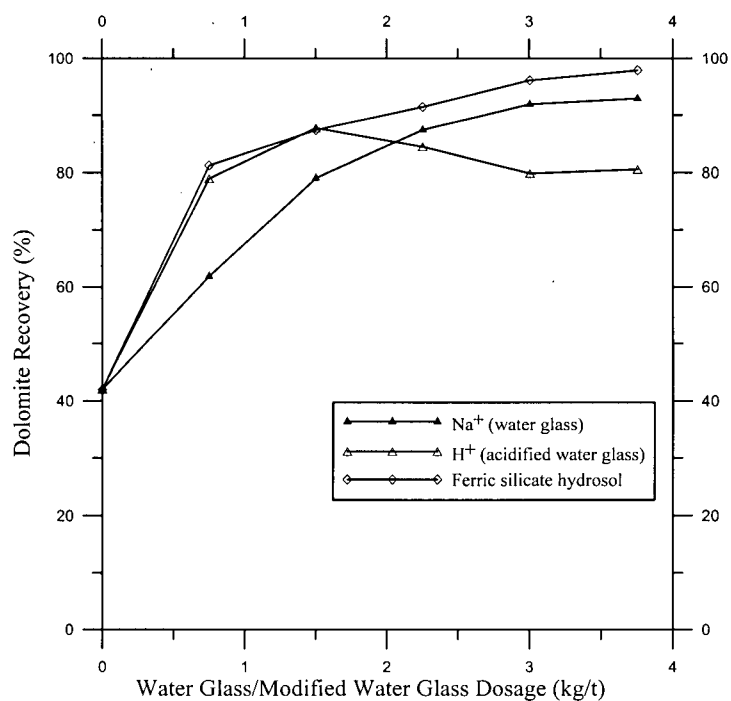
Figure 5.4   Effect of water glass and modified water glasses on dolomite flotation (DTAB 2.5kg/t, natural pH).

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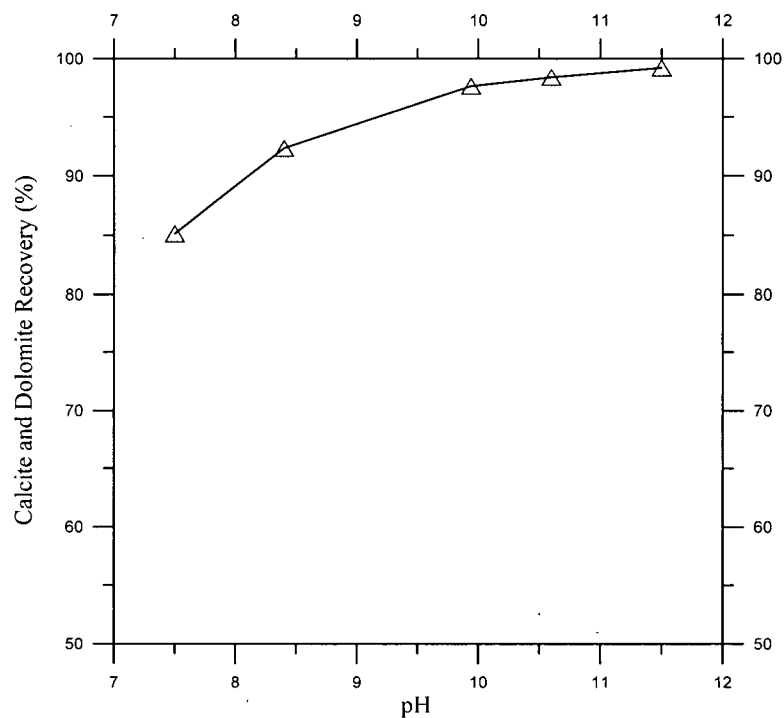
Figure 5.5   Effect of pH on the flotation of calcite and dolomite mixture
(calcite: dolomite =1:1, DTAB 2.5kg/t, ferric silicate hydrosol 3.75 kg/t).
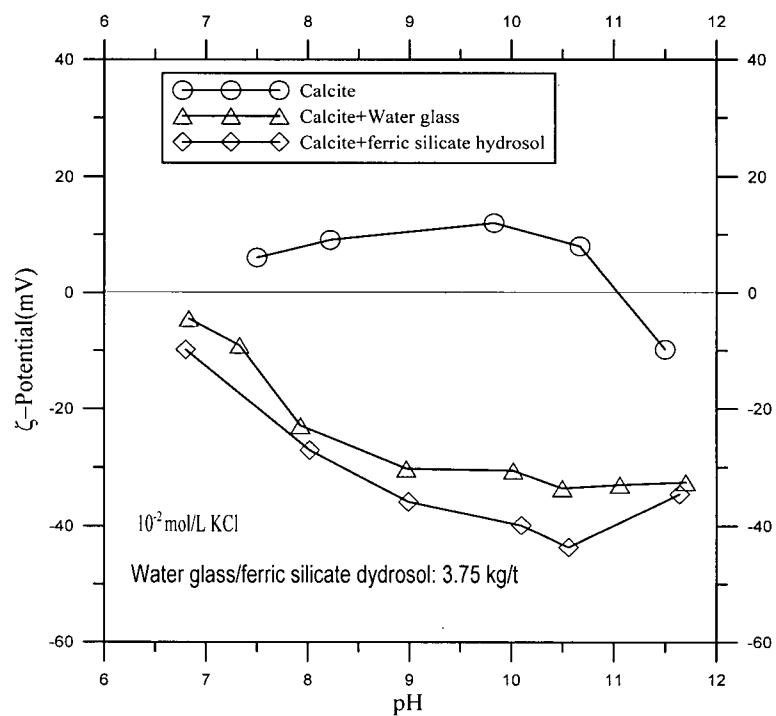
Figure 5.6   Effect of water glass and ferric silicate hydrosol on zeta potential of calcite.
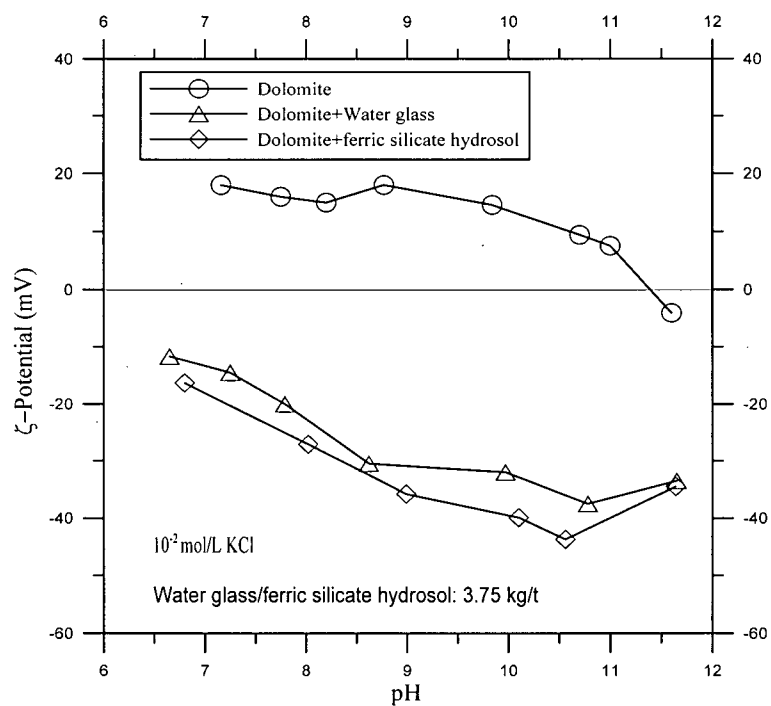
Figure 5.7   Effect of water glass and ferric silicate hydrosol on zeta potential of dolomite.
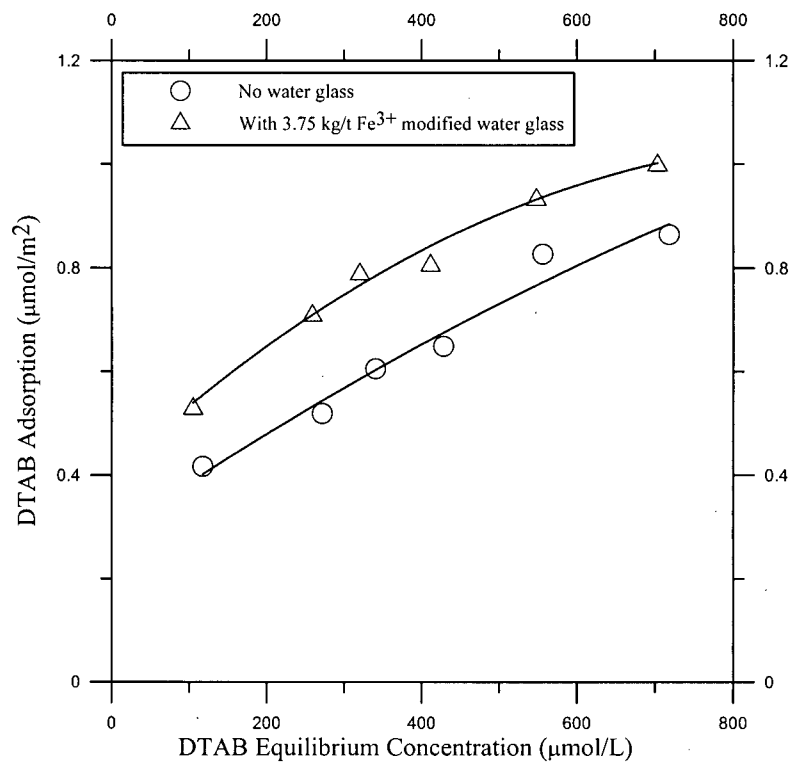
Figure 5.8   Adsorption of DTAB onto calcite at pH 10.4.
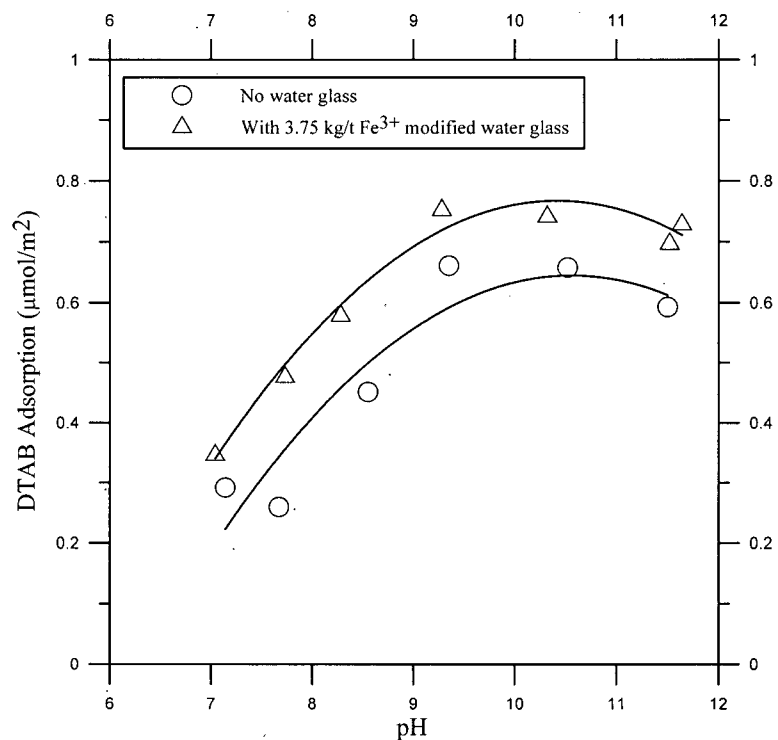
Figure 5.9   Effect of pH and water glass on adsorption of DTAB
on calcite (initial DTAB concentration 4.86×10^{-4} mol/L).
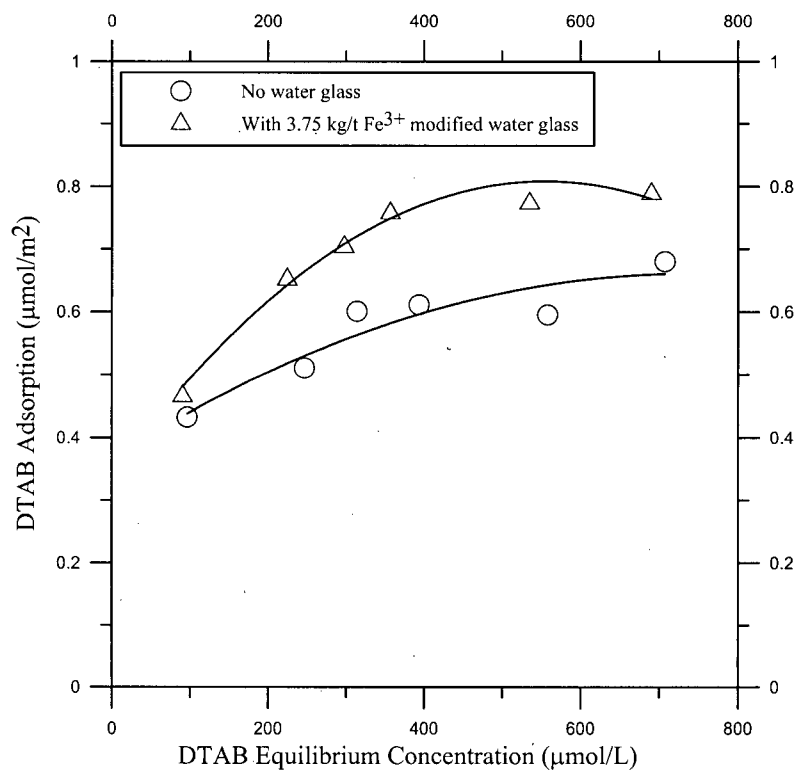
Figure 5.10   Adsorption of DTAB onto dolomite at pH 10.4.
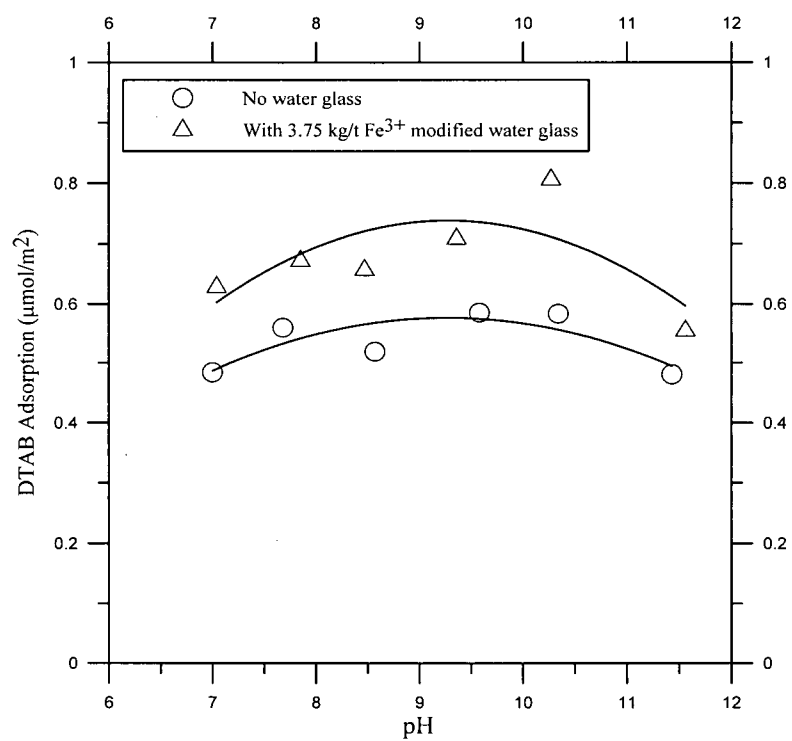
Figure 5.11   Effect of pH and water glass on adsorption of DTAB
on dolomite (initial DTAB concentration 4.86×10^{-4} mol/L).

CHAPTER 6   SEPARATION OF A MIXTURE OF SUBBITUMINOUS COAL AND GANGUE MINERALS

6.1 Introduction

One of the objectives of this research was to develop a reverse coal flotation process in which gangue is floated and coal particles are depressed. As shown in Chapter 5, the gangue (calcite and dolomite) flotation using amine as a collector was significantly improved with the addition of a modified water glass. In this part, 30 % of gangue minerals (calcite, dolomite and silica, each 10 %) were mixed with 70 % of a subbituminous LS20 coal (-0.216 mm) and the analyzed ash content of the coal and gangue mixture was 48.5 %. The conventional reverse flotation of the subbituminous coal/gangue mixture was carried out, in which the DTAC collector was conditioned for 5 minutes, and the effect of various factors on conventional coal reverse flotation was investigated. The flotation was carried out in a 2 L mechanical cell.

In this thesis, mineral/gangue product is referred to as reject which reported to the froth product, and coal product as concentrate which did not report to the froth product in reverse coal flotation.

6.2   Results and Discussion

6.2.1   DTAC stage addition

The effect of DTAC on raw coal/gangue mixture flotation was first tested. The collector was added in one dose. Even at very high dosages of the collector the quality of the concentrate was low, indicating that more gangue material needed to be floated (results shown in Figure 6.1). As can be seen, the yield of the reject increased only from 17.7 % to 23.7 % when dosages of DTAC increased from 5 kg/t to 6.5 kg/t. The ash content of the reject was between 59.3 % and 61.8 % indicating good selectivity, but the ash content of the concentrate was between 44.8 % and 47.0 %, therefore showing that quite a substantial amount of gangue particles was still left in the coal concentrate. It is interesting to note that increasing the collector dosages from 5 kg/t to 6.5 kg/t had little effect on both the yield

and the ash content of the products. The flotation of the gangue minerals did not improve much by increasing the collector dosages.

To reduce the amine adsorption onto coal, DTAC was added in two stages with 0.55 kg/t of the DTAC added in the second stage. As can be seen in Figure 6.2, only 26.6 % of gangue floated with a DTAC consumption of 5.55 kg/t (first addition 5 kg/t and second addition 0.55 kg/t). The ash content of the concentrate was 45.4 % which indicates that the dosage of the collector was insufficient. However, the reject yield increased dramatically to 54.0 % and the ash content of the concentrate decreased to 26.7 % with 6.05 kg/t of collector consumption (first addition 5.5 kg/t and second addition 0.55 kg/t). In comparison, the yield of the reject was only 21.7 % at an ash content of 44.8 %, in the concentrate, with 6 kg/t of DTAC added in one shot. Gangue flotation was further improved and the ash content of the concentrate further decreased when the collector was added in three or four stages, keeping, however, the overall collector dosage constant (as shown in Figures 6.3 and 6.4). For example, the reject yield of 67.3 % and the concentrate ash content of 23.6 % were obtained with four-stage additions (first addition 5 kg/t, second addition 0.55 kg/t, third addition 0.25 kg/t and fourth addition 0.2 kg/t). For the feed ash content of 48.5 %, and considering 10 % inherent ash, the quality of the concentrate was rather good. The results indicate that not only 30 % of the gangue minerals (calcite, dolomite and silica) added to the raw coal/gangue mixture reported to the reject, but the gangue initially contained in the raw coal was floated as well. The separation of the coal from gangue was shown to be possible through reverse flotation, but the consumption of DTAC was high. The effect of stage additions of DTAC on the yield of the reject is summarized in Figure 6.5.

The effect of stage addition of DTAC merits further discussion. The tested subbituminous coal was hydrophilic and had a tendency to adsorb high amount of amine (Pawlik and Laskowski, 2003a and 2003b). In the tests in which DTAC was conditioned for 5 minutes with pulp prior to flotation, the collector adsorption on coal surfaces under such conditions is apparently substantial leaving insufficient amount of the collector available to float gangue. Stage additions decrease collector adsorption on coal surface. It is also possible that the initial stage flotation had significantly removed the fines and thus, resulted in more efficient subsequent flotation.

Although the stage addition of collector could significantly improve gangue flotation, it is only effective when the dosage of the collector reaches a very high level, around 6 kg/t in this case. This indicates that a high dosage of this collector is needed to initiate the flotation and the high collector consumption results from the high adsorption of the collector onto coal surfaces and the effect of fines on flotation. If the adsorption of DTAC on coal surfaces could be reduced and the effect of fines on flotation could be eliminated, the consumption of the collector should decrease. This topic is further dealt with in Chapter 7.

In the subsequent tests, DTAC was added in four stages and the effect of dextrin and the ferric silicate hydrosol, and pH, on the reverse flotation of raw coal/gangue mixture was further investigated.

6.2.2 Effect of dextrin, ferric silicate hydrosol and pH on reverse flotation

The tests revealed that the addition of dextrin and ferric silicate hydrosol improves the selectivity of flotation by lowering the ash content of the concentrate. The results are shown in Figures 6.6 and 6.7. As seen from Figure 6.6, the ash content of concentrate decreased from 30.8 % to 20.9 % when the dosages of dextrin increased from 0 to 1.5 kg/t. Figure 6.7 indicates that the ash content of the concentrate decreased from 30.6 % to 21 % when the dosages of the ferric silicate hydrosol increased from 0 to 2 kg/t. The gangue flotation selectivity is improved following the addition of dextrin mainly due to its depressing action on coal while the ferric silicate hydrosol improves the cationic flotation of calcite and dolomite because of its activation as discussed in Chapter 5.

The effect of pH on the flotation of the raw coal/gangue is shown in Figure 6.8. The low ash content of the concentrate was obtained around pH 10.5. This seems to result from the optimum flotation of calcite and dolomite at that pH level, as discussed in Chapter 5.

It was observed that the conditioning time with the ferric silicate hydrosol also had an impact on the ash content of the concentrate. As shown in Figure 6.9, the ash content of the concentrate decreased from 24.6 % to 20.9 % when the conditioning time was

increased up to 20 minutes. The longer conditioning times with ferric silicate resulted in higher adsorption of silicate species onto calcite and dolomite. Since silicate adsorption promotes gangue flotation, the ash content of the concentrate thus decreased.

6.3 Summary

In the reverse flotation of a subbituminous coal/gangue mixture, good separation was achieved indicating that coal reverse flotation is possible at high dosages of DTAC. Although the stage additions of DTAC could decrease collector consumption, it was only effective when the collector dosage was not lower than 6 kg/t.

The addition of dextrin and the ferric silicate hydrosol improved the selectivity of the process. Dextrin was used to depress coal and ferric silicate hydrosol was used to activate calcite and dolomite for cationic flotation with DTAC. Conditioning with the ferric silicate hydrosol decreased the ash content of the concentrate.
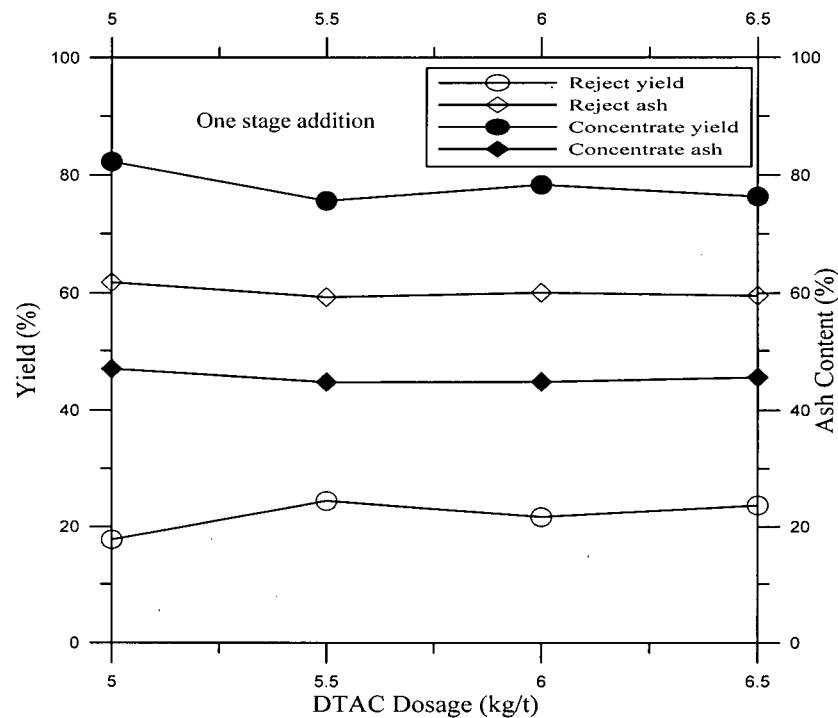
Figure 6.1   Effect of DTAC added in one stage on reverse flotation of raw coal/gangue mixture (ferric silicate hydrosol 2 kg/t, dextrin 1 kg/t, pH 10.4, feed ash 48.5%).
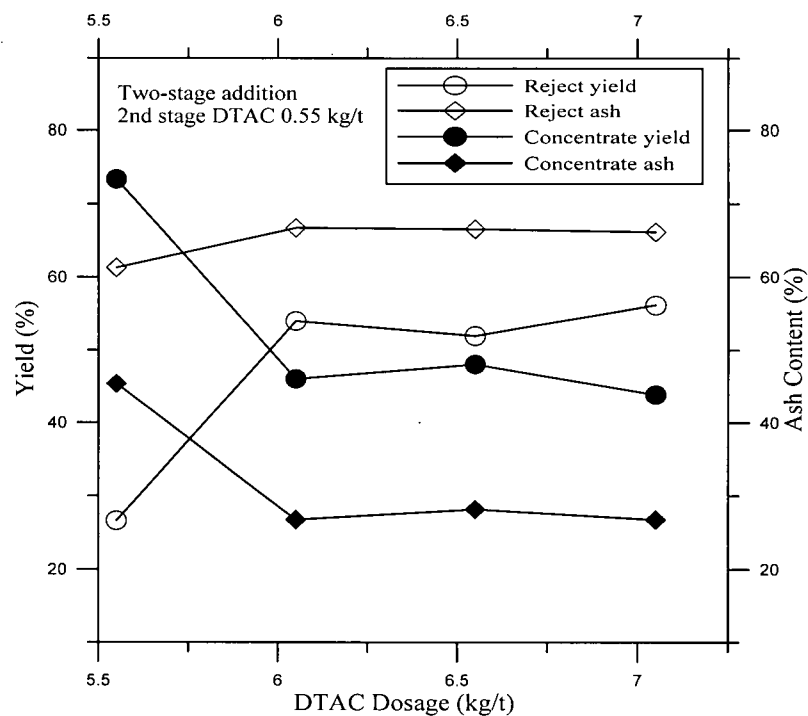
Figure 6.2   Effect of DTAC added in two stages on reverse flotation of raw coal/gangue mixture (ferric silicate hydrosol 2 kg/t, dextrin 1 kg/t, pH 10.4, feed ash 48.5%).
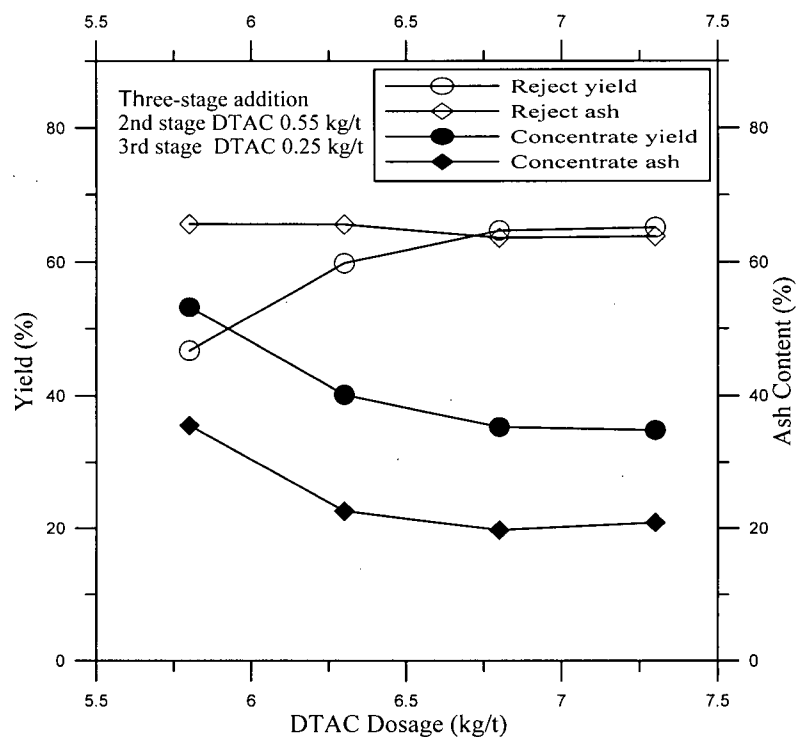
Figure 6.3   Effect of DTAC added in three stages on reverse flotation of raw coal/gangue mixture (ferric silicate hydrosol 2 kg/t, dextrin 1 kg/t, pH 10.4, feed ash 48.5%).
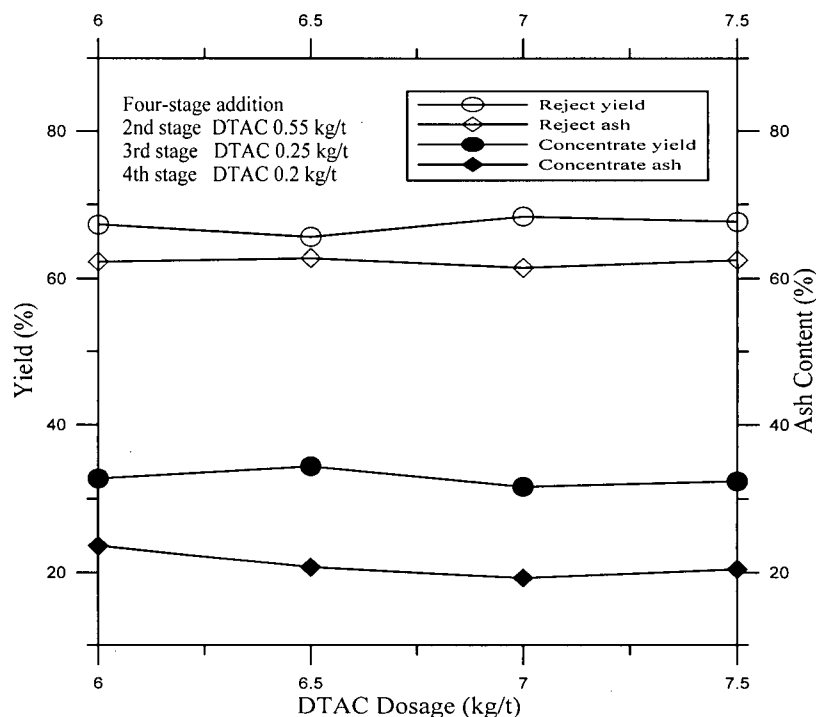
Figure 6.4   Effect of DTAC added in four stages on reverse flotation of raw coal/gangue mixture (ferric silicate hydrosol 2 kg/t, dextrin 1 kg/t, pH 10.4, feed ash 48.5%).

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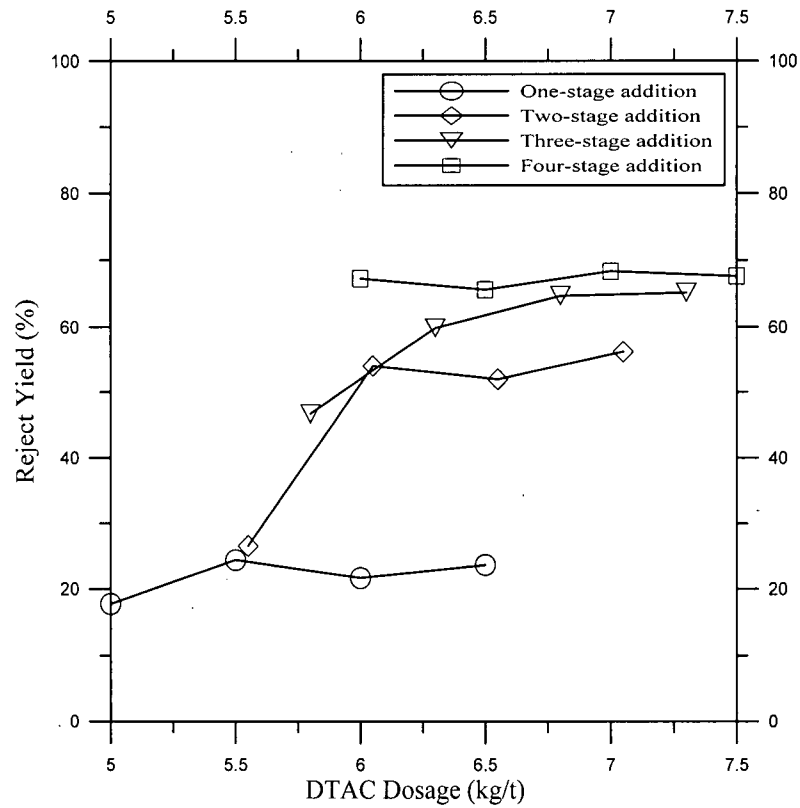
Figure 6.5   Effect of DTAC stage addition on raw coal/gangue mixture reverse
flotation (ferric silicate hydrosol 2 kg/t, dextrin 1 kg/t, pH 10.4, feed ash 48.5%).
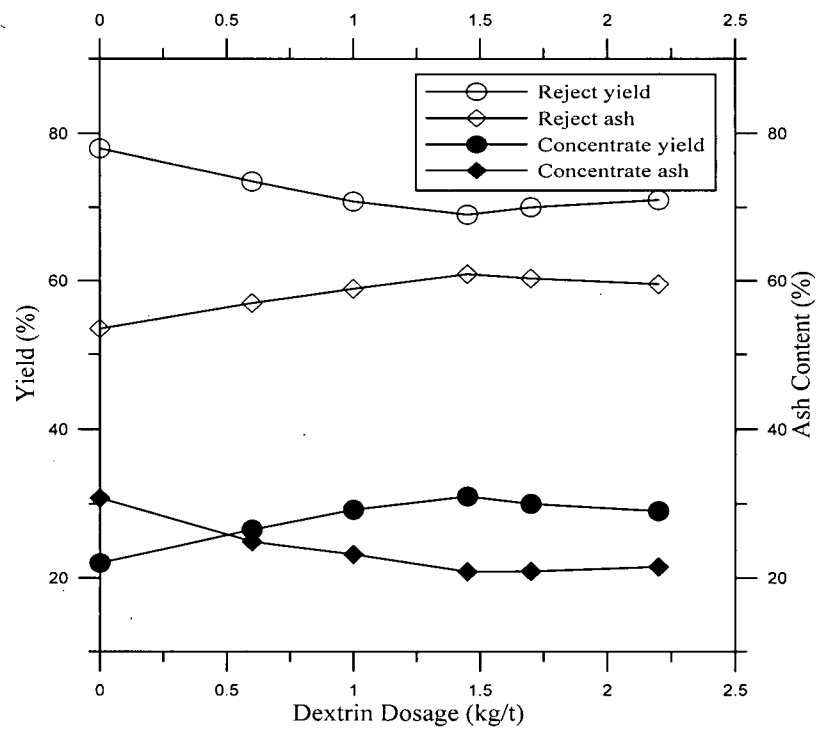
Figure 6.6   Effect of dextrin on reverse flotation of raw coal/gangue
mixture (DTAC 6 kg/t, ferric silicate hydrosol 2 kg/t, pH 10.4, feed ash 48.5%).
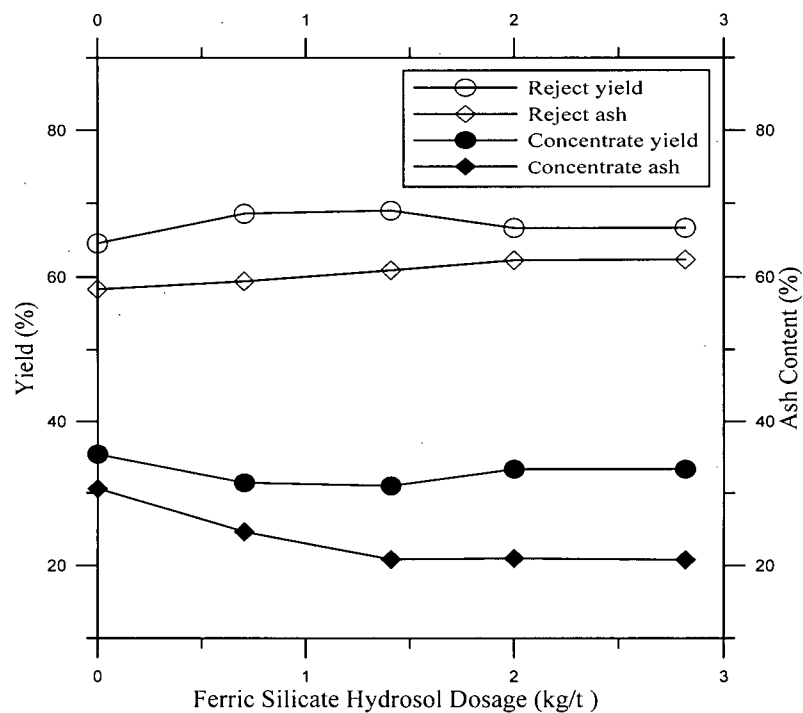
Figure 6.7   Effect of ferric silicate hydrosol on reverse flotation of raw coal/gangue mixture (DTAC 6 kg/t, dextrin 1 kg/t, pH 10.4, feed ash 48.5%).
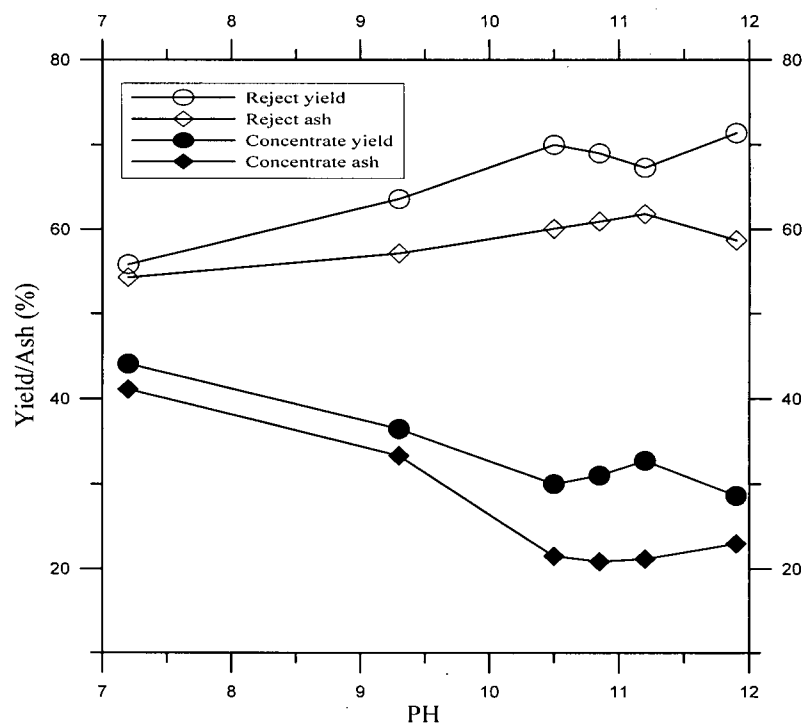
Figure 6.8   Effect of pH on reverse flotation of raw coal/gangue mixture (DTAB 6 kg/t, dextrin 1 kg/t, ferric silicate hydrosol 2 kg/t feed ash 48.5%).

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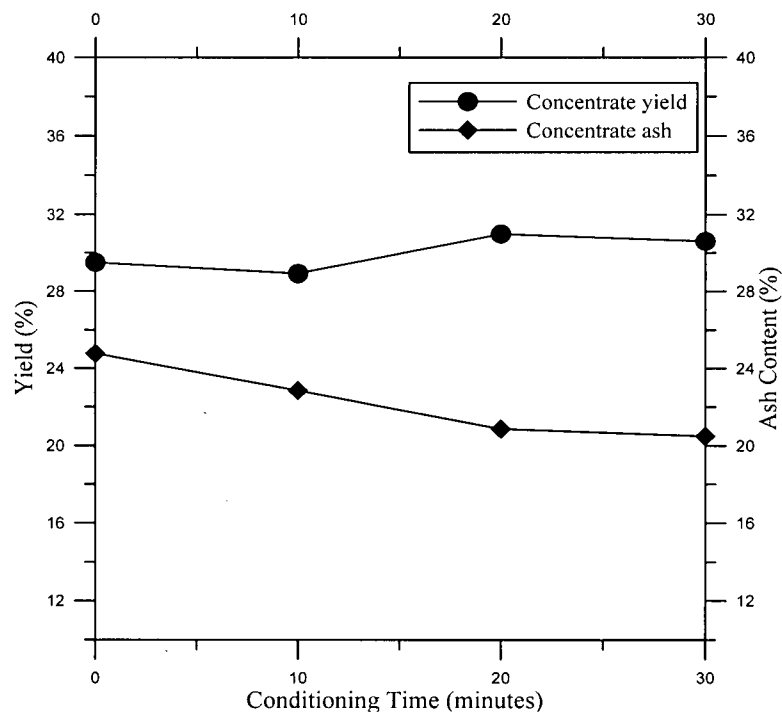
Figure 6.9 Effect of conditoning time of ferric silicate hydrosol on reverse flotation of raw coal/gangue mixture (DTAC 6 kg/t, dextrin 1 kg/t, ferric silicate hydrosol 2 kg/t, pH 10.4, feed ash 48.5%).

CHAPTER 7   THE USE OF THE ZERO CONDITIONING TIME CONCEPT IN CLEANING A SUBBITUMINOUS COAL

7.1 Introduction

As the results of Chapter 6 indicated, the reverse flotation of a raw coal/gangue mixture is possible with good selectivity, but only up to 6 kg/t of DTAC and the separation could only be achieved through stage addition of the collector. These results were obtained while working with a mixture of raw coal and gangue minerals and the preliminary flotation tests indicated that there was a significant difference between the reverse flotation of the raw coal/gangue mixture and the raw coal itself. When the raw coal was floated under the optimum flotation conditions established for the raw coal/gangue mixture, not enough gangue material floated indicating that the dosage of the collector was still not sufficient. This is reasonable since 30 % of the perfectly liberated gangue minerals (calcite, dolomite and silica) were mixed with 70 % of the raw coal in the flotation of the mixture, and the adsorption of DTAC onto these gangue minerals is much lower than onto coal. The reduced amount of coal in the feed decreases the adsorption of the collector onto coal, leaving more collector available to float the gangue. When only raw coal is used instead, more collector is apparently adsorbed by the coal so that much higher collector dosages are required to separate the gangue minerals from coal particles. The ferric silicate hydrosol was used to activate calcite and dolomite in the reverse flotation of raw coal/gangue mixture, but preliminary tests showed that its addition had no effect on the reverse flotation of raw coal itself.

Two methods of dealing with the problem of high DTAC consumption were considered. First, a polymer (A100 polyacrylamide) was used as a blinder, and second, the zero conditioning time flotation method was employed. Unless specified, in all zero conditioning time reverse flotation tests, direct DTAC addition method was used (in which the air valve of the 2 L mechanical flotation cell was opened prior to the DTAC addition).

For comparison, conventional reverse coal flotation tests were first carried out (in which the DTAC collector was conditioned for 5 minutes prior to flotation).

The LS20 raw coal (-0.216 mm) was used in the experiments.

7.2 Results and discussion

7.2.1 Effect of DTAC and PAM on conventional reverse coal flotation

The effect of DTAC and PAM (A100) on conventional reverse flotation of LS20 coal is shown in Figures 7.1-7.4. DTAC was conditioned for 5 minutes in all of these tests. As can been seen from Curve 1 (Figure 7.1), the yield of reject increased with increasing DTAC dosages, but only 24.4 % of the gangue material was recovered into the reject with a DTAC consumption of 5 kg/t. However, the yield of reject was dramatically increased with the addition of PAM. For example, a reject yield of 23.1 % was obtained with a DTAC consumption of 2 kg/t in the presence of 500 g/t of PAM, as shown by Curve 2 (Figure 7.1).

The addition of dextrin slightly decreased the yield of reject (Curves 3 and 4 in Figure 7.1), but significantly improved selectivity. As Figure 7.2 shows (Curves 1 and 2), without the addition of dextrin, the highest ash contents of the rejects were 58.5 % and 57.5 % in the absence and presence of PAM respectively, but the ash contents of the rejects increased to 68.7 % and 68.9 %, respectively, after the addition of 1 kg/t of dextrin.

The yield and ash contents of the concentrate are presented as a function of collector dosages in Figures 7.3 and 7.4. Both parameters decreased with increasing DTAC consumption because more gangue material reported to the reject. A concentrate of 24.9 % ash at 73.4 % yield was obtained at 3 kg/t DTAC, 1 kg/t dextrin and 500 g/t PAM. The feed ash of the raw coal was 34.6 %.

These results are significant since they indicate that the addition of PAM greatly reduces the consumption of DTAC. More than a half of DTAC was saved by adding 500 g/t of PAM (Figure 7.1) to obtain rejects at the same yield. Although DTAC consumption in conventional reverse coal flotation was greatly reduced from 6 kg/t down to 3 kg/t by the addition of PAM, the dosage was still considered high.

7.2.2 Effect of DTAC and PAM on zero conditioning time reverse coal flotation

The zero conditioning time flotation method was tested to reduce further the consumption of the collector. The results are shown in Figures 7.5-7.8. A reject yield of 58.8 % was obtained at a DTAC dosage of 5 kg/t under zero conditioning situation (Curve 1 in Figure 7.5), compared with only 24.4 % of the reject yield obtained in the conventional flotation test (Curve 1 in Figure 7.1). The use of the zero conditioning time technique increased the yield from 24.4 % to 58.8 % (these results were obtained without any PAM). When PAM was used (500 g/t), as Curve 2 (Figure 7.5) shows, the yield of the reject jumped to 84.8 % with a DTAC consumption of 1.375 kg/t, compared with only 13.7 % yield of the reject at a DTAC consumption of 1.5 kg/t under conventional conditions (Curve 2 in Figure 7.1). These results demonstrate that the collector consumption can be greatly reduced with the use of the zero conditioning method, which in combination with a dose of PAM reduces further the required dosage of the collector.

The addition of dextrin reduces the yield of reject (Curves 3 and 4 in Figure 7.5) but improves the selectivity of flotation (so that the ash content of the reject increases, Curves 3 and 4 in Figure 7.6). The results indicate that dextrin is necessary in this process to maintain high selectivity.

The concentrate yield and ash content decreased with increasing DTAC consumption in the reverse flotation process with zero conditioning (Figures 7.7 and 7.8). A concentrate with 19.9 % ash at 50.2 % yield was obtained at 1.375 kg/t DTAC, 500 g/t PAM and 1 kg/t dextrin.

The significance of these results is obvious. First, the results show that the reverse flotation of a sub-bituminous coal is possible, and that with the zero conditioning method along with the use of PAM, high dosage of DTAC can be reduced to a much lower level. Second, since amines are also widely used in potash and phosphate industry, the zero conditioning time concept may have much broader implications.

7.2.3 Effect of dextrin and tannic acid on zero conditioning time reverse coal flotation

The effect of dextrin on zero conditioning time reverse coal flotation is further investigated and the results are shown in Figures 7.9 and 7.10. As these figures show, the addition of dextrin reduced the yield of reject and increased its ash content. It is interesting to note that the addition of tannic acid helped increase the yield of reject by about 5 % (Curve 2 in Figure 7.9) without affecting the ash content of the reject (Curve 3 in Figure 7.9). Therefore, the ash content of the concentrate decreased by a few percent (Curve 1 in Figure 7.10) and a concentrate containing 16.7 % ash was obtained. For the coal, whose inherent ash content is 10 %, this is not a bad performance. The tested sub-bituminous coal is not very hydrophobic and it contains a large amount of clay minerals. The addition of tannic acid improved the dispersion of particles in the pulp. The effect of tannic acid on ash content and yield of the products is shown in Figures 7.11 and 7.12.

7.2.4 Effect of PAM and pH on zero conditioning time reverse coal flotation

PAM plays a critical role in the studied reverse coal flotation process. The addition of PAM significantly reduced DTAC consumption. As curve 1 in Figure 7.13 shows, with 1.375 kg/t of DTAC only 2.7 % of the reject was recovered without using PAM. The yield of the reject increased dramatically with increasing dosages of PAM up to 500g/t at which the reject yield was 54.3 %. A further increase in PAM dosages resulted in a reduced reject yield. Because more gangue material was floated, the concentrate quality was also improved. As Figure 7.14 indicates, a concentrate of 16.8 % ash content was obtained when PAM dosages were in the 400-500 g/t range. The action mechanism of PAM on reverse coal flotation needs further tests.

The effect of pH on the reverse coal flotation is also significant. For this coal the optimum flotation was achieved over the pH range of 7.5 - 8.5 (this is a natural pH for this coal). The tests reveal that a further increase of pH, by adding sodium hydroxide into the pulp, resulted in a sharp decrease of the yield of the reject (Figures 7.15 and 7.16). The

reasons for these changes are not clear at this moment. One possibility is that since it is a subbituminous coal, humic acids may have been extracted from it in an alkaline solution and their presence adversely affected cationic flotation.

7.2.5 Effect of DTAC conditioning time on reverse coal flotation

The effect of conditioning time of DTAC on reverse coal flotation was tested and the results are shown in Figures 7.17 and 7.18. Since the addition of tannic acid improved the quality of concentrate, 1 kg/t of tannic was added in the tests. Other reagents included 1.375 kg/t of DTAC, 1 kg/t of dextrin and 400 g/t of PAM. Flotation was carried out at natural pH.

As can be seen from Figure 7.17, the yield of reject decreased sharply from 48.4% to 17.5% when the conditioning time with DTAC was increased from 0 to 2.5 minutes. A further increase of the conditioning time (with DTAC) resulted in even lower recovery of the gangue material. The results demonstrate that even short period of conditioning significantly reduces the amount of floated materials.

Since conditioning with DTAC results in reduced flotation of gangue minerals, more gangue was left with coal as a concentrate so that the ash content of the concentrate increased. As Figure 7.18 shows, the ash content of concentrate increased from 16.8 % to 31.3 % when the conditioning time was increased from 0 to 10 minutes.

7.2.6 Effect of MIBC addition on zero conditioning time reverse coal flotation

Since DTAC is also a good frother, MIBC was not utilized in the previous reverse flotation tests. The purpose of investigating the effect of MIBC on reverse coal flotation is to see whether the addition of MIBC could further reduce the DTAC consumption. The results are shown in Figures 7.19 and 7.20.

The addition of MIBC had little effect on zero conditioning time reverse coal flotation when DTAC dosage was 1.375 g/t or higher. This was the optimum dosage of DTAC without any MIBC. However, the addition of MIBC played a role when DTAC dosage was lower than 1.375 kg/t. For example, the yield of reject increased from 7.9 % to 27.7 % with 100 g/t of MIBC (DTAC 0.5 kg/t), and increased to 31.3 % with 200 g/t of

MIBC. Increasing further the MIBC consumption to 300 g/t had little effect on the reject yield (30 %) at the same DTAC dosage. Although the addition of MIBC resulted in lower DTAC dosage, the quality of the concentrate was also affected, as shown in Figure 7.20, and this resulted from reduced gangue flotation.

7.2.7 Effect of direct or through-sparger addition of DTAC on zero conditioning time reverse coal flotation

As discussed in Chapter 4, the zero conditioning time method can be carried out either by direct addition of DTAC into a flotation cell without any conditioning step prior to flotation, or with the amine introduced into the flotation system with a stream of bubbles through a sparger. The previous zero conditioning time reverse flotation tests were all carried out by direct addition of DTAC into the cell. The results obtained with the addition through a sparger are given in Figures 7.21 and 7.22 along with the results obtained with direct addition for comparison. As can been seen from Figure 7.21, the flotation of gangue was slightly improved with the sparger addition of DTAC, but the difference was insignificant.

7.3   Summary

A large amount of amine (DTAC) was needed to float gangue minerals from coal by the reverse flotation when only amine was used. The addition of a polyacrylamide (A100) significantly reduced the collector consumption. The application of the zero conditioning method along with the use of PAM further reduced collector consumption. The collector consumption was further lowered by the addition of a frother (MIBC).

Dextrin is necessary to improve the selectivity of this process. The addition of a dispersant (tannic acid) decreased the concentrate ash content by a few percent, improving further the quality of the concentrate. The best separation was achieved over a natural pH range of 7.5-8.4 for this coal.
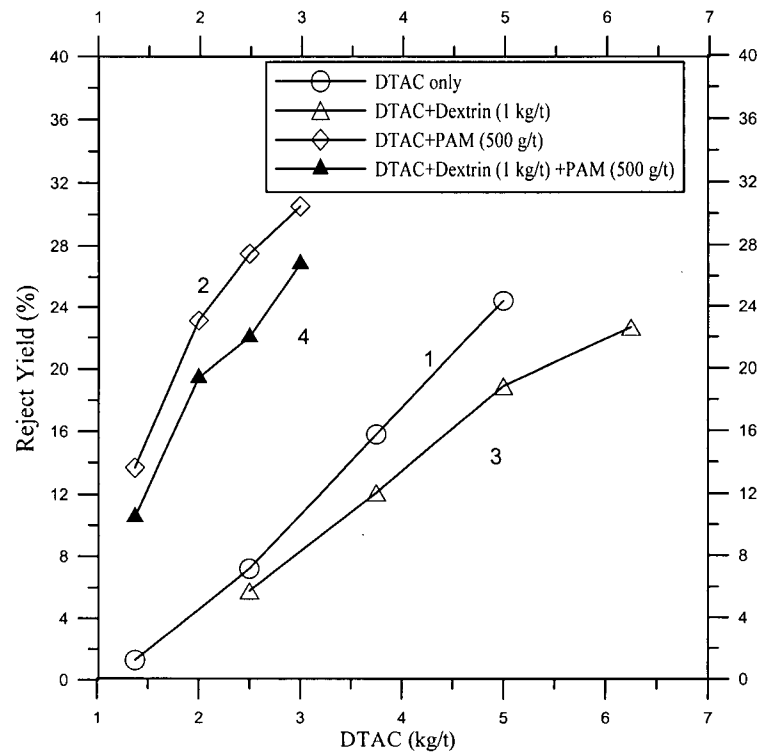
Figure 7.1   Effect of DTAC and PAM on reject yield in reverse
flotation of coal (DTAC conditioning time 5 minutes, natural pH).
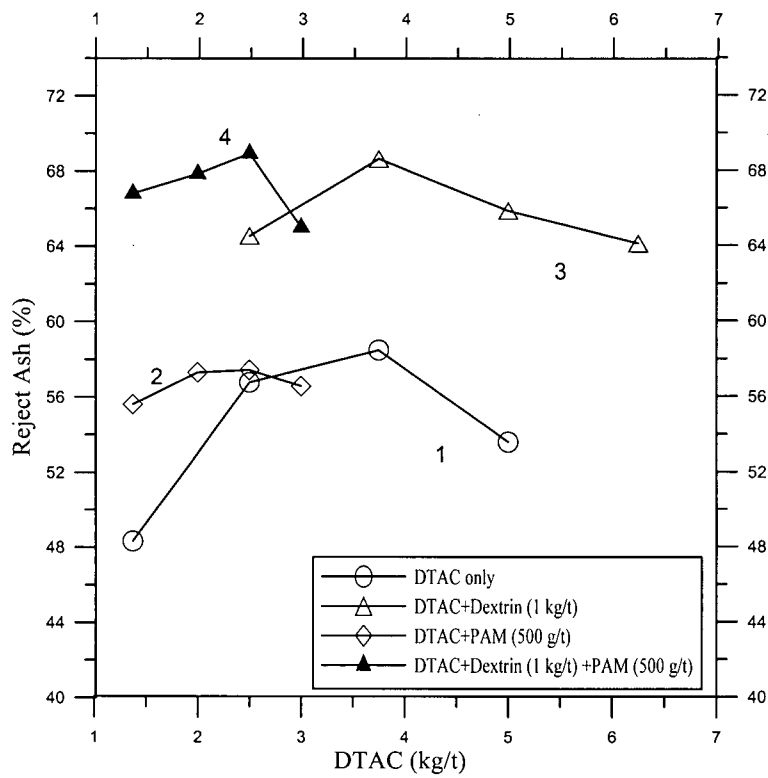
Figure 7.2   Effect of DTAC and PAM on reject ash in reverse
flotation of coal (DTAC conditioning time 5 minutes, natural pH).

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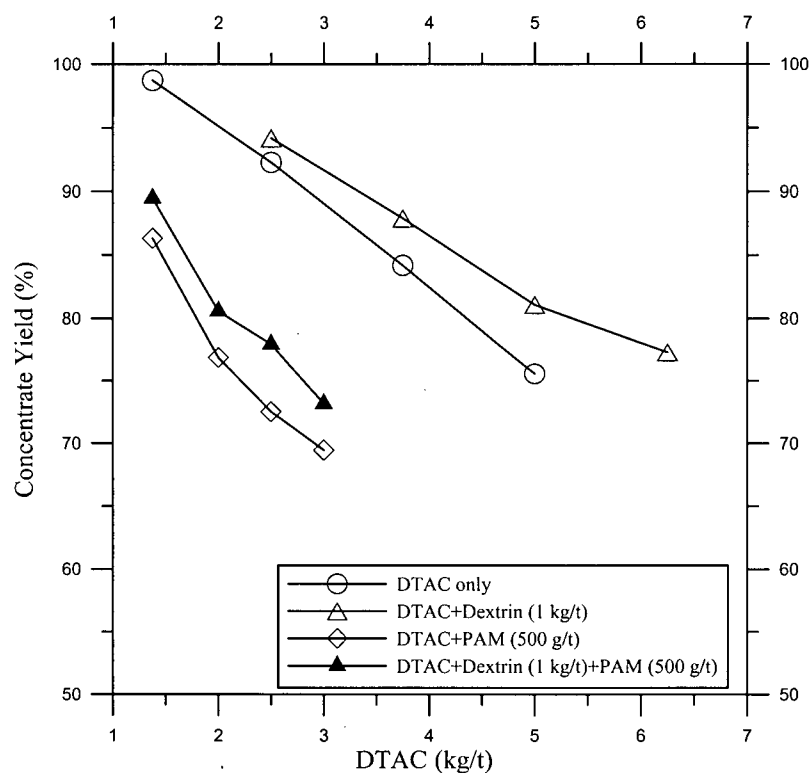
Figure 7.3   Effect of DTAC and PAM on concentrate yield in reverse
flotation of coal (DTAC conditioning time 5 minutes, natural pH).
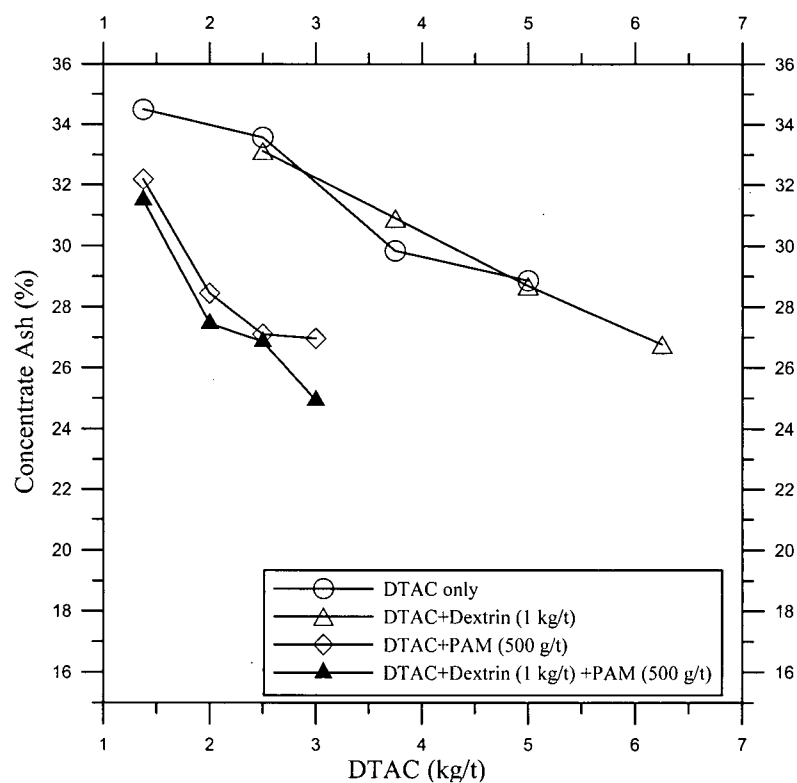
Figure 7.4   Effect of DTAC and PAM on concentrate ash in reverse
flotation of coal (DTAC conditioning time 5 minutes, natural pH).

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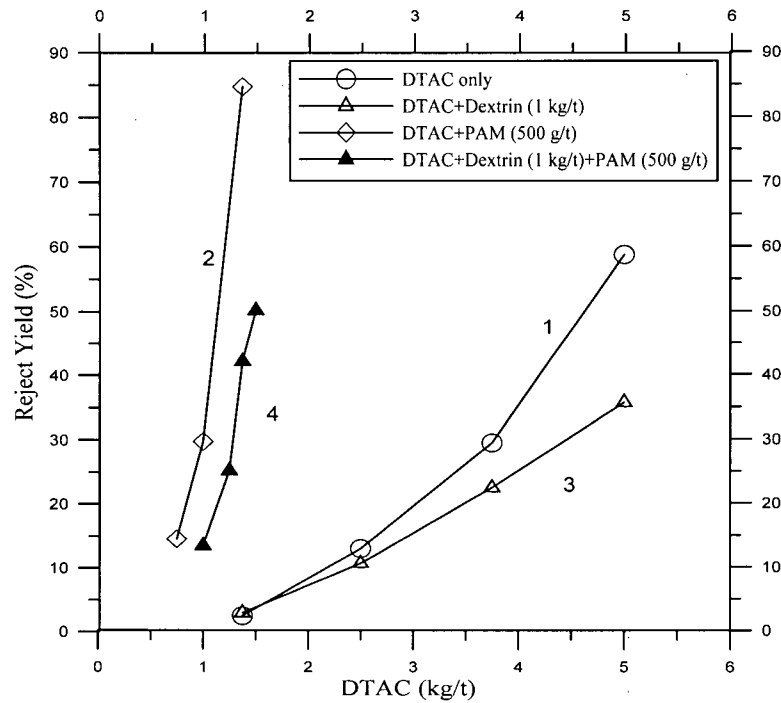
Figure 7.5 Effect of PAM and of zero conditioning on reject yield in reverse flotation of coal (DTAC conditioning time 0 minute, natural pH).
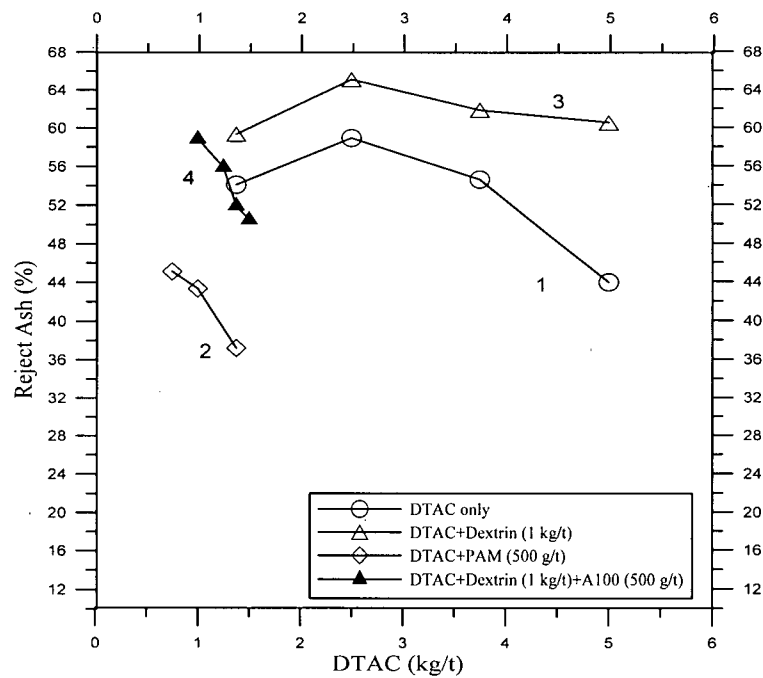
Figure 7.6 Effect of PAM and of zero conditioning on reject ash in reverse flotation of coal (DTAC conditioning time 0 minute, natural pH).
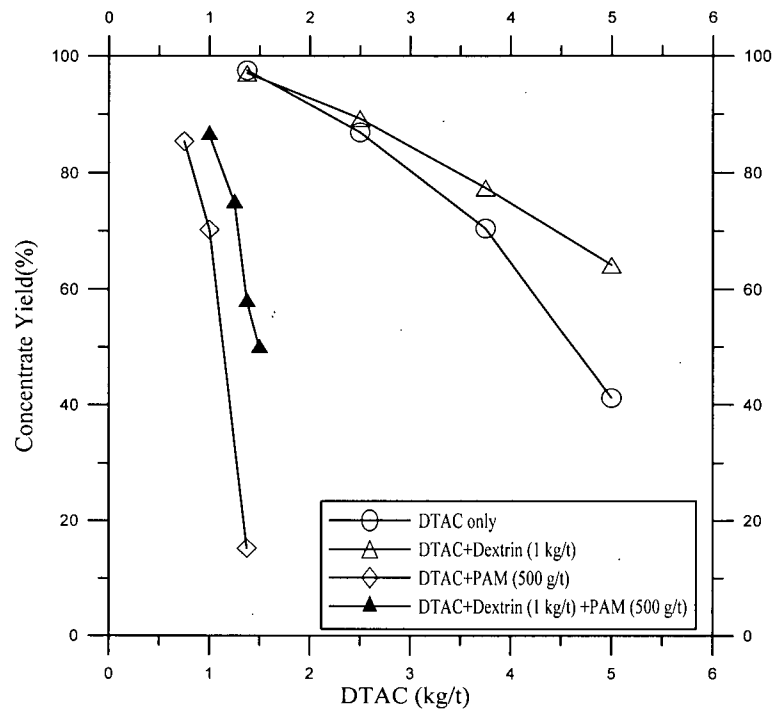
Figure 7.7 Effect of PAM and of zero conditioning on concentrate yield
in reverse flotation of coal (DTAC conditioning time 0 minute, natural pH).
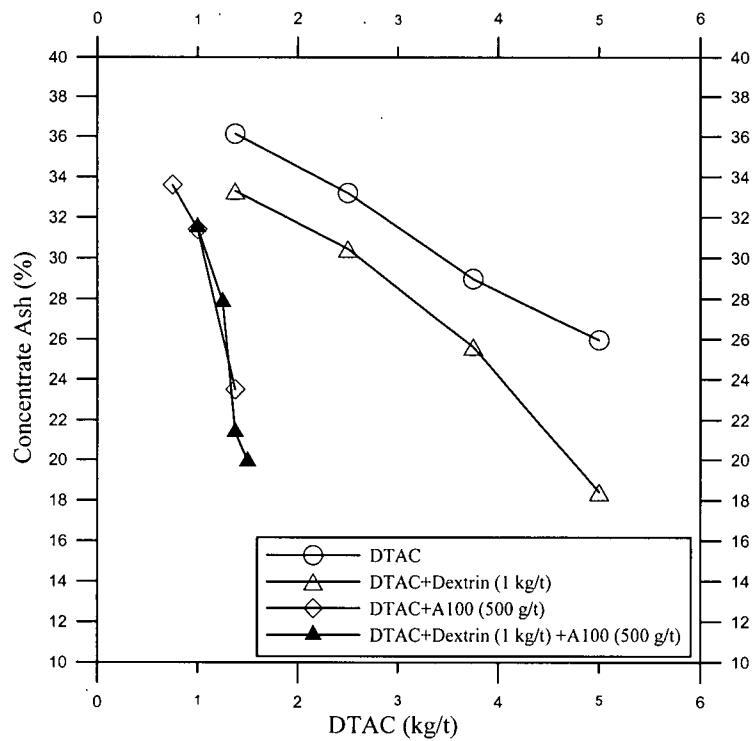
Figure 7.8 Effect of PAM and of zero conditioning on concentrate ash
in reverse flotation of coal (DTAC conditioning time 0 minute, natural pH).

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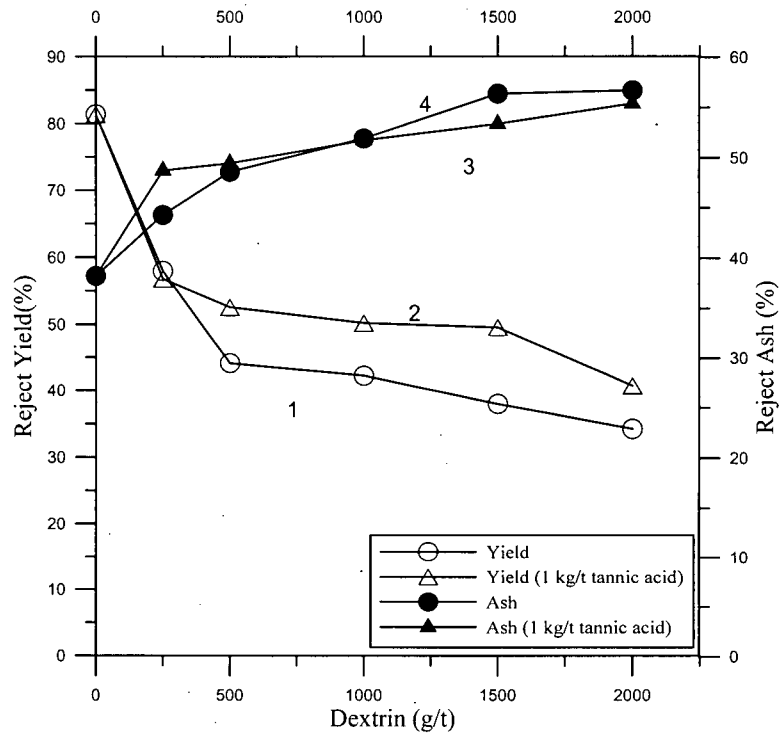
Figure 7.9   Effect of dextrin on reject yield/ash in reverse flotation of coal
(DTAC 1.375 kg/t, PAM 500 g/t, DTAC conditioning 0 minute, natural pH).
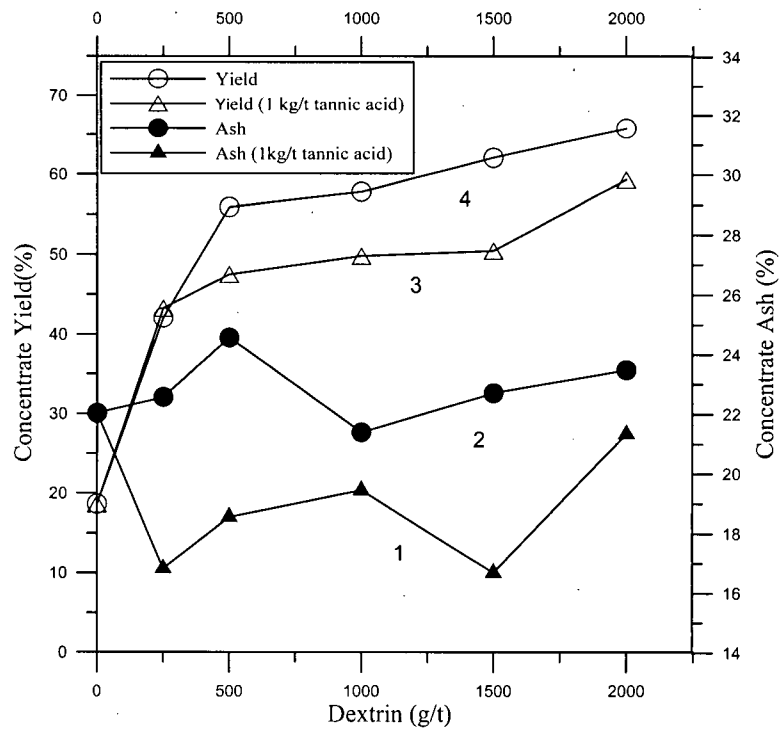
Figure 7.10   Effect of dextrin on concentrate yield/ash in reverse flotation of coal
(DTAC 1.375 kg/t, PAM 500 g/t, DTAC conditioning 0 minute, natural pH).

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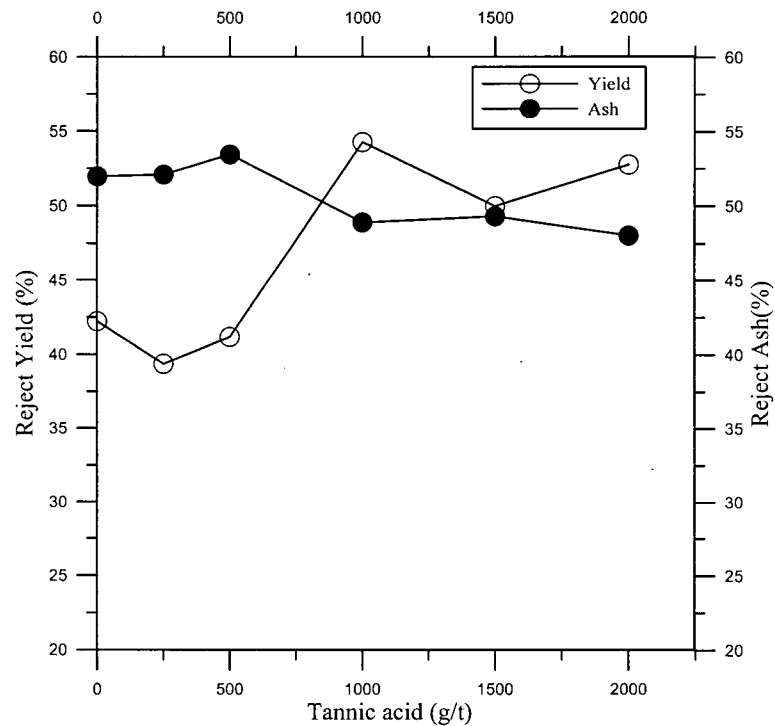
Figure 7.11   Effect of tannic acid on reject yield/ash in reverse flotation of coal
(DTAC 1.375 kg/t, PAM 500 g/t, dextrin 1 kg/t, DTAC conditioning 0 minute, natural pH).
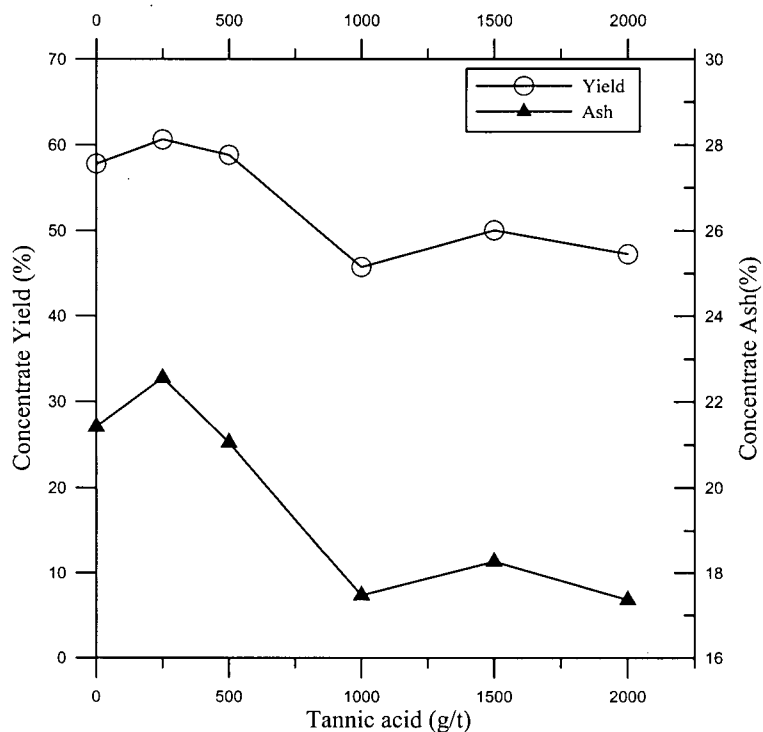
Figure 7.12   Effect of tannic acid on concentrate yield/ash in reverse flotation of coal
(DTAC 1.375 kg/t, PAM 500 g/t, dextrin 1 kg/t, DTAC conditioning 0 minute, natural pH).

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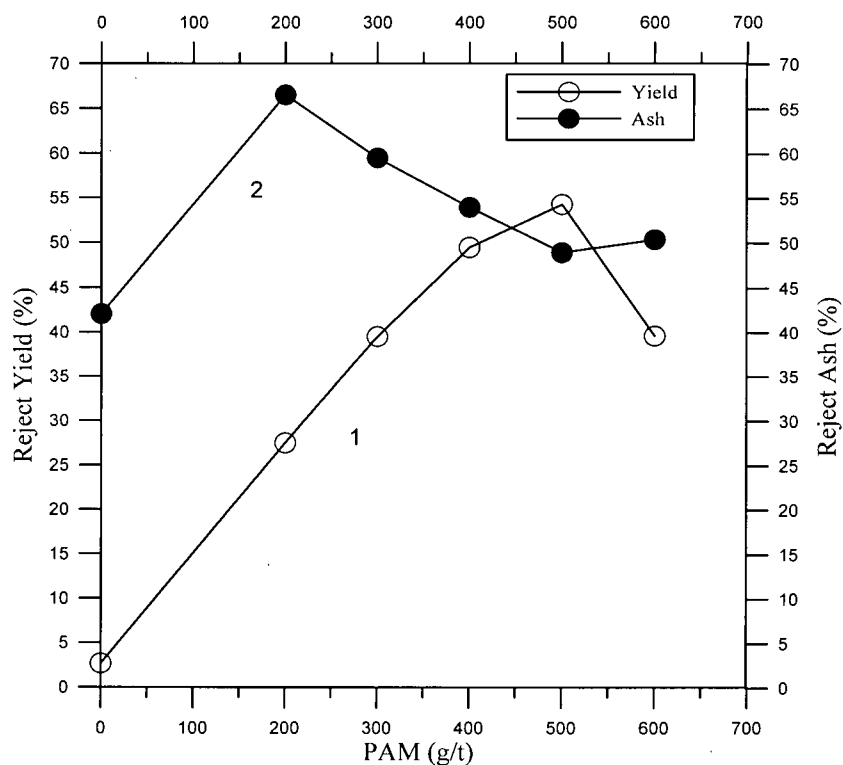
Figure 7.13   Effect of PAM dosage on reject yield/ash in reverse flotation of coal
(DTAC 1.375 kg/t, dextrin 1 kg/t, tannic acid 1 kg/t, DTAC conditioning 0 minute, natural pH).
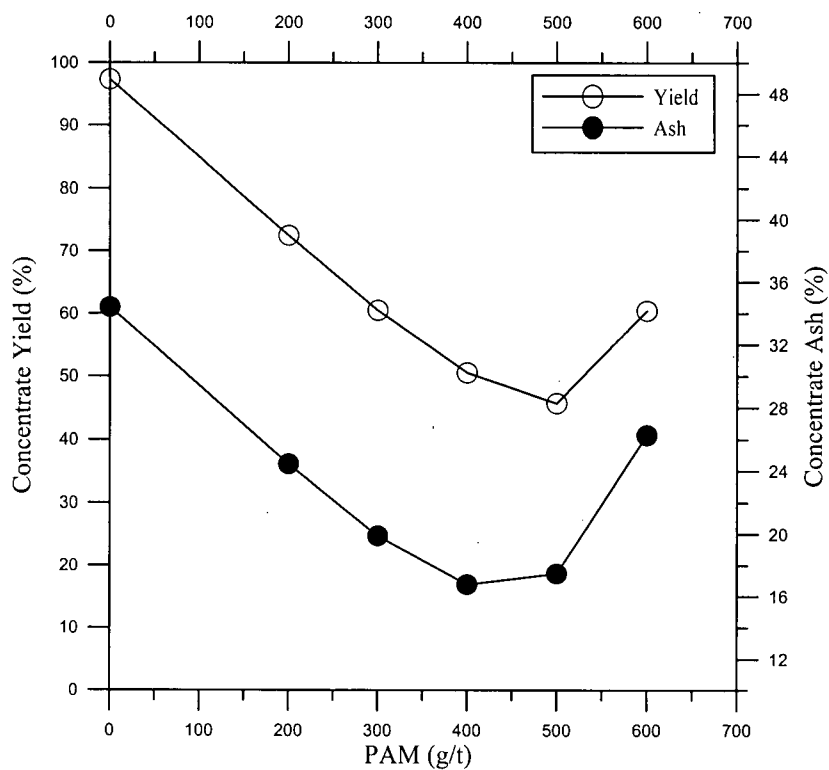
Figure 7.14   Effect of PAM dosage on concentrate yield/ash in reverse flotation of coal
(DTAC 1.375 kg/t, dextrin 1 kg/t, tannic acid 1 kg/t, DTAC conditioning 0 minute, natural pH).

116
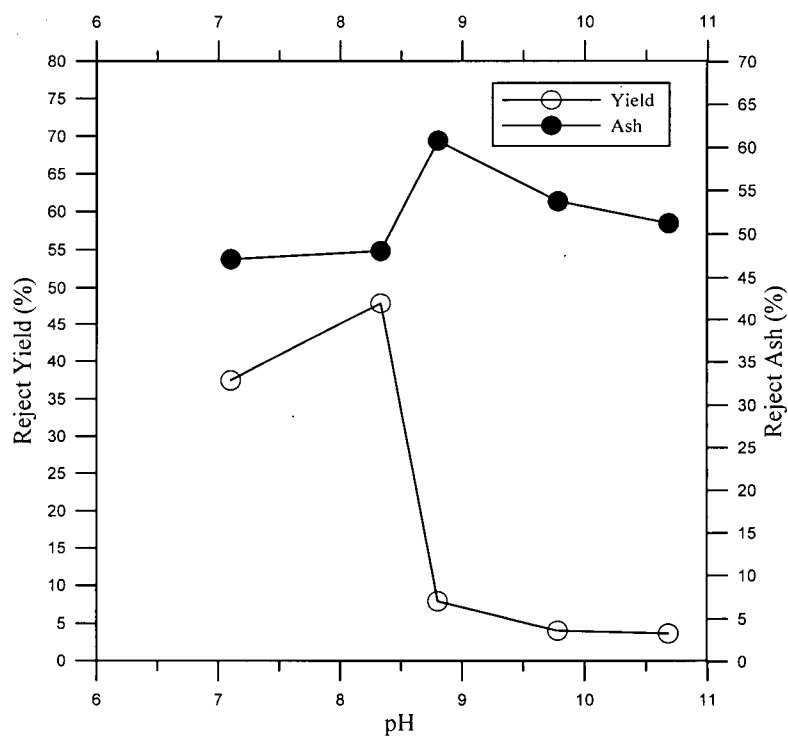
Figure 7.15   Effect of pH on reject yield/ash in reverse flotation of coal (DTAC 1.375 kg/t, dextrin 1 kg/t, tannic acid 1kg/t, PAM 400g/t, DTAC conditioning time 0 minute).
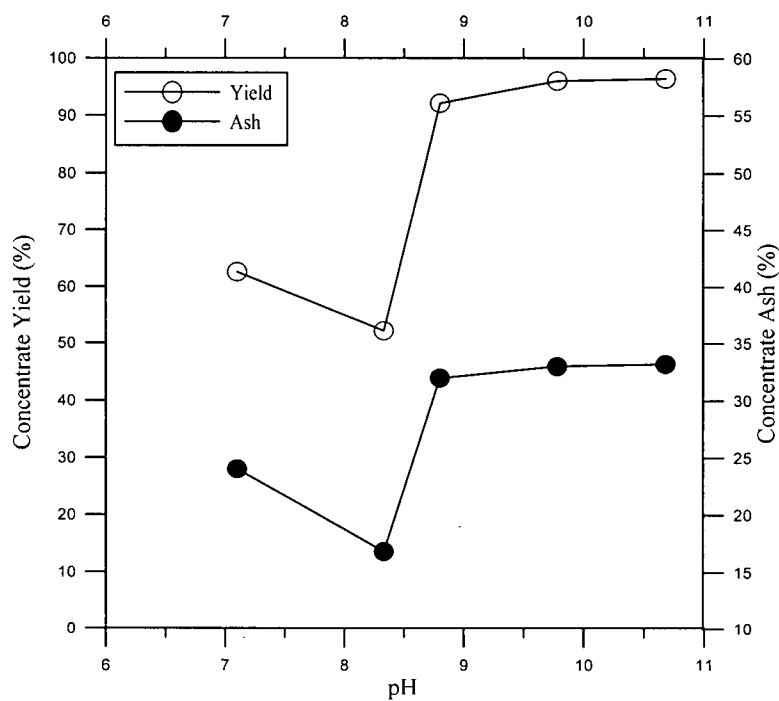
Figure 7.16   Effect of pH on concentrate yield/ash in reverse flotation of coal (DTAC 1.375 kg/t, dextrin 1 kg/t, tannic acid 1 kg/t, PAM 400g/t, DTAC conditioning time 0 minute).
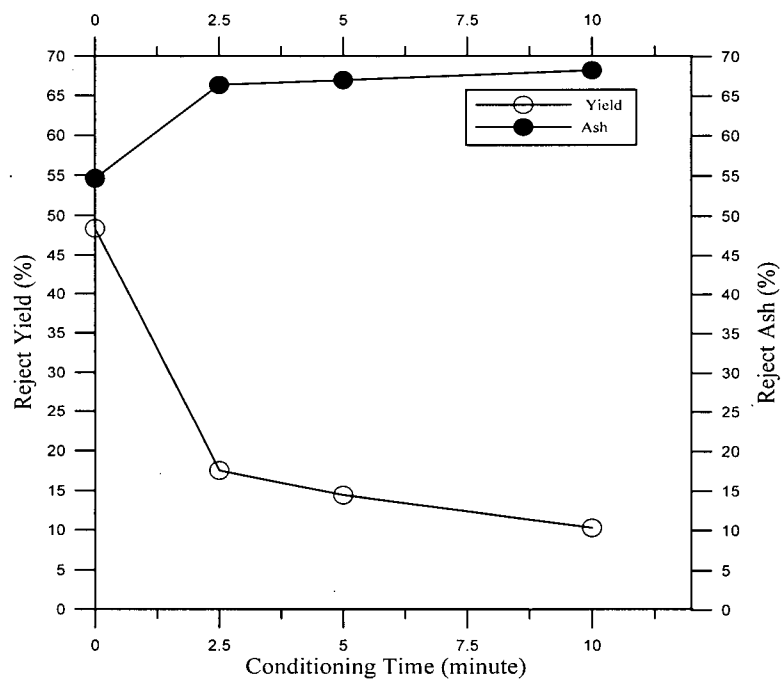
Figure 7.17   Effect of conditionign time with DTAC on reject yield/ash
in reverse coal flotation (DTAC 1.375 kg/t, dextrin 1 kg/t, tannic acid 1 kg/t, PAM 400g/t)
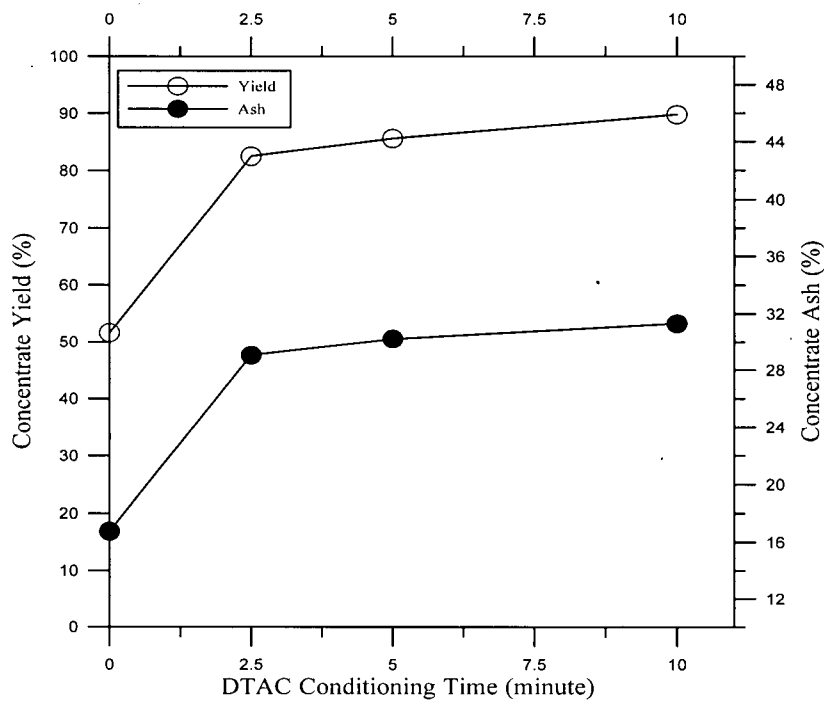
Figure 7.18. Effect of conditioning time with DTAC on concentrate yield/ash
in reverse coal flotation (DTAC1.375 kg/t, dextrin 1 kg/t, tannic acid 1 kg/t, PAM 400 g/t).

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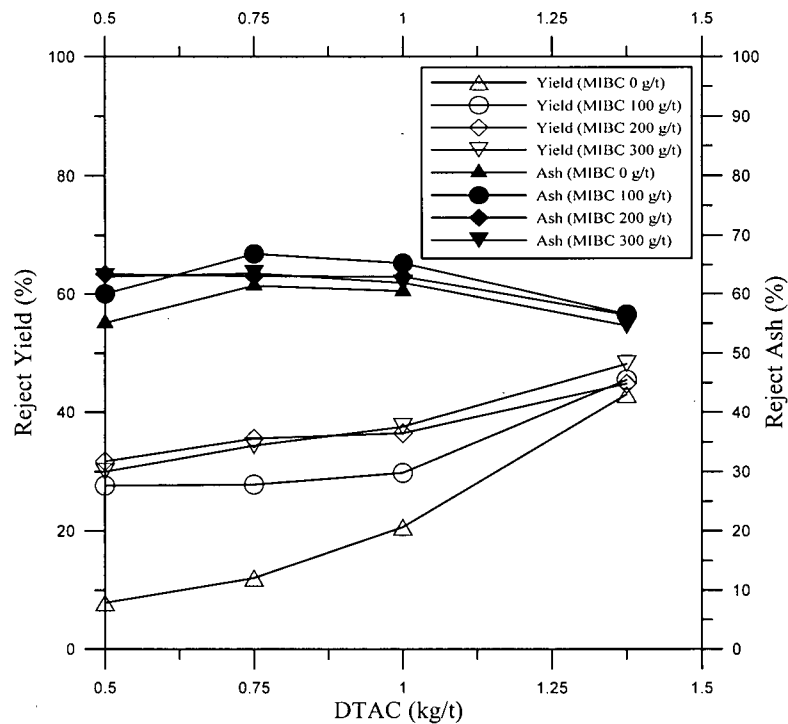
Figure 7.19   Effect of MIBC addition on reject yield/ash in reverse coal flotation (dextrin 1 kg/t, tannic acid 1 kg/t, 400 g/t of A100 , DTAC conditioning time 0 minute, natural pH).
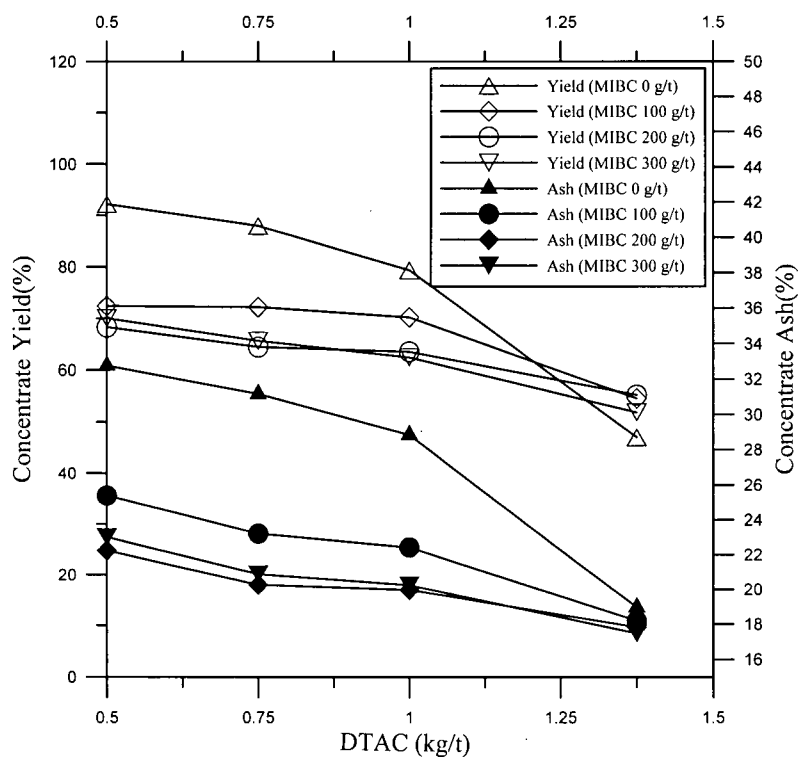
Figure 7.20 Effect of MIBC addition on concentrate yield/ash in reverse coal flotation (dextrin 1 kg/t, tannic acid 1 kg/t, 400 g/t of A100, DTAC conditioning time 0 minute, natural pH).
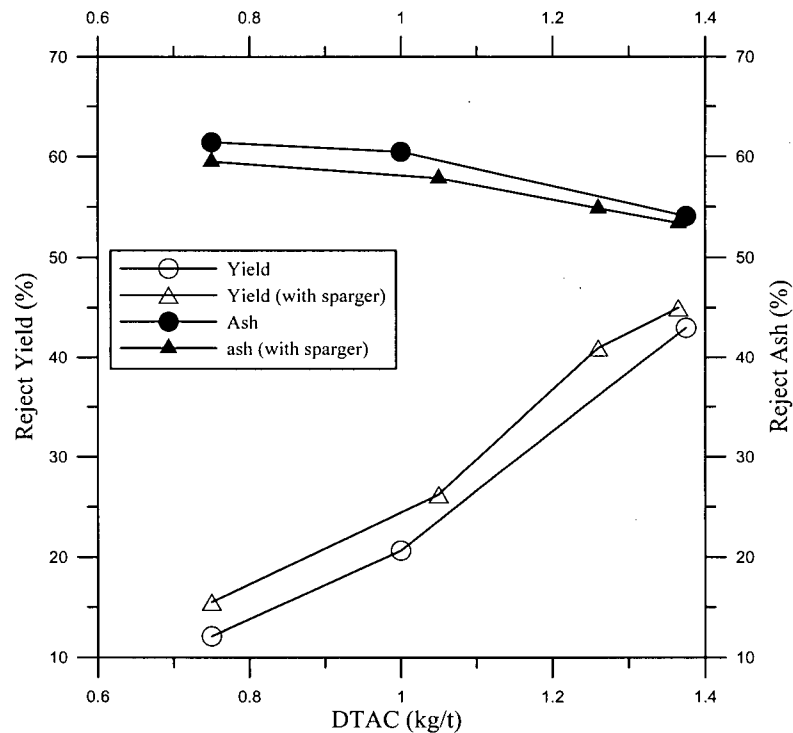
Figure 7.21 Effect of direct or through sparger addition of DTAC on reject yield/ash in reverse coal flotation (tannic 1 kg/t, dextrin 1 kg/t, 500 g/t of A100, DTAC conditioning time 0 minute, natural pH).
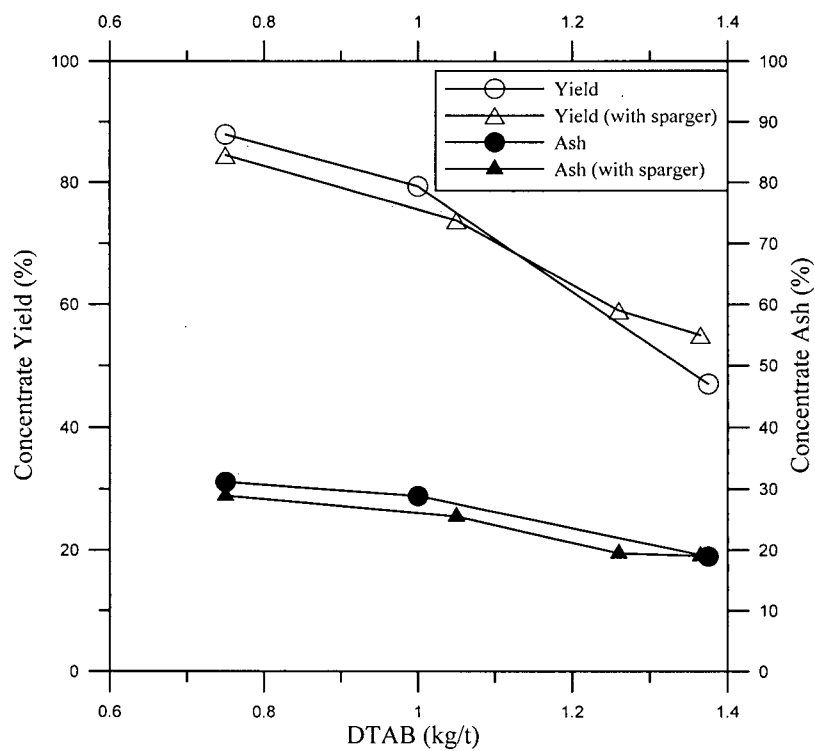
Figure 7.22   Effect of direct or through sparger addition of DTAC on concentrate yield/ash in reverse coal flotation (tannic 1 kg/t, dextrin 1 kg/t, 500 g/t of A100, DTAC conditioning time 0 minute, natural pH).

CHAPTER 8   SELECTION OF POLYACRYLAMIDES IN THE REVERSE COAL FLOTATION

8.1 Introduction

As it has been already shown, the use of a polyacrylamide (A100) in coal reverse flotation significantly decreases the consumption of the amine (collector). With the use of the "zero-conditioning time technique" and the polyacrylamide, amine consumption can be reduced further.

However, preliminary flotation tests revealed that only certain polyacrylamides can reduce the amine consumption in reverse coal flotation. In order to find out which polyacrylamides can be used in this application, a number of polyacrylamides with a different molecular weight and electrical charge were chosen for further tests.

The zero-conditioning time flotation technique (direct DTAC addition) was employed and the best flotation conditions found for the reverse flotation of a subbituminous coal were maintained without any changes in these tests.

Flotation was carried out in a 2 L mechanical cell and the LS20 (-0.216 mm) raw coal was used.

8.2 Results and Discussion

8.2.1 Effect of different polymers on reverse coal flotation

The tested polymers included non ionic, anionic and cationic polymers with a molecular weight ranging from 10,000 to approximately 20 million Daltons and the electrical charge ranging from 0 to about 70 %. It was found that only a few polyacrylamides improved gangue flotation in this process. The results showed that: 1) the cationic polyacrylamides, regardless of their molecular weight and electrical charge, did not improve gangue flotation; 2) the non-ionic polyacrylamides with a molecular weight over 600,000 Daltons improved gangue flotation; 3) for the anionic polyacrylamides only the polymers with a 7 % degree of anionicity or less had a significant effect on gangue

Flotation.

Polymers, which can promote gangue flotation, include N100, N300, N300LMW, A100, A100HMW, and PAMs 5-8, with A-100HMW and A-100 being the most effective ones (Table 4.2). The addition of other polymers such as A-110, A-110HMW, A-120LMW, A-120, A-120HMW, A-130, A-130HMW, A-137, A-150 LMW, A-150, A-150 HMW, C-444, C-494, PAMs 1-4, regardless of their molecular weight and charge, had no effect on gangue flotation. For clarity, only the results obtained with ten polymers are plotted in Figures 8.1-8.4.

The yield of reject increased significantly with the addition of A-100HMW or A-100. As can be seen from Figure 8.1, a reject yield of 58.4 % and 45.1 % was obtained with the addition of the two polyacrylamides (500 g/t), respectively, at a DTAC dosage of 1.375 kg/t. The yield was only approximately 3 % without the addition of those two polyacrylamides. The addition of N-100, N-300 and PAM7 also improved the gangue flotation. It was immediately apparent that the polyacrylamides improving gangue flotation were either non-anionic (PAM 5-8) or slightly hydrolyzed anionic (N100, N300, A-100 and A-100HMW). Their degrees of anionicity were 7 % or lower, but with a very different molecular weight ranging from over 600,000 to about 20,000,000 Daltons. In this group of polyacrylamides, only the one with a very low molecular weight (PAM 4 at 10,000 Daltons) did not improve gangue flotation. The results indicated that increasing the degree of anionicity resulted in a loss of their "activation" ability. For example, A-100, A-110, A-120 and A-150 have the same molecular weight (around 15,000,000 Daltons) but different degrees of anionicity. Only the addition of A-100 (which has a low degree of anionicity of about 7 %) increased gangue flotation. The addition of other PAMs did not improve flotation at all (their degree of anionicity is between 16 % and 50 %).

The reject ash and the concentrate yield /ash are shown in Figures 8.2-8.4. A concentrate with 54.9 % yield at 19.0 % ash was obtained with a DTAC consumption of 1.375 kg/t and the addition of 500 g/t of A100. If 10 % inherent ash is considered, the quality of the concentrate is rather good. When no A100 is added, flotation cannot be initiated at this collector consumption. To initiate flotation without adding these effective polyacrylamides, over 6 kg/t of DTAC was needed, as reported previously (Chapter 7).

8.2.2 Effect of degree of anionicity of polyacrylamide on reverse coal flotation

As discussed earlier, the degree of anionicity determined whether polyacrylamides could improve gangue flotation or not. To investigate further their effect on reverse coal flotation, a group of polymers with roughly the same high molecular weight (15,000,000 Daltons) but different degrees of anionicity was tested for comparison. These are N-100, N-300, A-100, A-110, A-120, A-130 and A-150 (all from Cytec). The results are shown in Figures 8.5 and 8.6.

As can be seen from Figure 8.5, only the polymers with a low degree of anionicity improved gangue flotation and the most effective polymer in this process turned out to be A100 (7 % degree of anionicity). The yield of reject decreased sharply when the degree of anionicity exceeded 7 %. When the degree of anionicity was over 16 %, the activating power was completely lost. It should be noted that the results listed in Figure 8.5 were obtained with high molecular weight polymers.

Low molecular weight polymers with a degree of anionicity higher than 7 % (e.g. PAM1 and PAM2 which have a degree of anionicity of 10 % and 70 %, respectively), were also tested and it was found that they could not improve flotation either.

8.2.3 Effect of molecular weight of polymers on reverse coal flotation

In order to compare the effect of the molecular weight of polymers on reverse coal flotation, only non-anionic polyacrylamides were used. These are polyacrylamides with a molecular weight ranging from 10,000 to 15,000,000 Daltons. The results are shown in Figures 8.7 and 8.8. As can been seen from Figure 8.7, the addition of a low molecular weight polymer (PAM 4 at 10,000 Daltons) did not improve gangue flotation (the reject yield was only about 3 %). The addition of other polymers with molecular weight ranging from 600,000 to 15,000,000 Daltons worked well. The yield of reject dramatically increased from about 3 % to about 23.9-30.4 % due to the addition of those polymers. It should be noted that these results were obtained with non-anionic polyacrylamides. When slightly hydrolyzed polymers such as A-100 (7 % degree of anionicity) were used, an even

higher yield of reject was obtained. The yield and ash content of concentrate are shown in Figure 8.8.

For polyacrylamides with the same degree of anionicity, the polymers with higher molecular weight produced better gangue flotation. Both A-100 and A-100HMW (they have the same 7 % anionicity degree) improved gangue flotation, as indicated in Figure 8.1. Their molecular weight is around 15 million and 20 million Daltons, respectively. The A-100HMW provides about 10 % higher yield of reject. The results are shown in Figure 8.9. For example, a reject yield of 58.4 % was obtained at 1.375 kg/t of DTAC and 500 g/t of A100 HMW polyacrylamide. The yield was 45 % when the same amount of A-100 was used. The concentrate ash content was 16.1 % and 19 %, respectively, with the addition of these two polyacrylamides at a collector consumption of 1.375 kg/t (Figure 8.10).

8.2.4   *Effect of polyacrylamide solution ageing on reverse coal flotation*

The impact of polyacrylamide flocculant solution ageing on flocculation performance has also been a subject of many investigations (Shyluk and Stow, 1969; Gardner, Murphy and Geehan, 1978 ; Chmelir et al. 1980; Henderson and Wheatley, 1987; Farrow and Swift, 1996a, b; Owen et al. 2002). These publications showed that the dosages required to achieve measurable flocculation decreased as flocculant solution ageing time was increased up to 72 hours. This indicates that aqueous solutions of high molecular weight polyacrylamides, used to flocculate mineral slurries, undergo time-based changes in their properties and with time are more completely dissolved. The ageing of the polymer stock solutions was carried out by gently stirring the stock solutions with a magnetic stirrer for a given time interval at a natural pH. The effect of addition of aged polyacrylamide stock solutions on reverse coal flotation was investigated and it was found that the flotation was not affected at all by aging. The results are shown in Figure 8.11. As seen from this figure, both the yield and ash content of the products did not change when the added A100 stock solutions were aged between 20 and 120 hours.

8.3   Summary

The discussed results show that some high molecular weight polyacrylamides can be used to promote gangue flotation in the reverse coal flotation process. This effect is determined by their molecular weight and degree of anionicity. Generally speaking, the addition of cationic polyacrylamides cannot improve gangue flotation, but non-anionic polymers with a molecular weight of over 600,000 Daltons work well. For anionic polyacrylamides, their effectiveness depends on their degree of anionicity and those with a 7 % degree of anionicity or lower are all effective polymers in promoting gangue flotation. The aging of the polymer solution does not affect flotation.

This work does leave some questions unanswered. It is well known that high molecular weight polyacrylamides are effective flocculants, and cause total nonselective flocculation. The total nonselective flocculation should not improve flotation. In contrary it should actually depress flotation. Since our reverse flotation experiments revealed that the use of some polyacrylamides dynamically improved this process there must be a reasonable explanation of the observed phenomenon. This is further studied in Chapter 10.
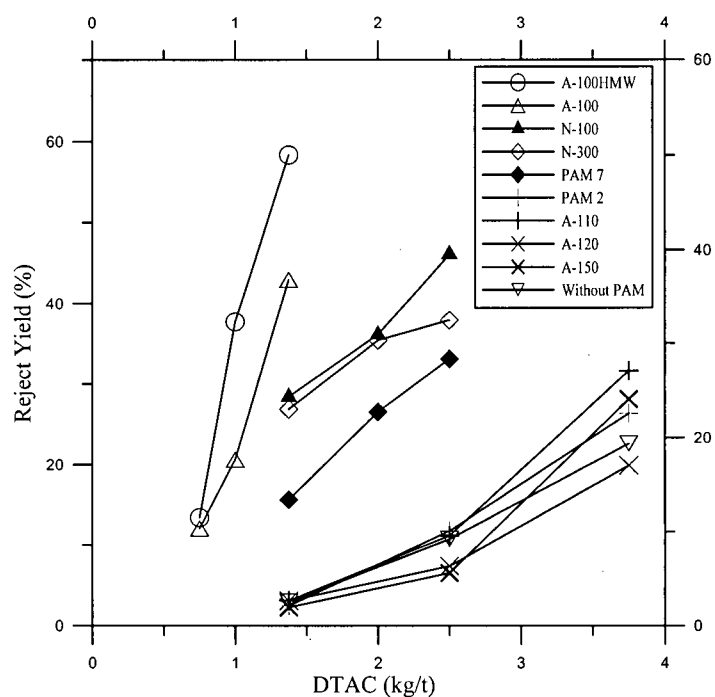
Figure 8.1 Effect of PAMs on reject yield in reverse flotation of coal (tannic acid 1 kg/t, dextrin 1 kg/t, PAM 500 g/t, DTAC conditioning time 0 minute, natural pH).
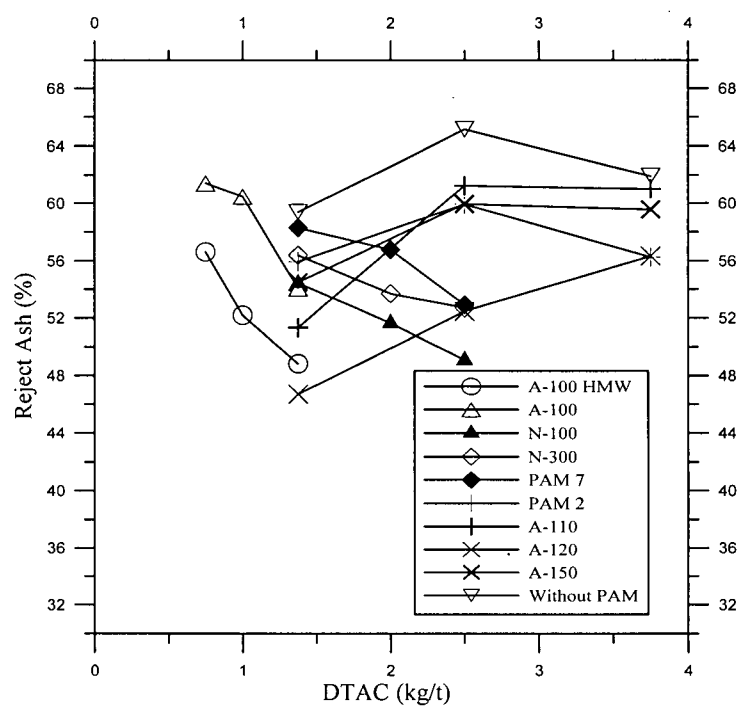
Figure 8.2 Effect of PAMs on reject ash in reverse flotation of coal (tannic acid 1kg/t, dextrin 1 kg/t, PAM 500 g/t, DTAC conditioning time 0 minute, natural pH).
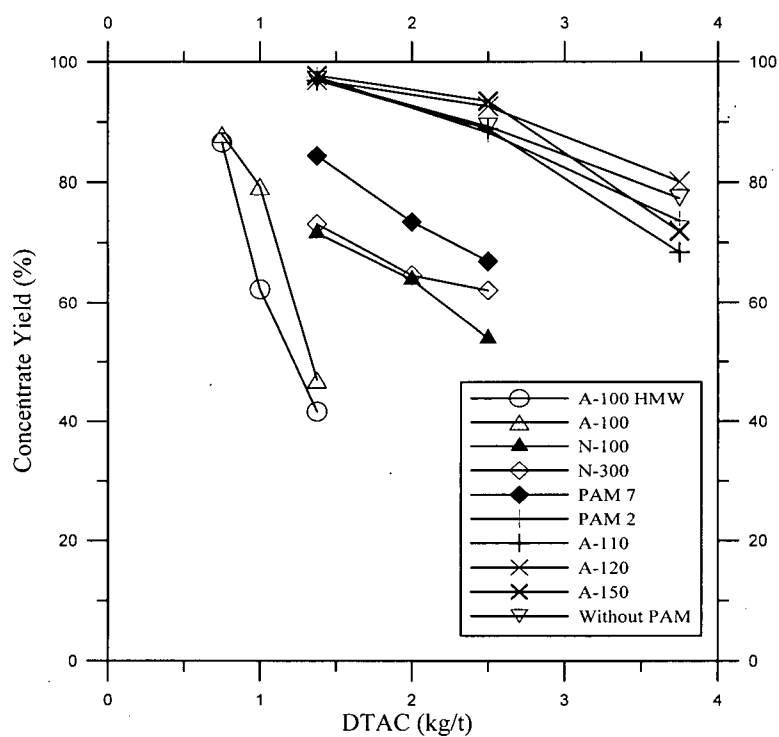
Figure 8.3   Effect of PAMs on concentrate yield in reverse flotation of coal (tannic acid 1 kg/t, dextrin 1 kg/t, PAM 500 g/t, DTAC conditioning time 0 minute, natural pH).
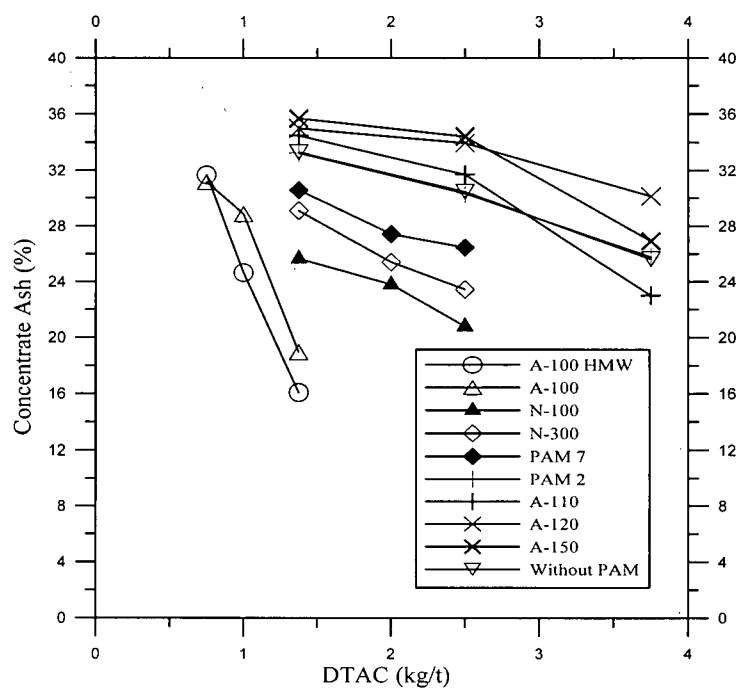
Figure 8.4   Effect of PAMs on concentrate ash in reverse flotation of coal (tannic acid 1 kg/t, dextrin 1 kg/t, PAM 500 g/t, DTAC conditioning time 0 minute, natural pH).
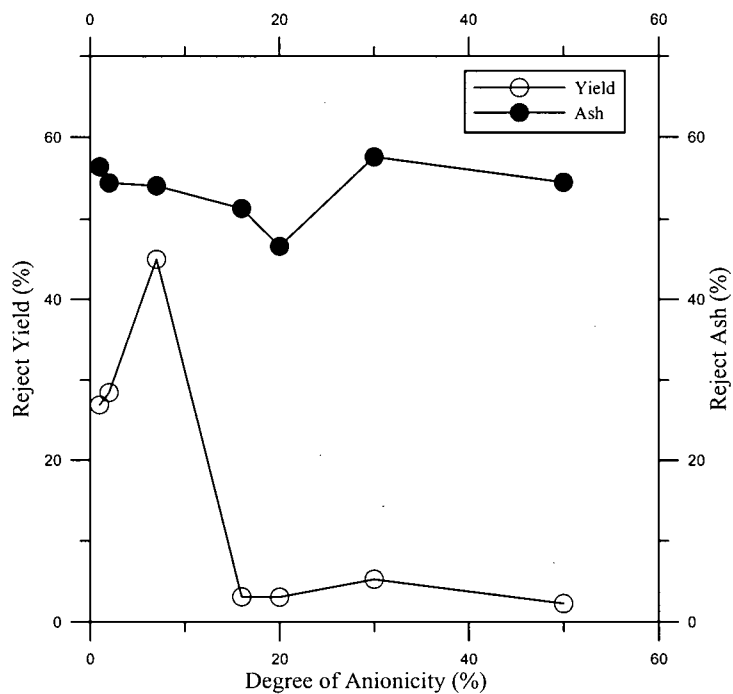
Figure 8.5   Effect of PAM's degree of anionicity on reject yield/ash in reverse coal flotation, DTAC 1.375 kg/t, dextrin 1 kg/t, tannic acid 1 kg/t, PAM 500 g/t, DTAC conditioning time 0', natural pH.
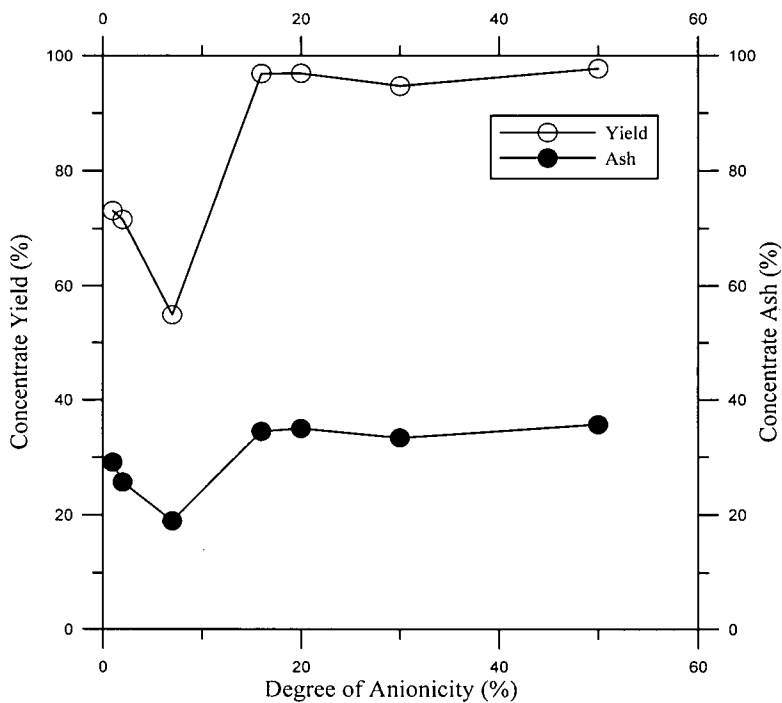
Figure 8.6 Effect of PAM's degree of anionicity on concentrate yield/ash in reverse coal flotation (DTAC 1.375 kg/t, dextrin 1 kg/t, tannic acid 1 kg/t, PAM 500 g/t, DTAC conditioning time 0 minute, natural pH).
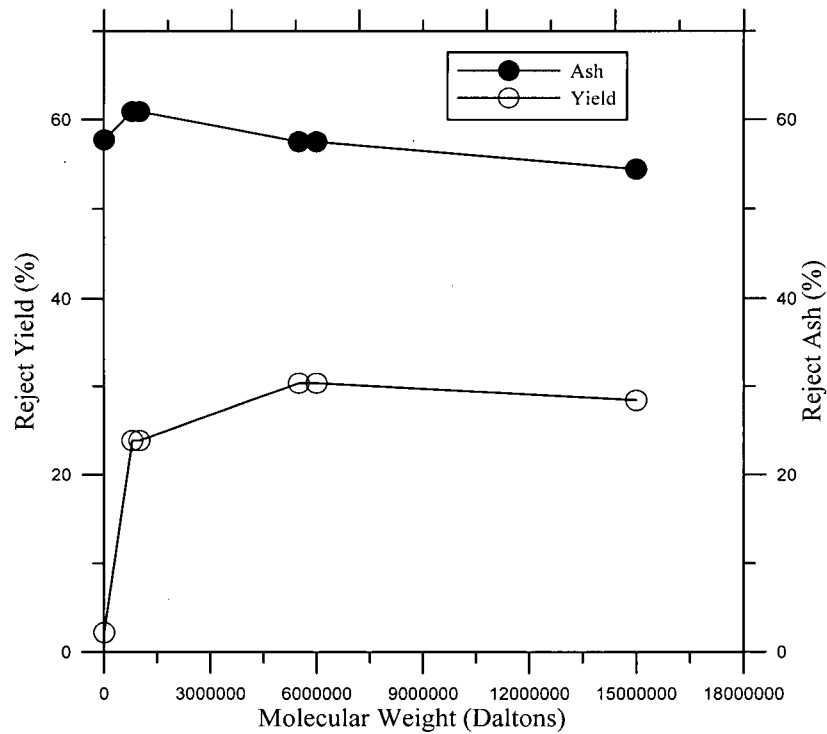
Figure 8.7 Effect of PAM's molecular weight on reject yield/ash in reverse coal flotation (DTAC 2.75 kg/t, dextrin 1kg/t, tannic acid 1kg/t, PAM 500 g/t, DTAC conditioning time 0 minute, natural pH).
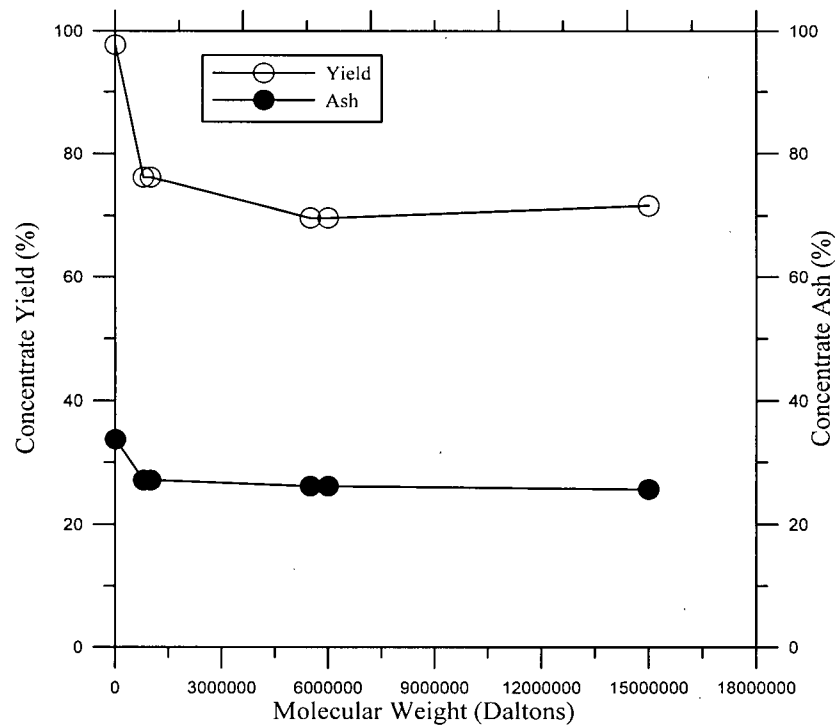
Figure 8.8 Effect of PAM's molecular weight on concentrate yield/ash in reverse coal flotation (DTAC 2.75 kg/t, dextrin 1 kg/t, tannic acid 1 kg/t, PAM 500 g/t, DTAC conditioning time 0 minute, natural pH).

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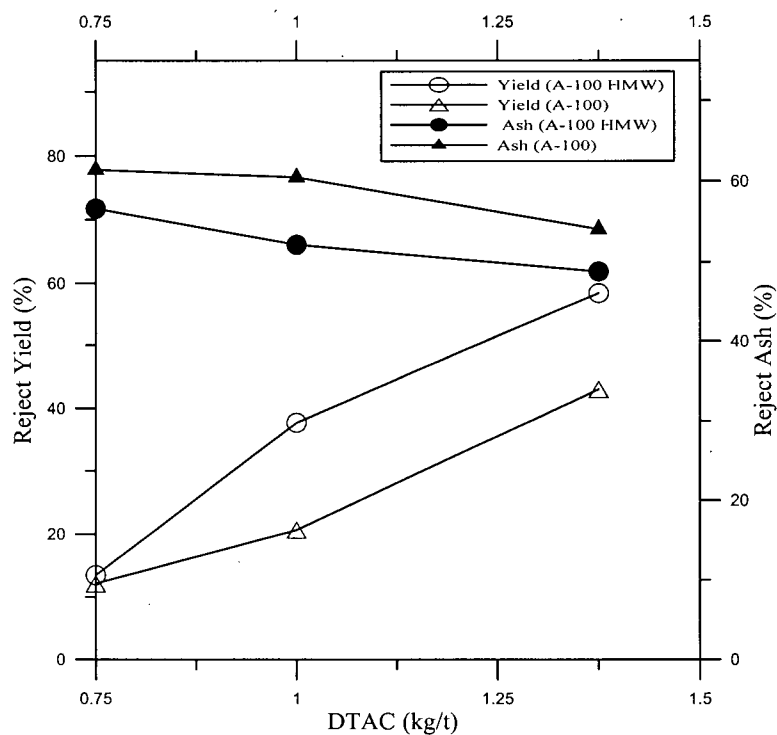
Figure 8.9. Effect of molecular weight of A100 on reject yield/ashin reverse coal flotation
(tannic acid 1 kg/t, dextrin 1 kg/t, PAM 500 g/t, DTAC conditioning time 0 minute, natural pH).
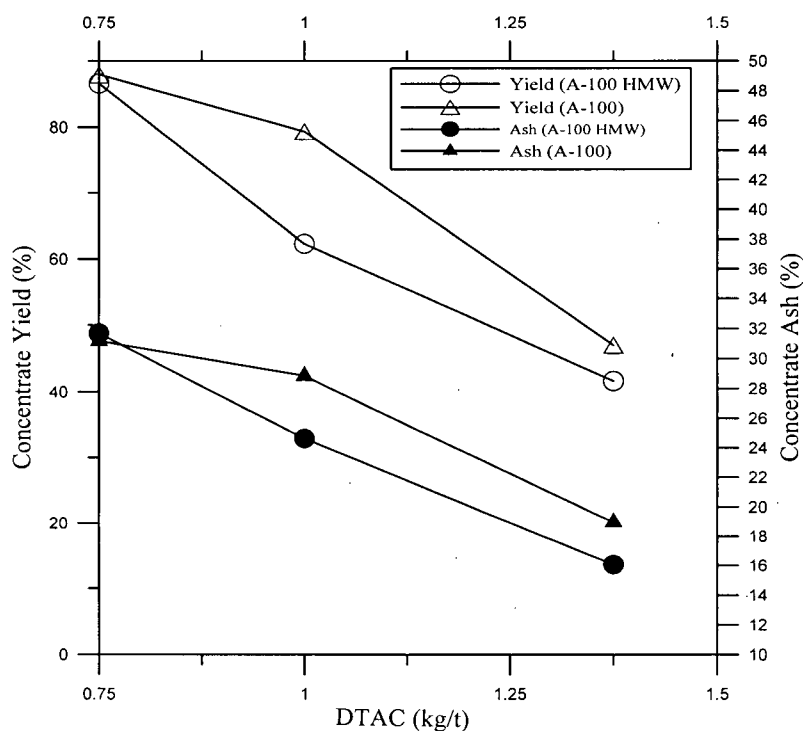
Figure 8.10 Effect of molecular weight of A100 on concentrate yield/ash in reverse coal flotation
(tannic acid 1 kg/t, dextrin 1 kg/t, PAM 500 g/t, DTAC conditioning time 0 minute, natural pH).

130
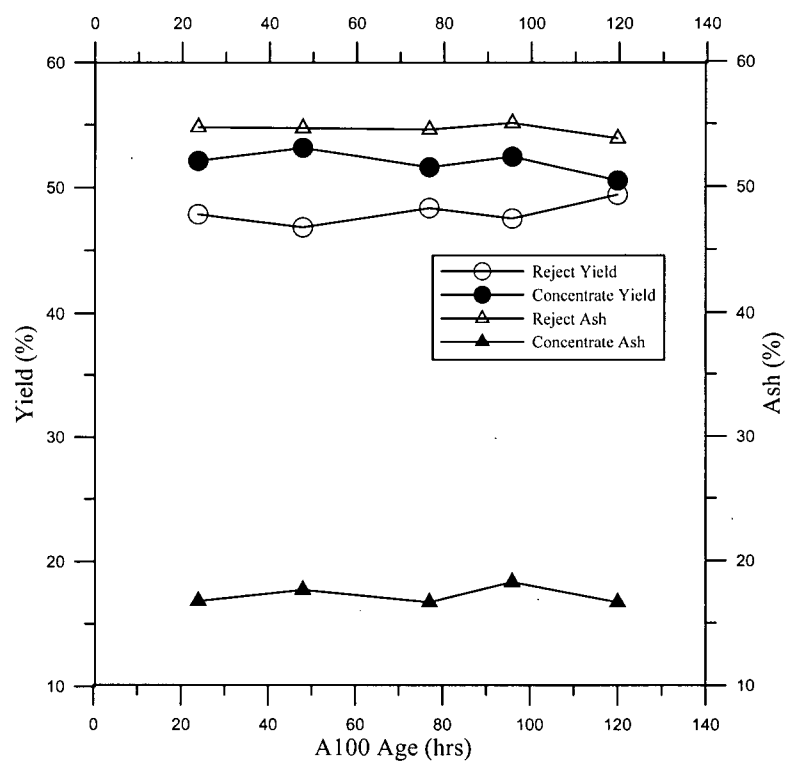
Figure 8.11 Effect of A100 age on reverse flotation of coal (DTAC 1.375 kg/t, dextrin 1 kg/t, tannic acid 1 kg/t, 400 g/t of A100, DTAC conditioning time 0 minute, natural pH)

CHAPTER 9　　DTAC ADSORPTION STUDIES

9.1　Introduction

As the flotation results indicate, a large amount of amine (DTAC) is needed to initiate the reverse coal flotation process when the zero conditioning time method and the A100 polyacrylamide are not employed. These conditions should correspond to a high adsorption density of amine on coal. The amine consumption significantly decreased with the application of the zero conditioning method, and the adsorption of amine on coal should also decrease.

The addition of the A100 polyacrylamide improved gangue flotation and reduced the amine consumption. Whether the use of A100 polyacrylamide really resulted in a decrease of amine adsorption onto coal needs to be investigated.

pH greatly affected gangue flotation in the reverse coal flotation process. An increase in pH from about 8.4 to 9.2 resulted in almost a complete depression of gangue flotation (Chapter 7). Thus, the effect of pH on amine adsorption onto coal should also be studied.

In the zero-conditioning time flotation concept, the idea is that the collector could be brought to the mineral surfaces by bubbles carrying the collector. In other words, the adsorption of amines on mineral surfaces should be higher in the presence of bubbles.

To better answer these questions, adsorption measurements under various conditions were carried out.

9.2　DTAC adsorption on coals and silica

The adsorption of DTAC on LS20 raw coal, LS20 clean coal and silica is shown in Figure 9.1. As this figure reveals, the adsorption of DTAC on coal is much higher than its adsorption on silica. This confirmed that the major portion of amine is adsorbed by coal in the reverse flotation system. Therefore, when the collector dosage was not sufficiently high, the gangue flotation cannot be initiated. Previous flotation tests demonstrated that over 6 kg/t of DTAC was needed to initiate gangue flotation and that this consumption was

greatly reduced to 1.375 kg/t with the application of the zero-conditioning time technique and the use of polyacrylamide. It is obvious that reducing conditioning time decreases amine adsorption onto coal, although the role of PAM is not clear yet.

It is interesting to note that the adsorption densities of DTAC in moles per unit area onto raw coal and onto clean coal are practically the same (Figure 9.1). Since the specific surface area of raw coal (6.75 m^2/g) is more than 6 times larger than that of the clean coal (0.98 m^2/g), the raw coal adsorbs more than 6 times as much DTAC as clean coal for the same amount of material (Figure 9.2). The large specific surface area of raw coal is determined by a high content of fines. As Table 4.4 shows (Chapter 4), 55.4 % of the raw coal was under 74 μm and 37.4 % was under 38 μm. Due to the large specific surface area of the fine particles, the adsorption density of DTAC (in mol/g) on raw coal is extremely high. When these fine particles were removed, for example by using a shaking table, the adsorption in mole/g decreased considerably (Figure 9.2). The adsorption of DTAC on silica was negligible compared to that on coals.

It seems now that the fine fractions are responsible for the high DTAC consumption in reverse coal flotation. Therefore, eliminating the fines should significantly decrease the amine consumption.

The high adsorption of DTAC on raw coal in moles per unit mass basis was well demonstrated by adsorption measurements. With the tested highest initial DTAC concentration of 1600 mg/L (corresponding to a DTAC consumption of 16 kg/t in flotation tests), only a residual concentration of 30 mg/L was detected. When the raw coal was cleaned using a shaking table, the adsorption of DTAC on the clean coal was reduced. With an initial DTAC concentration of 250 mg/L (corresponding to a DTAC consumption of 2.5 kg/t in flotation tests), a residual concentration of 30 mg/L was measured.

Since the initial DTAC concentration must be high enough to detect any residual DTAC in the adsorption tests on raw coal, only clean coal was used in the following adsorption tests.

9.3 Effect of conditioning time with DTAC on its adsorption onto clean coal and silica

DTAC adsorption onto clean coal is shown in Figure 9.3. Three different conditioning times were tested: 5 minutes, 1 minute and 5 seconds. The results revealed that the longer the DTAC conditioning time, the more DTAC was adsorbed. Reducing DTAC conditioning time decreased considerably its adsorption onto clean coal. Since 5 seconds of conditioning is the minimum time which could be employed in the tests (the mixture was manually vigorously shaken), it is reasonable to expect that the adsorption of DTAC onto clean coal/raw coal could be further significantly decreased if a zero-conditioning time technique was utilized. And this was confirmed by the flotation tests as discussed in Chapter 7.

The conditioning time has negligible effect on DTAC adsorption onto silica. Irrespective of the conditioning time employed, the adsorption onto silica is much lower than that onto coal (Figure 9.4).

The adsorption of DTAC onto clean coal is plotted as a function of time in Figure 9.5. An increase in adsorption with time of conditioning was insignificant with the exception of the first short period. An adsorption density of 6.6 $\mu mol/m^2$ was recorded after 5 seconds of conditioning. The DTAC adsorption on silica was very fast and was not affected by the conditioning time as indicated in Figure 9.6. There was not much difference after 5 seconds conditioning. These results also confirmed that amine flotation is very quick and only a very short conditioning time is needed.

9.4 Effect of pH on DTAC adsorption on clean coal

The effect of pH on DTAC adsorption onto clean coal was also tested. As can be seen from Figure 9.7, the amine adsorption density increased with increasing pH. In the reverse coal flotation process, gangue minerals are floated and clean coal is depressed. Since lower pH reduces the DTAC adsorption on coal, it should promote the reverse flotation process and decrease the DTAC consumption. However, the natural pH of the pulp prepared from this coal was around 8.3, any attempt to adjust the pH to a lower value

than 8.3 would result in a high consumption of acid. A pH change from about 8.5 to 9 resulted in a sharp decrease of the flotation yield as discussed in Chapter 7. This may have resulted from the increased adsorption of DTAC on coal, but there is no sharp increase of amine adsorption density on coal in the pH range. Thus, the effect of pH on flotation needs further clarification.

9.5   Effect of PAM on DTAC adsorption on clean coal

As already demonstrated in Chapter 7, the addition of PAM (A100) contributed significantly to a decreased consumption of DTAC. With the addition of 400 g/t of A100, the DTAC consumption was reduced from over 6 kg/t to 1.375 kg/t when the zero conditioning time flotation technique was applied. In order to investigate the effect of PAM on DTAC adsorption onto clean coal, the adsorption measurements were also carried out in the presence of PAM at different DTAC conditioning times. It was found that DTAC adsorption on clean coal was only very slightly affected by the addition of A100 (Figures 9.8-9.10). The detected difference, however, was too small to draw any definite conclusion from these tests. With 5 minutes conditioning of DTAC, the adsorption of DTAC was practically the same as without the addition of A100. The difference became slightly larger as the DTAC conditioning time was reduced to 5 seconds. The addition of PAM, with a higher degree of anionicity (A130), made no difference on the DTAC adsorption (Figure 9.11). Since the amine adsorption onto coal is not affected by the addition of PAM, the effect of PAM on reverse coal flotation thus needs further explanation. Since PAM is a flocculant and causes flocculation of fines particles, and thus reduces the surface area of the finest fractions, it is quite possible that the effect of PAM on reverse flotation results from the reduced amine adsorption that makes possible significant reduction of amine dosage.

9.6   Effect of air bubbles on DTAC adsorption on clean coal and silica

To test the idea that bubbles can bring more collector to mineral surfaces, two series of adsorption tests were carried out: one in the presence of bubbles (conditioning

carried out in a cell with air valve open) and the other without bubbles (conditioning carried out in a sealed bottle). The results are shown in Figures 9.12 and 9.13. The adsorption of DTAC onto coal is practically the same whether air is introduced or not, but its adsorption onto silica is almost doubled in the presence of air bubbles. This may suggest a different adsorption mechanism of amine onto coal and silica as discussed in Chapter 13. It may also indicate that the tests carried out in the absence of air bubbles should be repeated with a more carefully de-aerated system.

9.7 Summary

The adsorption of DTAC on LS20 coal is extremely high and reducing conditioning time with DTAC significantly reduces its adsorption on the coal. This confirmed that the application of the zero conditioning time method in reverse coal flotation can reduce the amine consumption. DTAC adsorption on silica is negligible.

The addition of the A100 does not result in a decrease in DTAC adsorption on the coal. This indicates that the mode of action of PAM in reverse coal flotation must involve some other phenomena and possibly results from the reduced surface area of the finest size fraction flocculated by PAM.

The adsorption density of DTAC on coal increases with increasing pH, but there is no sharp increase in adsorption density in the pH range of 8.4 to 9.0 in which gangue flotation is almost completely depressed (Figure 7.15). The effect of pH on reverse coal flotation in this pH range also requires further investigation.

The adsorption of DTAC on silica is almost doubled in the presence of air bubbles. This supports the theory that a significant amount of the collector is brought onto the silica surface by air bubbles.
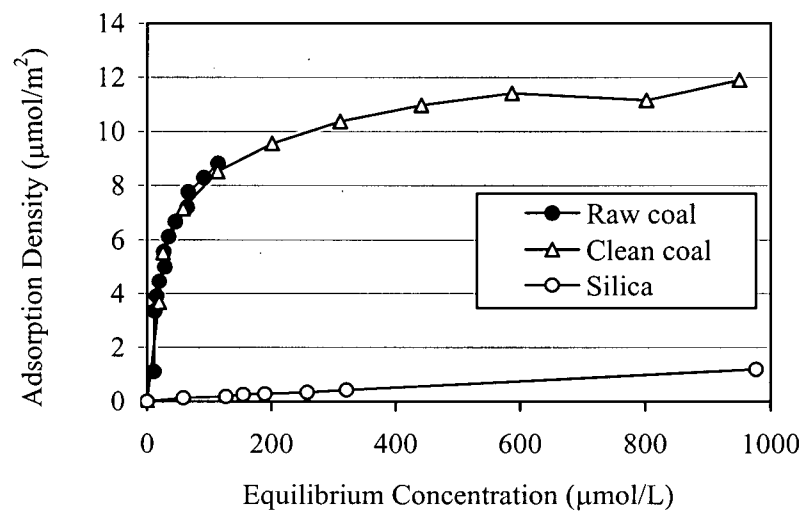
Figure 9.1 Adsorption isotherms of DTAC onto raw coal, clean coal and silica calculated on $\mu mol/m^2$ basis (DTAC conditioning time 5 minutes, natural pH).
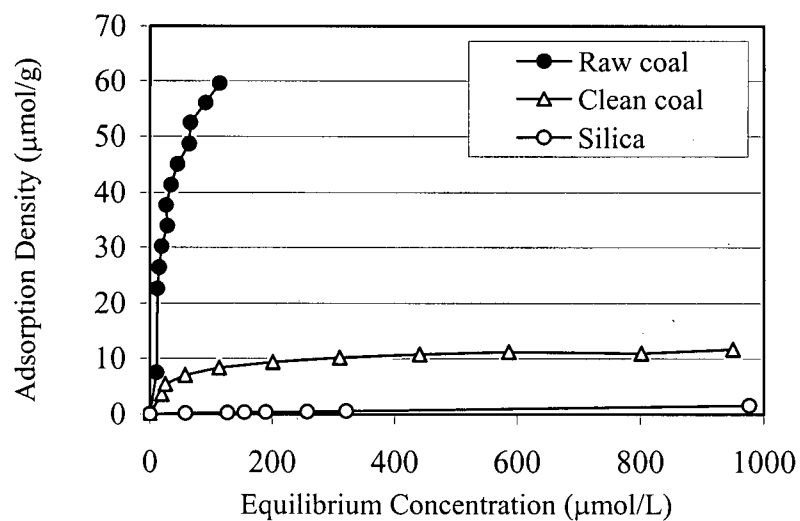
Figure 9.2 Adsorption isotherms of DTAC onto raw coal, clean coal and silica calculated on $\mu mol/g$ basis (DTAC conditioning time 5 minutes, natural pH).

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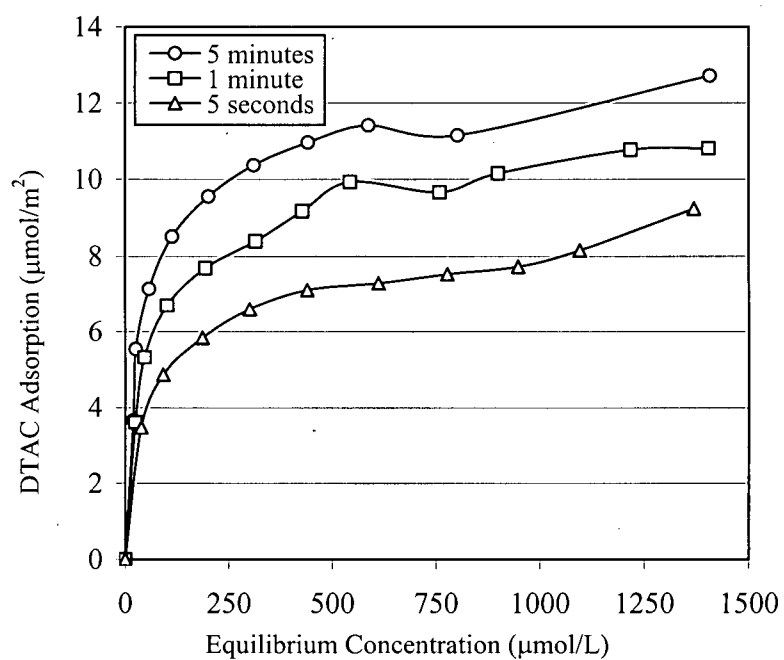
Figure 9.3 Adsorption isotherms of DTAC onto clean coal (natural pH).
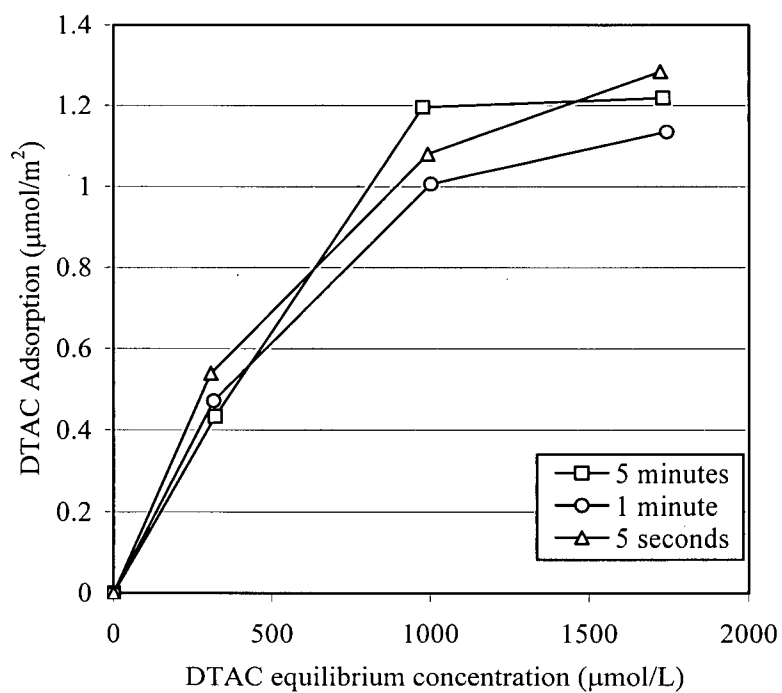
Figure 9.4 Adsorption isotherms of DTAC onto silica (natural pH).

138
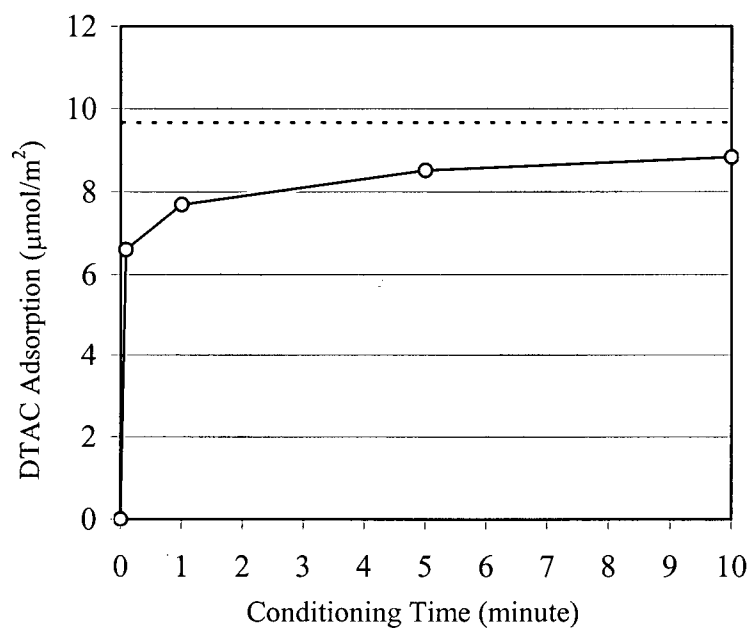
Figure 9.5 Adsorption kinetics of DTAC onto clean coal (initial DTAC concentration 9.47×10^{-4} mol/L, natural pH).
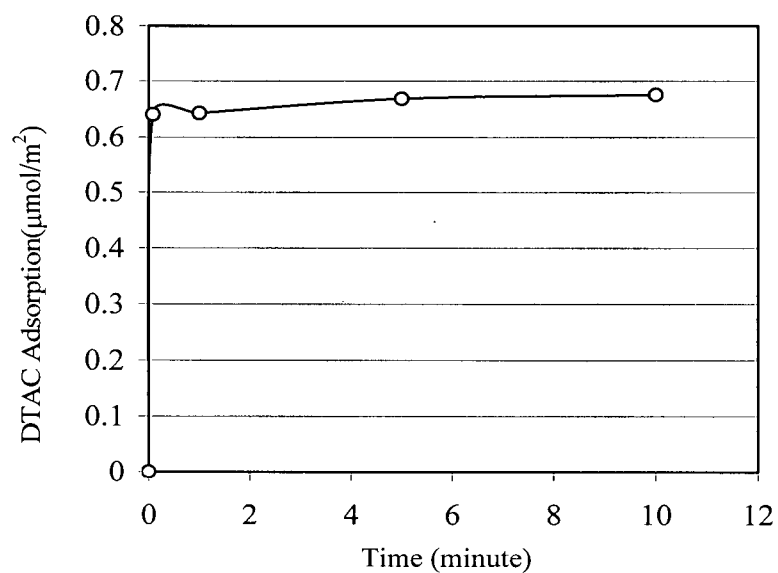
Figure 9.6 Adsorption kinetics of DTAC onto silica (initial DTAC concentration 5.68×10^{-4} mol/L, natural pH).
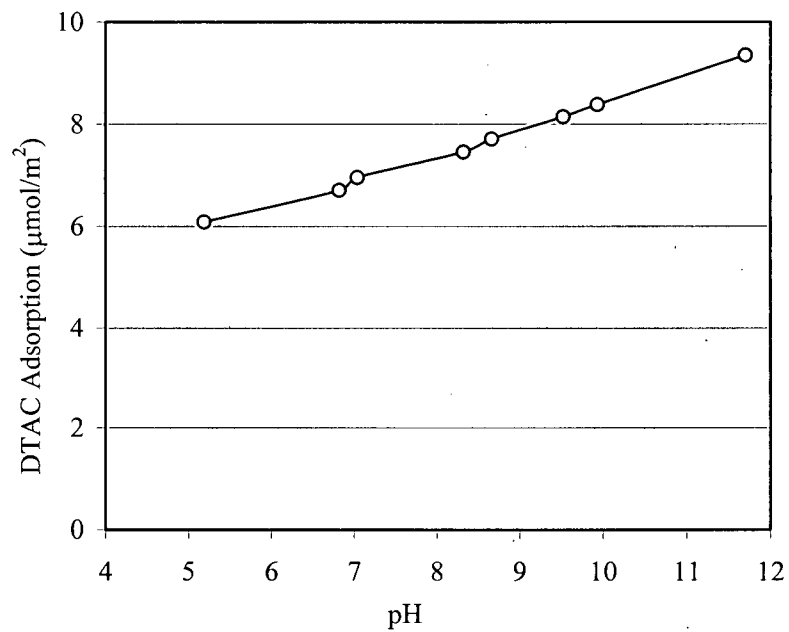
Figure 9.7   Effect of pH on DTAC adsorption onto clean coal (initial DTAC concentration 9.47×10^{-4} mol/L, 1 minute conditioning).
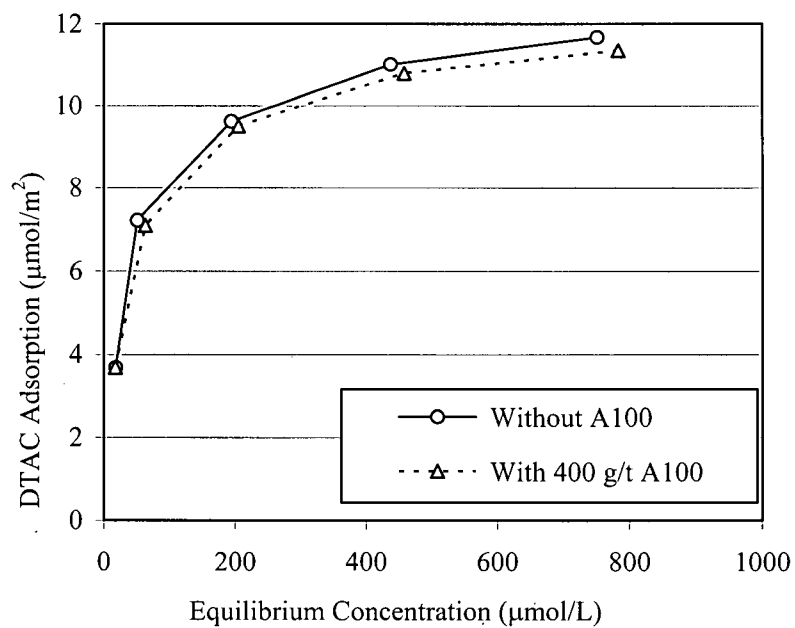
Figure 9.8   Effect of A100 on DTAC adsorption onto clean coal (DTAC conditioning time 5 minutes, natural pH).

140
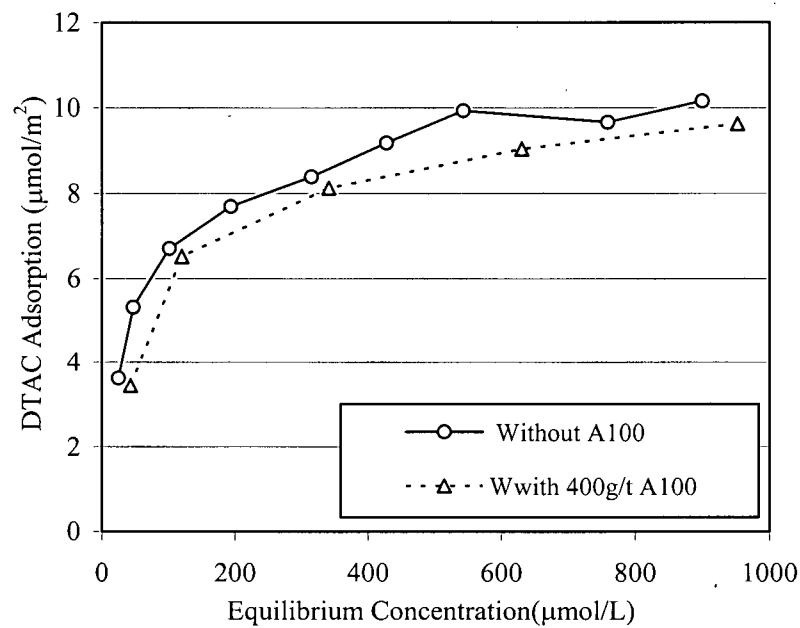
Figure 9.9   Effect of A100 on DTAC adsorption onto clean coal (DTAC conditionig time 1 minute, natural pH).

Figure 9.10   Effect of A100 on DTAC adsorption onto clean coal (DTAC conditioning time 5 seconds, natural pH).

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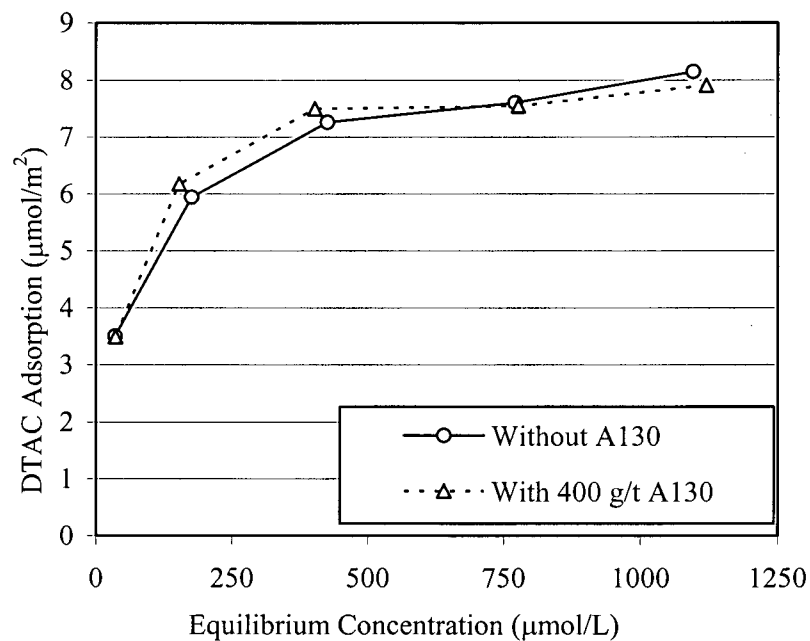
Figure 9.11   Effect of A130 on DTAC adsorption
onto clean coal (DTAC conditioning time 5 seconds,
natural pH).
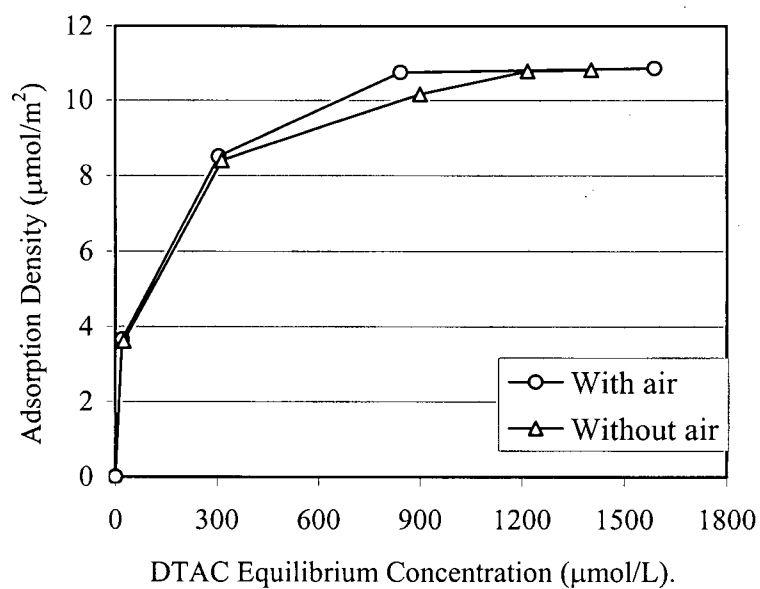
Figure 9.12 Adsorption isotherms of DTAC onto clean
coal (DTAC conditioning time 1 minute, natural pH).
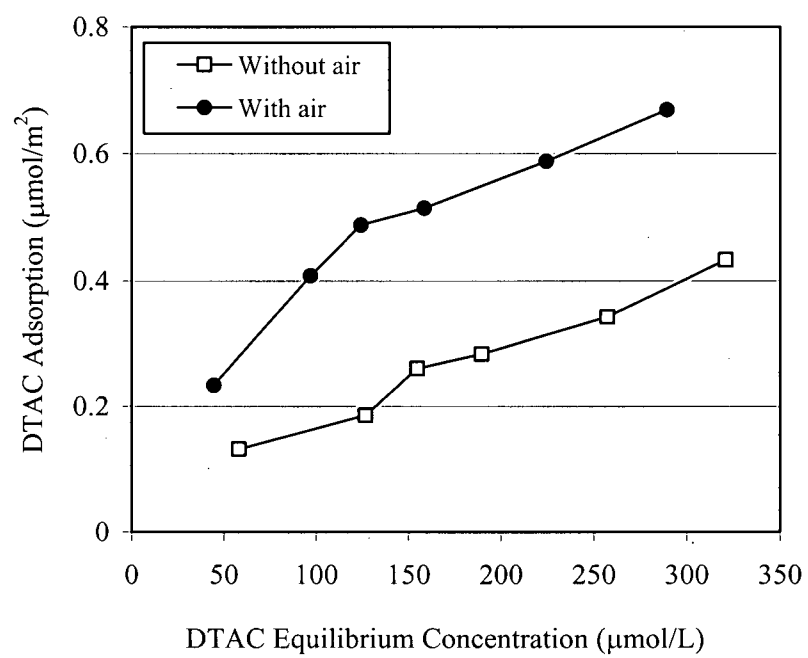
Figure 9.13 Adsorption isotherms of DTAC onto silica (DTAC conditioning time 5 minutes, natural pH).

CHAPTER 10   FLOCCULATION STUDIES

10.1   Introduction

The addition of the A100 polyacrylamide significantly reduced the collector consumption in reverse coal flotation (Chapter 7). This polyacrylamide has a high molecular weight (15 million Daltons) and a 7 % degree of anionicity. Further flotation tests showed (Chapter 8) that not all polyacrylamides can be used for this purpose and only those with a 7 % degree of anionicity or less (non-anionic or slightly hydrolyzed anionic polyacrylamides) promote the flotation of gangue. The polymers with a higher degree of anionicity are not effective at all. It is well known that all high molecular weight polyacrylamides are effective flocculants with those having a degree of anionicity between 10 % and 30 % being the most effective (Xu and Cymerman, 1999). However, the coal reverse flotation tests demonstrated that the addition of these most effective flocculants did not help reduce the DTAC consumption.

It is to be pointed out that different procedures are followed in flocculation and flotation tests. In the flocculation tests, pulp is moderately agitated to avoid breaking the flocs. In the flotation tests, however, the pulp is subjected to very intense conditioning (1500 rpm) and, under such conditions, the flocs are broken, at least to some extent. It was reported that the flocculation power of PAM was lost when the polymer stock solutions were subjected to intense conditioning but its depressing ability in flotation was not affected by the conditioning mode (Castro and Laskowski, 2004). Two kinds of conditioning must be considered: the effect of conditioning of PAM solution on its flocculating ability (polymer degradation) and the effect of conditioning of a PAM-mineral suspension on flocculation (breaking/rearranging flocs).

In this Chapter, three series of settling tests were carried out to investigate the effect of polyacrylamide on the reverse flotation of coal: (a) Settling tests in which unsheared PAM solutions were added into a gently agitated coal-water-slurry; (b) Settling tests in which polymer solutions were first sheared (degraded) in a flotation cell at 1500 rpm for 30 minutes and then added into a gently agitated coal-water slurry; and (c) Settling tests after conditioning unsheared PAM-coal suspensions in a flotation cell at 1500 rpm for 5

minutes.

Five polyacrylamides with different degrees of anionicity and roughly the same molecular weight were used. These are: N100, N300, A100, A130 and A150. Their degree of anionicity is around <1 %, < 2 %, 7%, 33 %, and 50 %, respectively (Table 4.2). N100, N300 and A100 were found to promote gangue flotation and A130 and A150 did not (Chapter 8).

10.2   Settling tests with unsheared PAM solutions

10.2.1 Effect of PAMs' dosage on flocculation of coal

In these tests, unsheared PAM solutions were added into gently agitated coal-water suspensions. The position of the sediment interface height is plotted as a function of settling time for different PAM dosages. The results are shown in Figures 10.1-10.5.

As these figures indicate, in the flocculant concentration range tested, the flocculation power of polyacrylamides increases with increasing degrees of anionicity, and A130 and A150 turned out to be the most effective flocculants. Their degrees of anionicity are 33 % and 50 %, respectively. This is consistent with industrial observations. For example, for N100 and N300, the boundary was first observed after 2 minutes of settling at a dosage of 50 g/t, but for A100 the dosage at which this happened was reduced to 12.5 g/t, indicating that A100 is much more efficient than N100 and N300. For A130 and A150, the boundary between the supernant and sediment was immediately observed even at a dosage as low as 12.5 g/t. These results reveal that for the tested PAMs the settling rate increases with increasing dosages until it reaches a certain concentration. Exceeding the dosage above this concentration does not increase the settling rate any further.

Flocculation efficiency is sometimes defined as the ratio of the amount of flocculated material to the total amount of solids in suspension. In other words, high flocculation efficiency means there is less solid material remaining suspended. Figure 10.6 shows the relationship between the yield of the suspended material and the PAM dosage. This graph again clearly shows that the flocculation efficiency depends on the degree of anionicity and dosage of the flocculant. For example, the yields of suspended material after

5 minutes of settling for N100 and N300 were 40.3 % and 54.3 %, respectively, at a dosage of 12.5 g/t. The yields decreased to 13.2 % for A100, 3.4 % for A130, and 2.1 % for A150 at the same dosage. The selected polyacrylamides are very efficient flocculants and the material was almost completely flocculated when a certain dosage was reached. The minimum PAM dosage needed for complete flocculation decreases with increasing degree of anionicity: 200 g/t for N100 and N300, 50 g/t for A100, and 12.5 g/t for A130 and A150.

Flocculation with the N300, N100 and A100 flocculants was somewhat selective before total flocculation occurred. The ash content of the suspended product was higher than that of the settled product. The suspended product ash increased with increasing PAM dosages, but the settled product ash did not change much and was around 29-33 %. Taking N300 as an example, the yield/ash was plotted as a function of its dosage and the results are shown in Figure 10.7. The ash contents of the suspended and settled products were 33.8% and 33.2%, respectively, without the addition of flocculants (at a yield of suspended and settled products of 63.3 % and 36.7 %, respectively). As the N300 dosage increased to 100 g/t, the yield of suspended product decreased from 63.3% to 2.9 % and its ash increased from 33.2 % to 50.8 %, but the settled product ash was between 29.5 % and 33.15 %. No such data could be obtained for A130 and A150 since total flocculation occurred even at the lowest dosage of 12.5 g/t.

10.2.2 Effect of pH on flocculation of coal

In the flotation tests (Chapter 7), it was shown that pH significantly affected the reverse flotation of coal when A100 polyacrylamide was added. The yield of the froth product decreased from 49.6 % to less than 8 % when pH was changed from a natural pH of 8.4 to over 9.

In the following tests, two polyacrylamides were chosen. One is A100, which turned out to be the most effective in coal reverse flotation, and the other is A130, which is the most efficient flocculant. In all of these tests, PAM solutions were not sheared and coal-polymer suspensions were just slightly agitated to avoid breaking the flocs during the addition of PAMs. The dosage of PAMs was kept at 400 g/t.

The effect of pH on the flocculation of coal was significant. Quite different settling

behaviors were observed with different PAMs. The results are shown in Figures 10.8 and 10.9.

As Figure 10.8 indicates, total flocculation was observed and the solution above the interface was clear when pH was between 7.5 and 8.6 for A100. As the pH increased from 9.2 to 11, a clear interface was still observed but the solution above the interface became increasingly turbid as more fines remained suspended. The yield of the suspended portion increased from 1.7 % to 7.3 %. An ash analysis of both the suspended and settled products revealed that selective flocculation occurred with increasing pH. The ash content of the suspended product increased from 49.1 % to 64.9 % in the pH range from 9.2 to 11.

The effect of pH on the flocculation of coal with A130 was even more significant, as can be seen in Figure 10.9. An interface was observed only over the pH range of 7.5-8.1. When the pH was higher than 8.6 (from 8.6 to 11), no interface was observed. Even in the pH range of 7.5-8.1, the solution above the interface was turbid and contained a low percentage of fines. The suspended portion yield increased significantly with increasing pH and was as high as 45.9 % at pH 10. While the ash content of the suspended material was between 36.7 % and 51.1 %, the ash content of the settled portion was between 26.8 % and 32.9 %, which indicates that flocculation was selective.

These results show that higher pH results in more solids remaining suspended and more selective flocculation. The effect of pH on the flocculation of coal with A130 was more obvious than with A100. The two polyacrylamides differed only in the degree of anionicity.

10.3 Settling tests with sheared PAM solutions

The effect of shear degraded polyacrylamide solutions on the flocculation of coal was investigated using A100 and A130 flocculants. In these tests, PAM solutions were conditioned in a 1 liter flotation cell at 1500 rpm for 30 minutes before use. Coal-water suspensions were just slightly agitated during the addition of the sheared polymer solutions.

As Figures 10.10 and 10.11 indicate, the shearing of PAM stock solutions for 30 minutes results only in a very slight decrease of flocculation power. The effect of

increasing dosages on the settling behavior of coal-water suspensions also became insignificant. This is quite different from the results obtained with the unsheared polymer solutions (Figures 10.3 and 10.4). For A100, no settling interface was observed at a dosage of 12.5 g/t during the entire 5 minutes of settling (the layer occurred after 2 minutes at the same dosage in the case of unsheared A100 solution). An interface was observed after 1 minute of settling at a dosage of 25 g/t, but further increase of dosages of A100 from 50g/t to 500g/t did not result in an increase in the settling rate of the interface. This effect became more apparent for A130, as shown in Figure 10.11. The settling curves were almost identical irrespective of dosage.

As Figure 10.12 shows, although the settling rate decreased after PAM stock solutions were sheared, the yields of the suspended material were not affected very much after 5 minutes of settling, as compared with Figure 10.6.

Flocculation was also somewhat selective for A100. The ash content of the suspended matter increased from 34.8 % to 55.6 % when the dosage increased from 0 g/t to 50 g/t, but the ash content of the settled product was between 30.1 % and 34.2 %. The results are shown in Figure 10.13. No ash data could be collected for A130 because of the complete flocculation of coal even at the lowest dosage of 12.5 g/t.

There are two important findings for the use of sheared PAM solutions in flocculation tests. The shearing of PAM stock solutions resulted in a decrease in the settling rate, and by increasing the dosage of the sheared PAM it was not possible to improve flocculation.

10.4   Settling tests with intensely conditioned polymer-coal suspensions

10.4.1   Effect of PAMs' dosage on flocculation of coal

In the reverse flotation tests polymer solutions were added to the flotation cell and the pulp was subjected to 5 minute-conditioning before the collector was introduced. As already discussed, only some polymers reduce the amine consumption. The previous flocculation tests showed that both the nonionic and anionic polymers were very good flocculants and the polymers with a high degree of anionicity, such as A130 (33 % degree

of anionicity) and A150 (50 % degree of anionicity), were the most efficient ones. An increase in pH resulted in a change in flocculation from non-selective to slightly selective with more fine clay minerals remaining suspended. The shearing of PAM solutions decreased polymer's flocculation power. The effect of dosage became insignificant after shearing.

In order to investigate the effect of vigorous conditioning of polymer-coal suspensions on the flocculation of coal, additional series of tests were carried out. Unsheared polymer solutions (A100 and A130) and coal pulp were added to a 1 liter flotation cell and were conditioned at 1500 rpm for 5 minutes. Then the suspensions were transferred to a 500 mL cylinder to carry out settling tests. The results are shown in Figures 10.14 and 10.15.

The intense conditioning of polymer-coal suspensions, in a flotation cell, had a tremendous impact on the settling behavior of the system, although the effect on flocculation with A100 and A130 was quite different. As Figure 10.14 indicates, the conditioning of the whole coal-flocculant system strongly affected flocculation with the A100 flocculant. A settling interface was observed only after 4 minutes of settling at an A100 dosage of 100 g/t (the interface was observed after 2 minutes for unsheared A100 at a dosage of 12.5 g/t, and after 1 minute for sheared A100 at a dosage of 25 g/t , Figures 10.3 and 10.10). Increasing the dosage of A100 caused more solid particles to flocculate. Although the conditioning of the polymer-coal suspensions broke the large flocs into smaller ones and slowed the settling rate, total flocculation was still possible at 400 g/t of A100. It should be noted that the A100 dosage required for total flocculation after conditioning corresponds with the optimum A100 dosage (the maximum reject yield is obtained at this PAM dosage in reverse coal flotation, Figure 7.13). It indicates that the addition of A100 PAM results in flocculation of fines and this promotes the gangue flotation.

The results were quite different for A130. Firstly, flocculation became selective and no total flocculation occurred in the tested dosage range, which was apparently different from the previous results. Secondly, increasing A130 dosage from 0 g/t to 100 g/t resulted in more solids flocculated, but further increasing the dosage from 100 g/t to 700 g/t increased the yield of the suspended matter. These results are shown in Figure 10.16 in

which the yield of the suspended matter is plotted as a function of A100 and A130 dosages. The yield decreased with increasing dosage for A100 and total flocculation occurred at an A100 dosage of over 400 g/t. For A130, the yield decreased with increasing dosage up to 100 g/t, but a further increase of the dosage increased the yield of the suspended matter. All previous flocculation tests showed that A130 was the most effective flocculant and that even at a very low dosage (12.5 g/t) total flocculation occurred. Intense conditioning of the polymer-coal suspensions made the flocculation with this polymer to some extent selective.

The yield and ash of the suspended and settled products after 5 minute-settling are shown in Figures 10.17 and 10.18. As Figure 10.17 indicates, the ash of the suspended matter is between 33.8 % and 48.0 % and the ash of the settled matter is between 28.8 % and 33.2 %, indicating that a level of selectivity can be achieved with A100. With increasing PAM dosage, the yield of the suspended matter decreased significantly and this made the ash content of the settled matter change very little (which was around 31.0 %). For A130, as its dosage increased from 0 g/t to 700 g/t, the ash of the settled matter decreased from 33.2 % to 26.5 %, and the ash of the suspended matter was between 34.0% and 46.5%, indicating also some degree of selectivity.

10.4.2 Effect of pH on flocculation of coal

As indicated in Section10.1.2, an increase in pH generated more material suspended with using unsheared PAM solutions added to a gently agitated coal-water slurry. This effect becomes much more significant with a strongly conditioned coal-flocculant system. The results are shown in Figures 10.19 and 10.20. As can be seen from Figure 10.19, total flocculation was observed in the pH range of 7.5-8.1 using A100. This yield of the suspended matter increased to 3.7 % at pH 8.6. The yield increased with increasing pH and a yield of 65.6 % was obtained at pH 11. The ash content in the suspended matter was between 35.2 % and 43.3 %, and the ash of the settled matter was between 29.2 % and 33.1 %. The ash of the suspended matter was higher than that of the settled matter indicating some degree of selectivity, but the difference in ash content became small over the pH range of 10 -11.

For A130, no total flocculation occurred in the whole pH range tested. The yield of the suspended matter increased significantly with increasing pH. Even at pH 7.5, a yield of 19.1 % was obtained. The yield increased to 70.1 % at pH 11. As can be seen from Figure 10.20, flocculation was selective when pH was lower than 8.6. Above pH 8.8, A130 actually acted as a dispersant.

10.5 Summary

All tested polyacrylamides, regardless of their degree of anionicity, were very good flocculants. Polymers having a high degree of anionicity (A130 and A150) were the most efficient when their stock solutions and the pulp were not subjected to strong conditioning. Flocculation was not selective at natural pH when total flocculation was observed.

pH had a significant effect on the flocculation of coal. Increasing the pH resulted in more selective flocculation with more fine particles remaining in suspension. The effect of pH on the flocculation of coal with A130 (33 % degree of anionicity) was more significant than with A100 (7 % degree of anionicity).

The shearing of polymer solutions turned out to have a significant effect on the flocculation of coal. The settling rate decreased and increasing the dosage had little effect on the settling rate. However, total flocculation was still observed after 5 minutes of settling, regardless of the polymer's degree of anionicity. Since this affects flocculation, it may also affect reverse coal flotation in a flotation cell. However, this correlation is not further addressed in this thesis.

The intense conditioning of a coal slurry after adding unsheared flocculant solution in a flotation cell resulted in a different flocculation behavior for polymers with different degrees of anionicity. For the polymer with a low degree of anionicity (such as A100), its flocculation power was partially lost, but increasing its dosage to over 400 g/t still led to total flocculation at pH values below 8.6. At pH higher than 8.6 more solids were dispersed and flocculation was somewhat selective. For polymers with a high degree of anionicity (such as A130), flocculation became more selective and the yield of the suspended matter initially decreased with increasing dosage, but further increasing the dosage resulted in an

increase of the yield. The effect of pH was also significant, higher pH made the polymer act as a dispersant rather than a flocculant.

These results indicate that the effect of PAM on coal reverse flotation results from both the degree of anionicity of a polymer and the hydrodynamic conditions created in the flotation cell. This leads to the conclusion that the reverse flotation of coal should be different in a mechanical cell and in a column. This was further studied and the results are presented in Chapter 11.
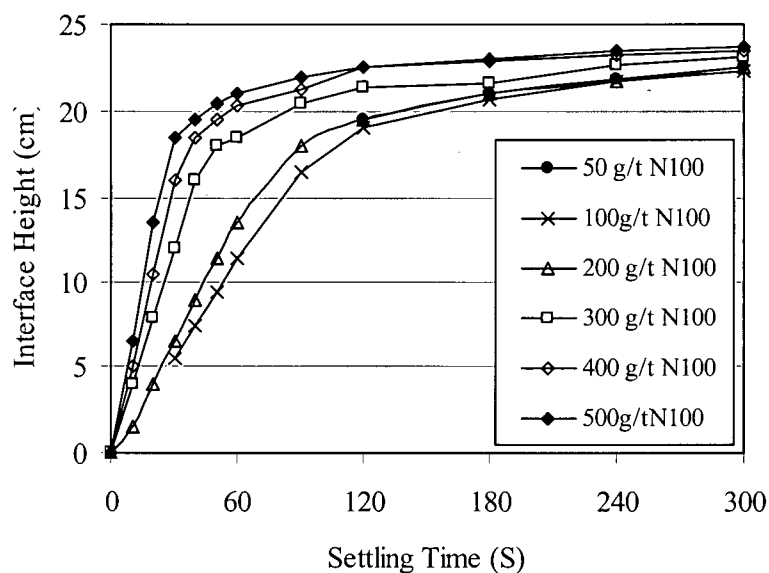
Figure 10.1 Settling curves for N100 polyacrylamide (25 g of LS20 coal in 500 mL water, natural pH).
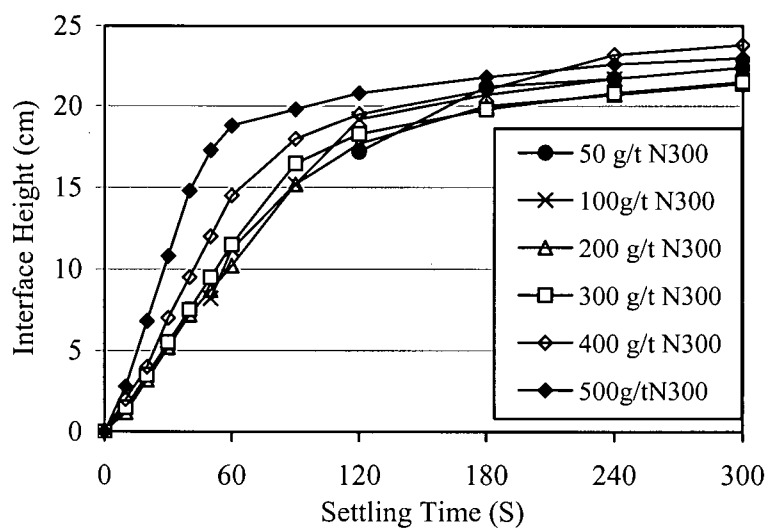
Figure 10.2 Settling curves for N300 polyacrylamide (25 g of LS20 coal in 500 mL water, natural pH).
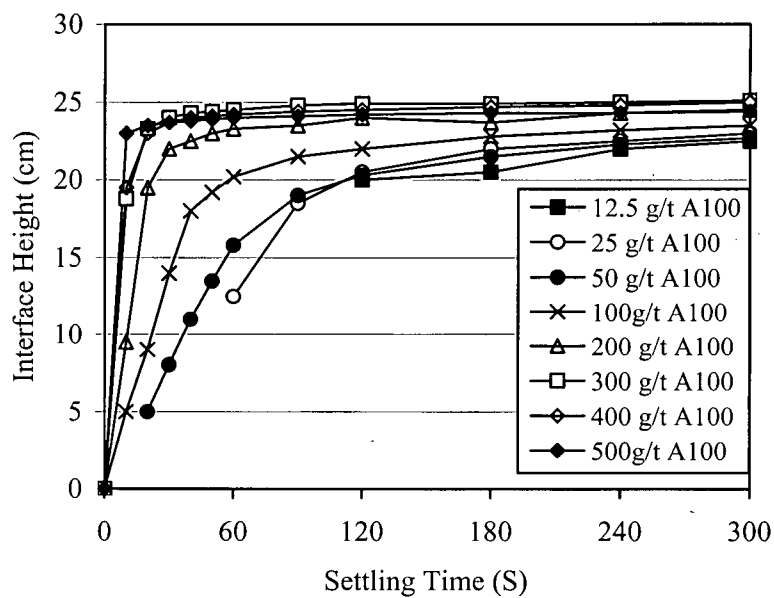
Figure 10.3   Settling curves for A100 polyacrylamide
(25 g of LS20 coal in 500 mL water, natural pH)
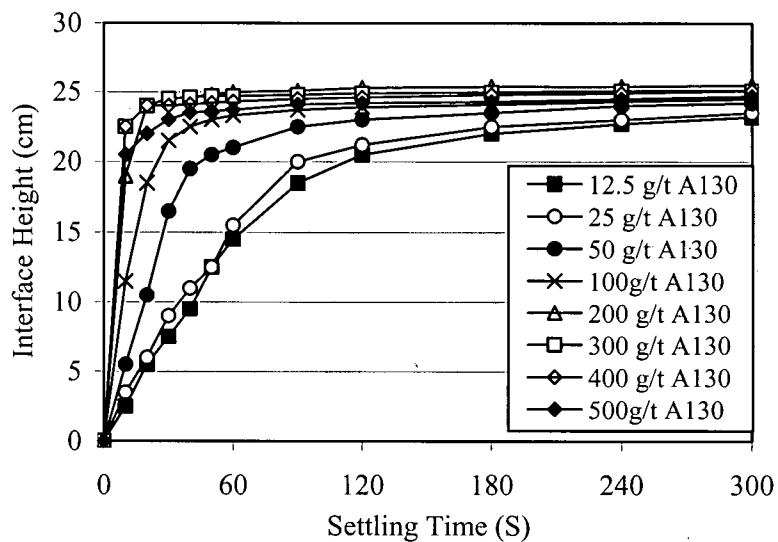
Figure 10.4   Settling curves for A130
polyacrylamide (25 g LS20 coal in 500 mL water,
natural pH).
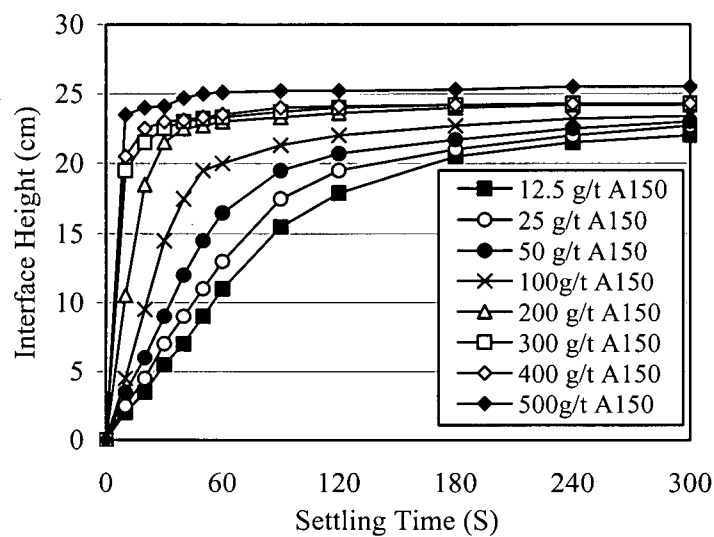
Figure 10.5   Settling curves for A150
polyacrylamide (25 g of LS20 coal in 500 mL water,
natural pH).
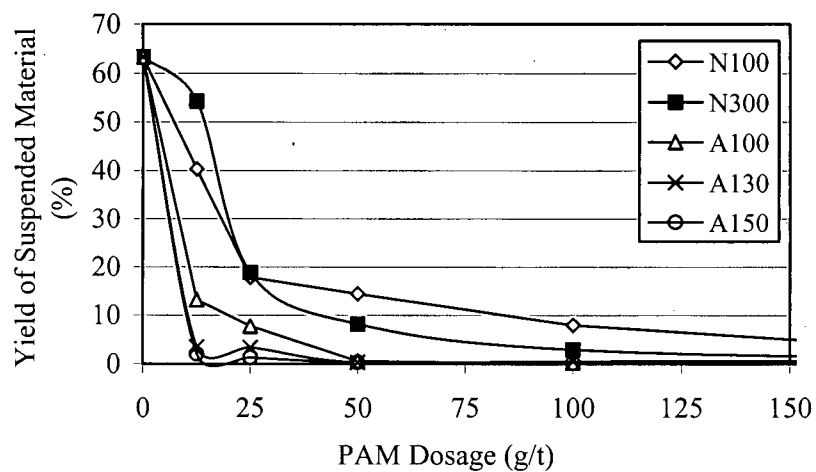
Figure 10.6   Effect of PAM on floccolation of coal
(25 g of LS20 coal in 500 mL water, after 5 minutes
settling).

Figure 10.7   Effect of N300 on flocculation of coal (25 g of LS20 in 500 mL water, natural pH, after 5 minutes settling).
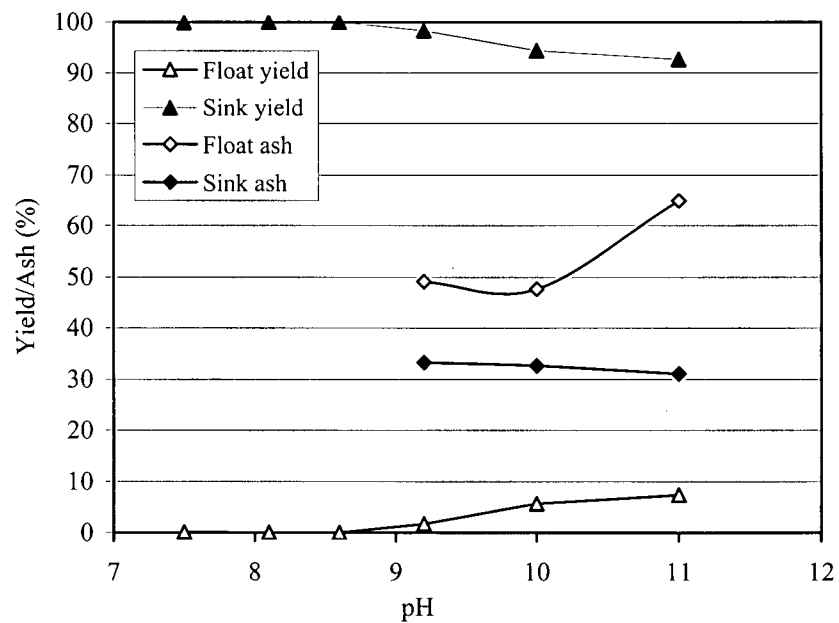
Figure 10. 8. Effect of pH on flocculation of coal with A100 (25 g of LS20 coal in 500 mL water, 400 g/t of A100, after 5 minutes settling).
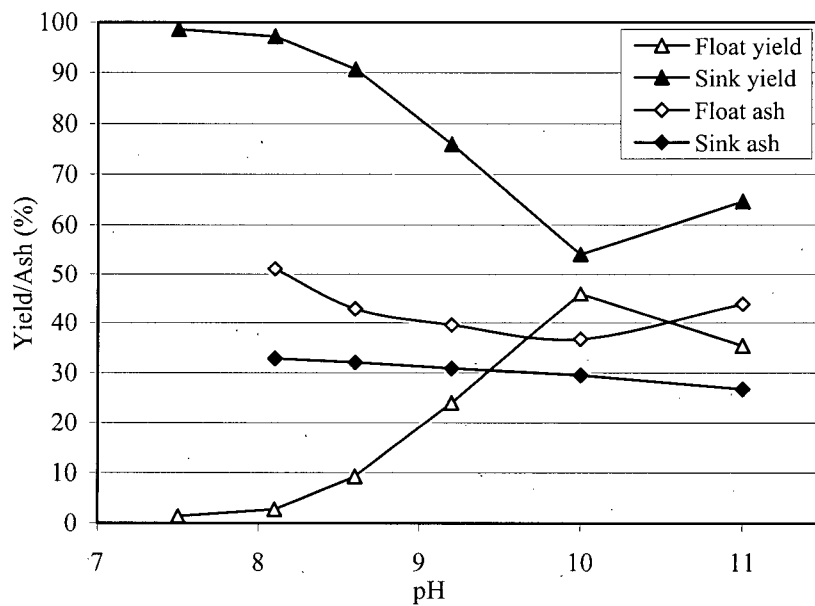
Figure 10.9 Effect of pH on flocculation of coal with A130
(25 g of LS20 coal in 500 mL water, 400 g/t of A130, after 5
minutes settling).
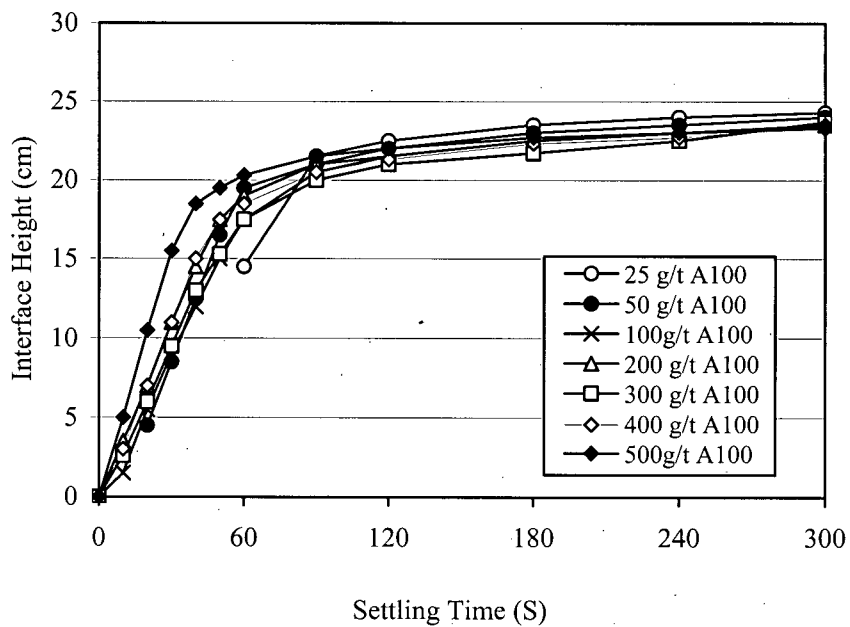
Figure 10.10 Settling curves for sheared A100
polyacrylamide (25 g of LS20 coal in 500 mL water,
natural pH).

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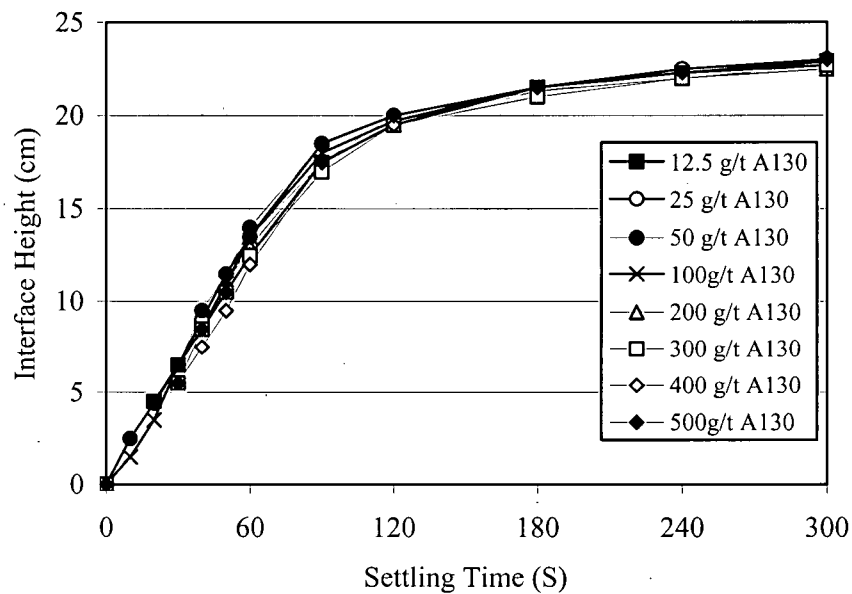
Figure 10.11 Settling curves for sheared A130 polyacrylamide (25 g of LS20 coal in 500 mL water, natural pH).
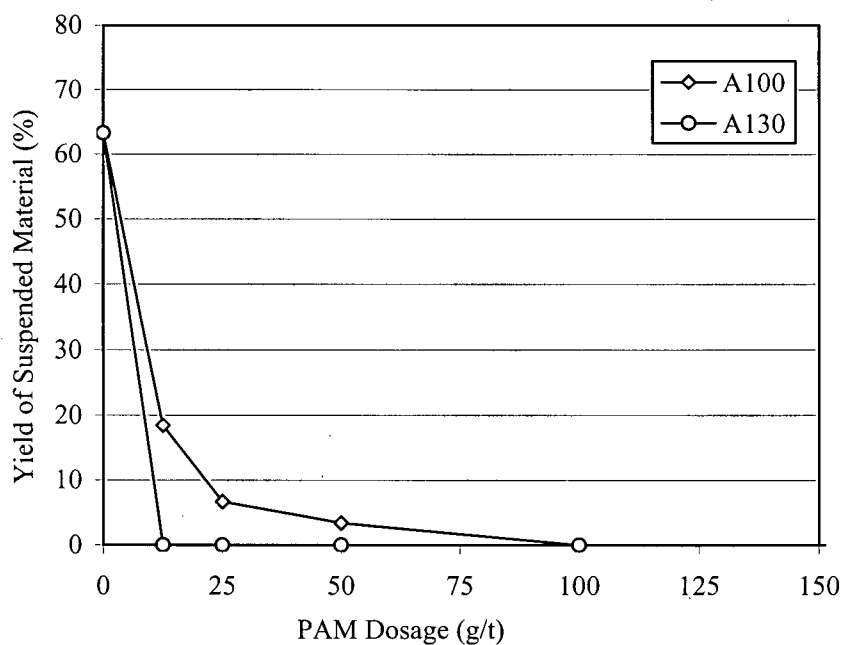
Figure 10.12 Effect of sheard PAMs on flocculation of coal (25 g of LS20 coal in 500 mL water, after 5 minutes settling).
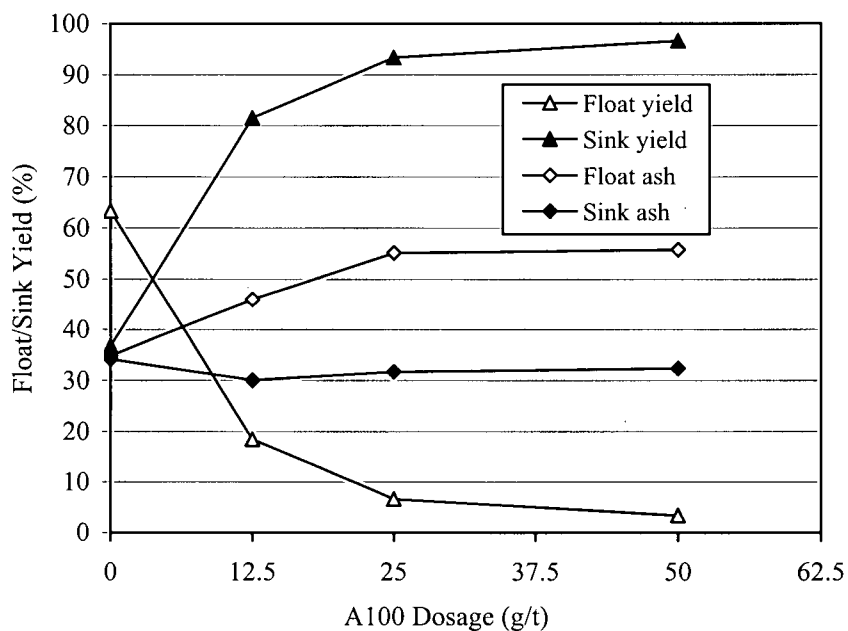
Figure 10.13 Effect of sheared A100 dosage on flocculation of coal (25 g of LS20 coal in 500 mL water, natural pH).
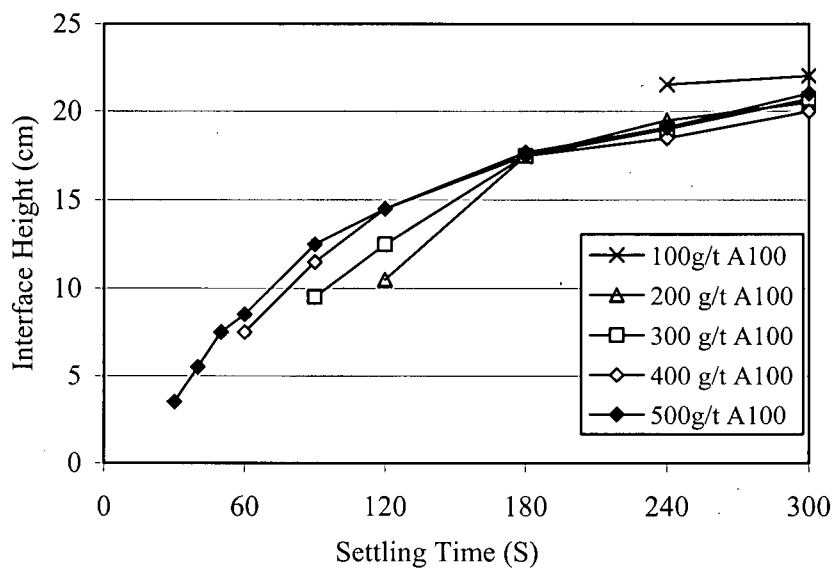
Figure 10.14 Settling curves for A100; after conditioning coal suspension in a cell at 1500 rpm for 5 minutes, natural pH.
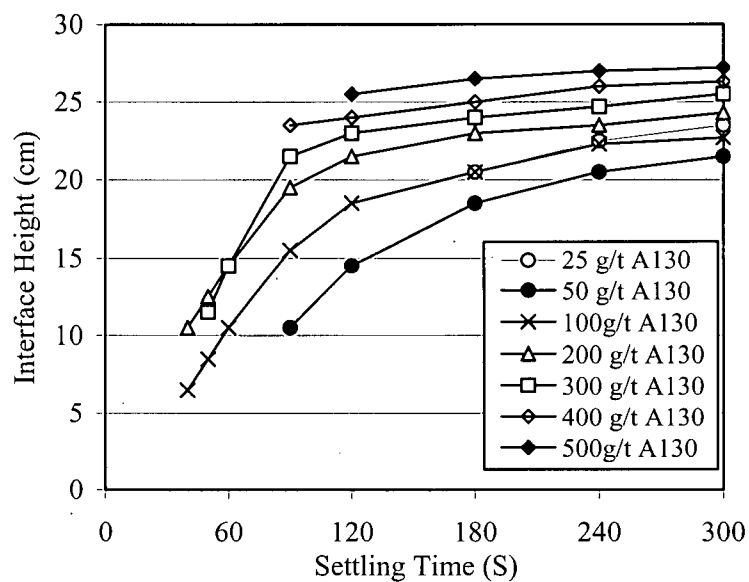
Figure 10.15   Settling curves for A130; after
conditioning coal suspension in a cell at 1500 rpm
for 5 minutes, natural pH.
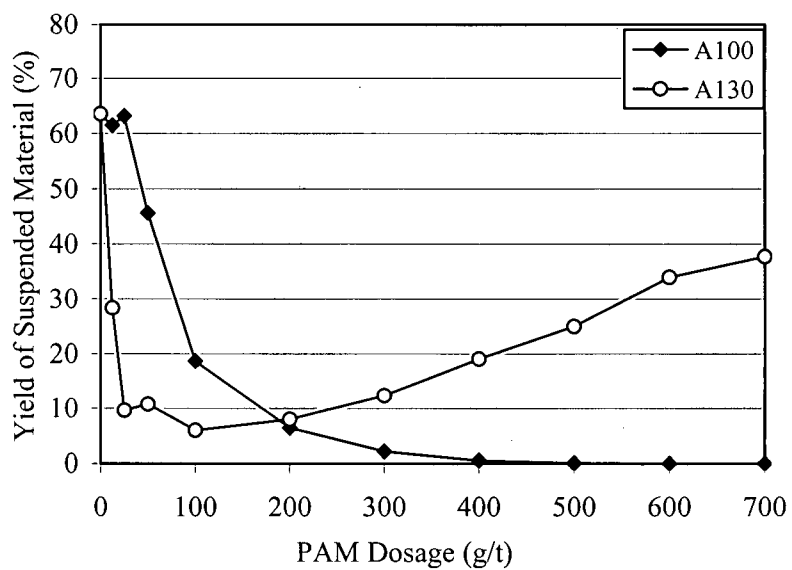
Figure 10.16   Effect of PAM on flocculation of coal
(suspension conditioned in a cell at 1500 rpm for 5
minutes, natural pH)
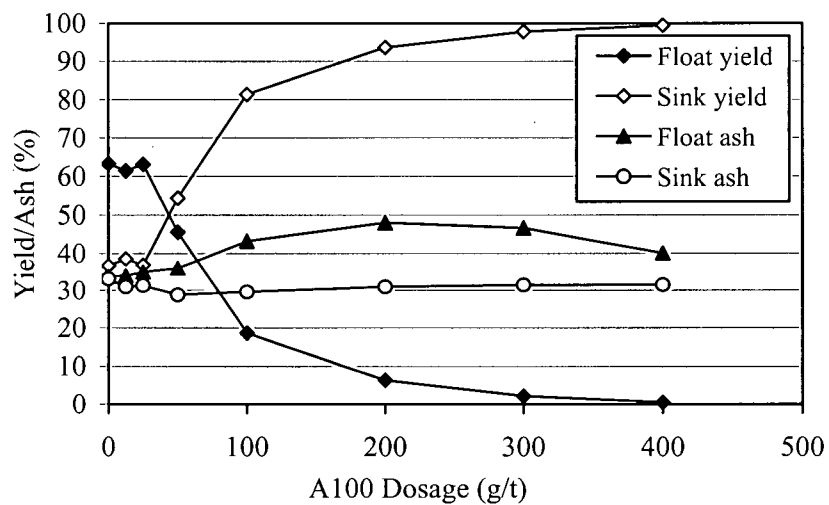
Figure 10.17 Effect of A100 on flocculation of coal (Suspension conditioned in a cell at 1500 rpm for 5 minutes, 25 g of LS20 coal in 500 mL water, natural pH, after 5 minutes settling).
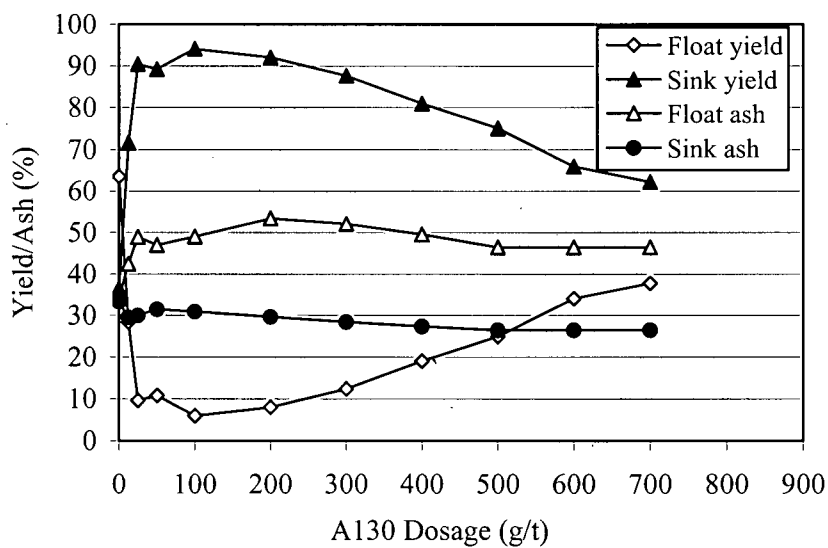
Figure 10.18   Effect of A130 on flocculation of coal (suspension conditioned in a cell at 1500 rpm for 5 minutes, 25 g of LS20 coal in 500 mL water, natural pH, after 5 minutes settling).
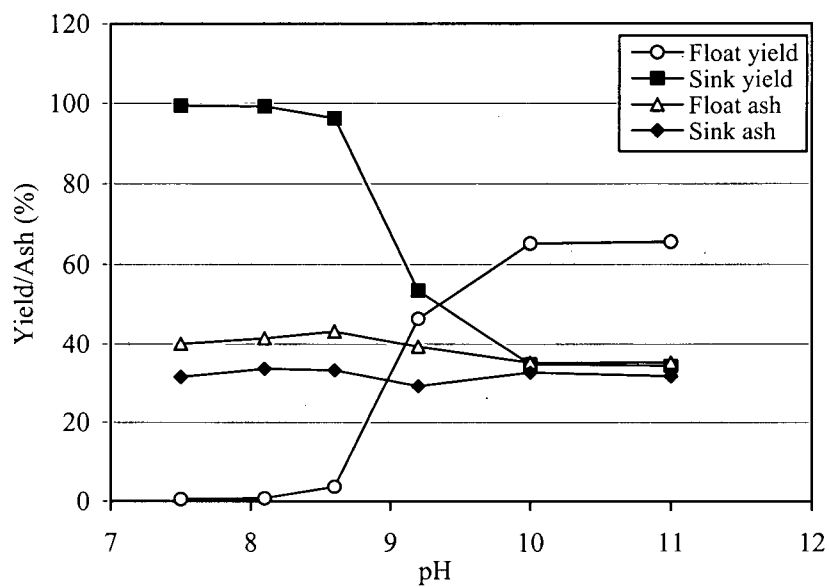
Figure 10.19 Effect of pH on flocculation of coal with A100 (suspension conditioned in a cell at 1500 rpm for 5 minutes, 25 g of LS20 coal in 500 mL water, 400 g/t of A100, after 5 minutes settling).
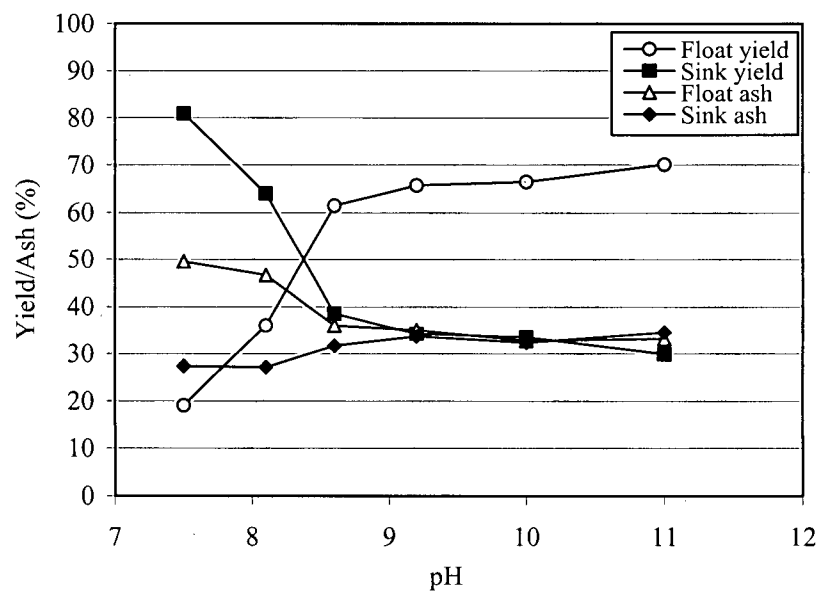
Figure 10. 20 Effect of pH on flocculation of coal with A130 (suspension conditioned in a cell at 1500 rpm for 5 minuts, 25 g of LS20 coal in 500 mL water, 400 g/t of A130, after 5 minutes settling).

CHAPTER 11   COLUMN FLOTATION

11.1   Introduction

The results of flocculation tests (Chapter 10) pointed out the importance of the hydrodynamic conditions in a flotation cell in flocculating coal with polyacrylamides. PAMs with different degree of anionicity responded quite differently to intense conditioning. The conditioning stage made PAM with a low degree of anionicity (such as A100) lose significantly its flocculation ability, but an increase in dosage still resulted in the total flocculation of the material. With intense conditioning small flocs (and not the large ones as observed in the standard flocculation tests) were produced and the addition of A100 polymer greatly improved gangue flotation. However, the strong conditioning in a cell with PAM of a high degree of anionicity resulted in redispersion of the flocculated solids, and the addition of such PAM did not improve gangue flotation. This shows that only the PAM that provides total flocculation, even after the PAM-coal system is subjected to an intense conditioning, can promote gangue flotation. If the effect of A100 on flotation depends on conditioning, the quality of the concentrate should strongly depend on conditioning in reverse coal flotation. This premise was tested in a flotation column.

As discussed in Chapter 3, reverse coal flotation should result in an increased column carrying capacity due to a decreased yield of the froth product in comparison with forward flotation. To test this idea, both forward and reverse column flotation tests were carried out to determine the column carrying capacity in each case.

11.2   Effect of conditioning with PAM on reverse coal flotation

In these tests, the intensity of conditioning with A100 polyacrylamide in a 30 L tank after addition of A100 into a coal slurry was maintained at two levels: either 400 r.p.m. or 1500 r.p.m. This was followed by pumping the pulp into the column to carry out the flotation tests. The flotation tests were carried out using dodecyltrimetyl ammonium chloride (DTAC) as collector with tannic acid as dispersant and dextrin as depressant. Further details on the selection of these reagents were discussed in Chapter 7 and the test

procedure was described in Chapter 4. Since the purpose of these tests was to investigate the effects of conditioning with PAM on column flotation, conventional reverse flotation method was used to simplify the process. Only air was introduced into the column through the sparger. The results are shown in Tables 11.1 and 11.2.

As the results of Table 11.1 demonstrate, the ash contents of the reject and concentrate were practically the same when the pulp was conditioned with A100 flocculant at 400 r.p.m. Reverse flotation under these conditions was completely non-selective implying total flocculation. Although the flocs were easily floated no separation was achieved since the flocs were produced during total non-selective flocculation. Increasing the intensity of conditioning from 400 r.p.m. to 1500 r.p.m. resulted in a significant improvement of the concentrate quality (Table 11.2). Its ash content decreased to around 17 % and the ash content of the reject increased to around 53 %. These results show that intense conditioning leads to the rearrangement of the large coal-fine gangue flocs into separately flocculated coal flocs and fine gangue flocs which are then floated with DTAC in the reverse flotation process.

To demonstrate the effect of conditioning with A100 on flotation, the column was selected since conditioning in this case is carried out in a conditioning tank and can be accordingly adjusted. The procedure was described in Section 4.3.1.3 of Chapter 4.

The reverse flotation tests with PAM carried out in a mechanical batch flotation cell (Denver) provided excellent results (Chapter 7) since conditioning was quite intense under such conditions, and this further confirms the premise that reverse flotation with PAM depends on intense conditioning.

The results demonstrate quite clearly how important hydrodynamic conditions are for selective flocculation. The often-reported failure in selective flocculation tests might also be a result of inadequate optimization of the hydrodynamic conditions in such studies. These findings open a somewhat neglected area of research.

11.3   Column carrying capacity of forward and reverse flotation

Column carrying capacity is defined as the maximum feed rate in mass per unit time per unit cross-sectional area of the column (t/h/m^2) without affecting its performance

(Finch and Dobby, 1990). In practice, the carrying capacity is measured through monitoring the froth rate by changing the feed rate. Increasing feed rate also increases the froth rate until a certain point at which further increase in feed rate results in a level-off or decrease of the froth rate. This point defines the carrying capacity of a column. The experimental results are shown in Figures 11.1-3.

As seen from Figure 11.1, the carrying capacity of the column is around 1.8 t/h/m^2 in the forward column flotation. Further increase in the feed rate does not improve the froth rate. At a higher throughput, both the yield of concentrate and the ash content of reject decreased considerably (Figures 11.2 and 11.3).

In the reverse column flotation, no maximum froth rate was obtained over the tested feed rate range (Figure 11.1), indicating that the carrying capacity was not yet reached. In the tested feed rate range, the change in ash content/yield of the products (concentrate and reject) was insignificant in the reverse flotation (Figures 11.2 and 11.3).

It should be noted that the ash content of the reject in reverse flotation is lower than that in forward flotation although the ash content of concentrate is approximately the same.

11.4 Summary

These tests show that conditioning is essential when high molecular weight polyacrylamides are used in reverse coal flotation in order to reduce the amine consumption. The intense conditioning produces selectively aggregated small flocs of coal and gangue particles, also making the flotation process selective. The flocculation of fines leads to a significant decrease in the surface area of the gangue to be floated, and in turn reduces the consumption of amine. Reverse coal flotation results in an increase in the column carrying capacity due to the decreased yield of the froth product.

Table11.1 Effect of conditioning with A100 polyacrylamide at 400 r.p.m. on reverse coal flotation (DTAC 2.75 kg/t, tannic acid 1 kg/t, dextrin 1 kg/t, 400 g/t of A100)

Feed rate (kg/h)	Reject yield (%)	Concentrate yield (%)	Reject ash (%)	Concentrate ash (%)
2.1	62.7	37.4	33.7	33.4
2.5	68.0	32.0	33.8	33.2
4.0	58.1	41.9	33.6	33.7

Table 11.2 Effect of conditioning with A100 polyacrylamide at 1500 r.p.m. on reverse coal flotation (DTAC 2.75 kg/t, tannic acid 1 kg/t, dextrin 1 kg/t, 400 g/t of A100).

Feed rate (kg/h)	Reject yield (%)	Concentrate yield (%)	Reject ash (%)	Concentrate ash (%)
2.2	45.8	54.2	54.6	16.8
3.8	47.9	52.1	53.9	16.9
5.3	47.4	52.6	52.9	17.5
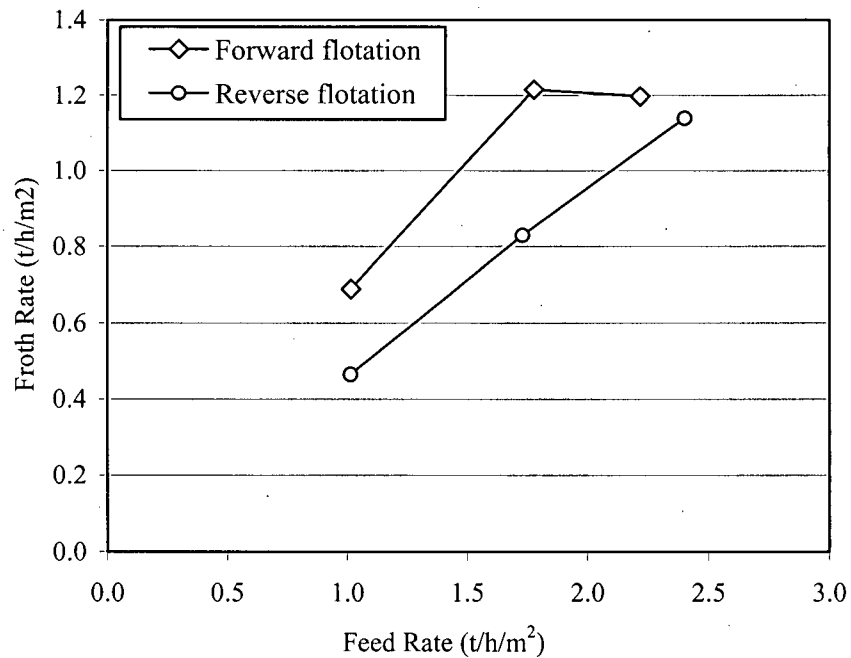
Figure 11.1 Column carrying capacity of forward and reverse flotation.
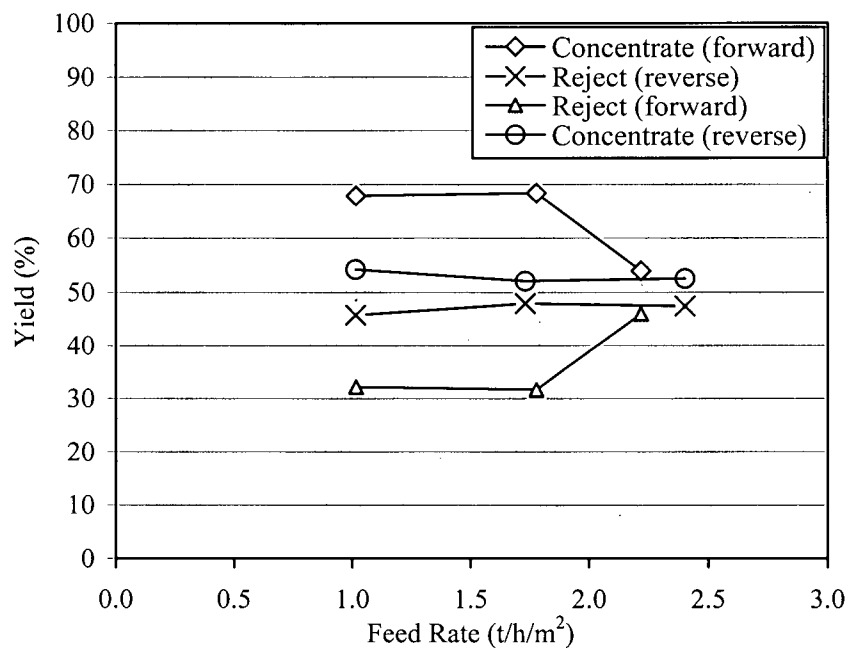
Figure 11.2 Effect of feed rate on yield in column flotation.
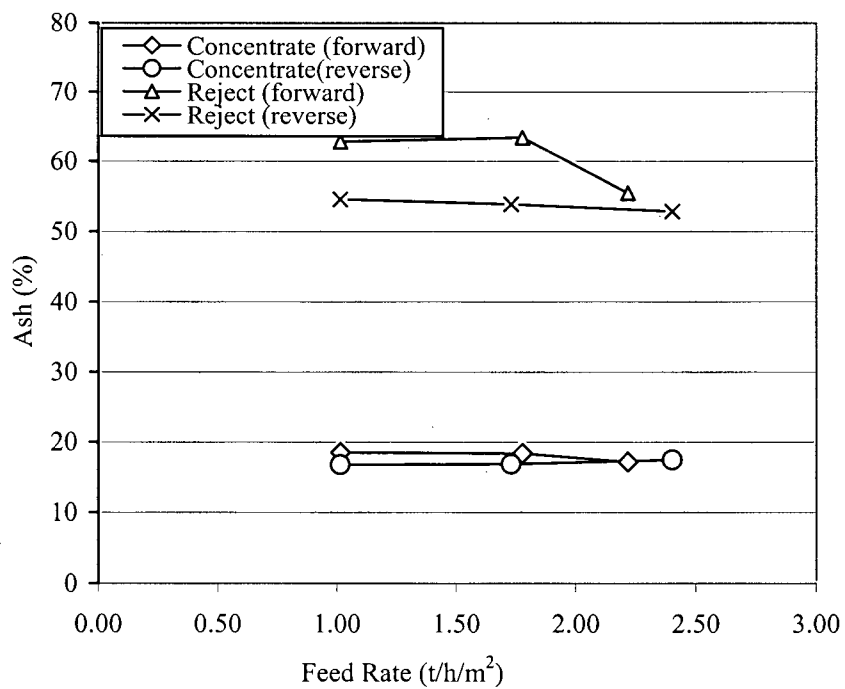
Figure 11.3 Effect of feed rate on ash in column flotation.

CHAPTER 12   RHEOLOGICAL MEASUREMENTS

12.1   Introduction

The LS20 coal is not very hydrophobic. Reverse flotation makes this coal even more hydrophilic by adsorbed depressant and dispersant (dextrin and tannic acid). The added A100 polyacrylamide is an anionic polymer and its adsorption onto the coal surface also increases hydrophilicity of the surface. As already discussed in Chapter 3, chemical additives are essential in the preparation of coal-water slurry to make the coal surface hydrophilic when the clean coal is prepared from forward flotation (forward flotation makes the coal surfaces more hydrophobic). This new reverse flotation process would make it easier to prepare a coal-water slurry because of the resulting surface properties of the coal particles. The chemical additives may not be needed when preparing coal-water slurry from the reverse coal flotation products since the particles are already made hydrophilic in the flotation stage. These ideas were tested and described in this chapter.

In the rheological measurements, two series of coal-water suspensions were prepared: one from the forward flotation concentrate (froth product) and the other from the reverse flotation concentrate. Initial rheological measurements were carried out using flotation concentrate obtained from a flotation feed ground below 0.216 mm. It was found that the concentrate settled quickly and the rheological measurements could not be carried out properly. Therefore, the -0.216 mm raw coal was reground and the flotation feed size was reduced to around 80 % below -74 μm to obtain a fine coal concentrate suitable for rheological measurements. Both forward and reverse flotation concentrates used for rheological measurements were produced in an 8 L mechanical cell, as described in Section 4.3.1.2 of Chapter 4.

The rheological measurements were then carried out in water, and in the presence of 0.5 % or 1 % PSS10 dispersant (per coal weight) at varying coal contents.

12.2   Results and discussion

The obtained rheological curves under various conditions are shown in Figures

12.1-12.6.

The apparent viscosity calculated at a shear rate of 100 Sec^{-1} was plotted as a function of coal content. The results are shown in Figures 12.7-12.9.

As can be seen from Figure 12.7, the apparent viscosity increases with increasing solids content for both suspensions, but the apparent viscosity of suspensions prepared from the forward flotation concentrate is much higher than that from the reverse flotation concentrate. The difference becomes even more significant at high solids contents. For example, the apparent viscosity is around 1300 mPa·sec and 409.3 mPa·sec, respectively, for these two suspensions at a solids content of 55.6 % in water. It should be noted that the clean coal products prepared from forward and reverse flotation have similar ash contents and size distributions as shown in Chapter 4.3.1.2.

The effect of a dispersant on the viscosity of suspensions prepared from forward flotation concentrate is shown in Figure 12.8. The addition of 0.5 % PSS10 (per coal weight) resulted in a decrease of the suspension viscosity and shifted the curve to the right. A further increase in the dosage of the dispersant to 1% (per coal weight) did not show further improvement, indicating that the addition of 0.5% dispersant was sufficient. The addition of 0.5% dispersant corresponds to a dosage of 5 kilograms per ton of coal concentrate.

It is interesting to observe that the addition of 0.5 % or 1 % dispersant to the suspensions prepared from the reverse flotation concentrate had little effect on the apparent viscosity, as Figure 12.9 shows. These results confirm the assumptions that coal-water slurries prepared from a reverse flotation concentrate should have better rheological properties than slurries produced from a forward flotation concentrate. Therefore, no chemical additives are needed in this case.

12.3   Summary

Coal reverse flotation is a better method of coal cleaning if coal is to be used to prepare coal-water slurries. The rheological measurements indicate that the clean coal product from reverse flotation might be suitable for direct preparation of coal-water slurries without any additional rheology modifiers.
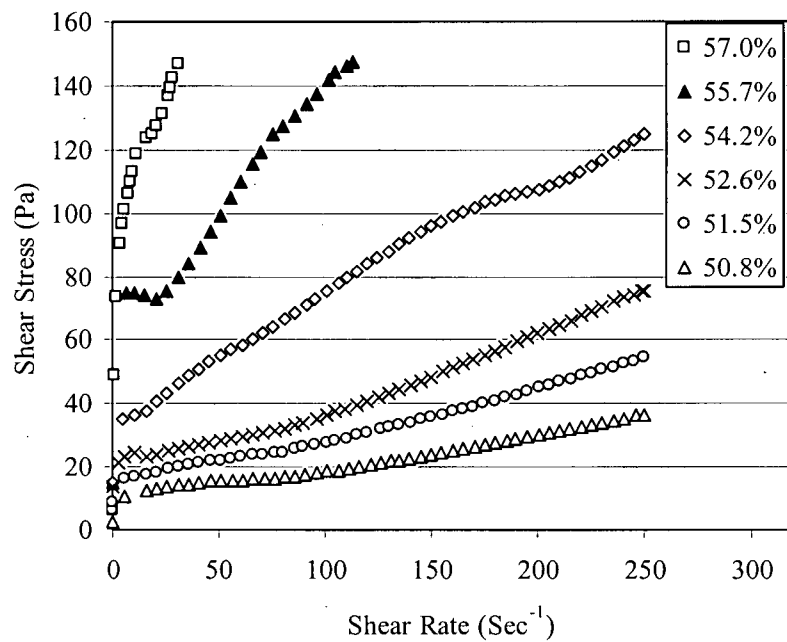
Figure 12.1 Flow curves for suspensions prepared
from the forward flotation concentrate in water at
various coal contents (weight % solids in suspension).
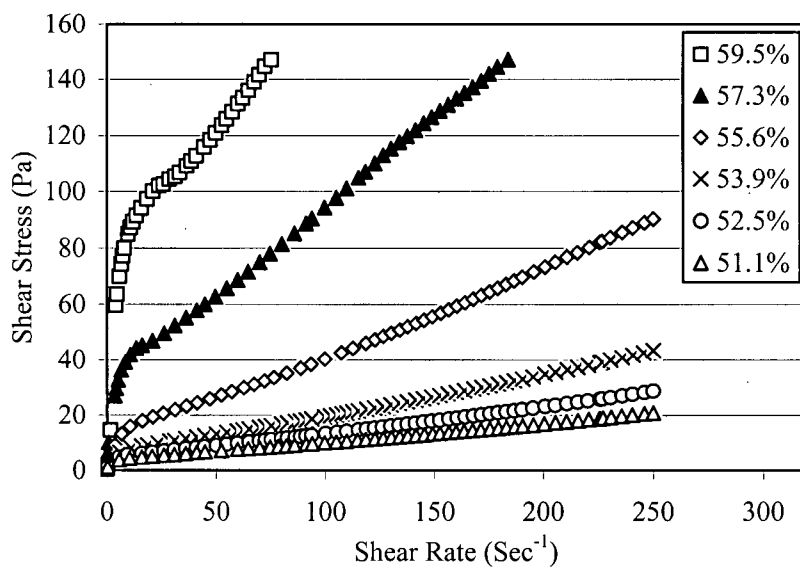
Figure12.2 Flow curves for suspensions prepared from
the forward flotation concentrate in the presence of 0.5 %
PSS10 at various coal contents (weight % solids in
suspension).
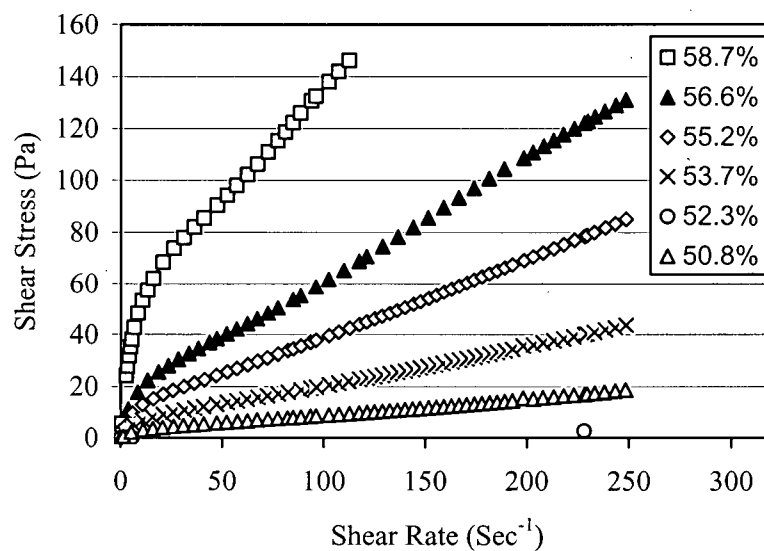
Figure 12.3. Flow curves for suspensions prepared
from the forward flotation concentrate in the presence
of 1 % PSS10 at various coal contents (weight %
solids in suspension).
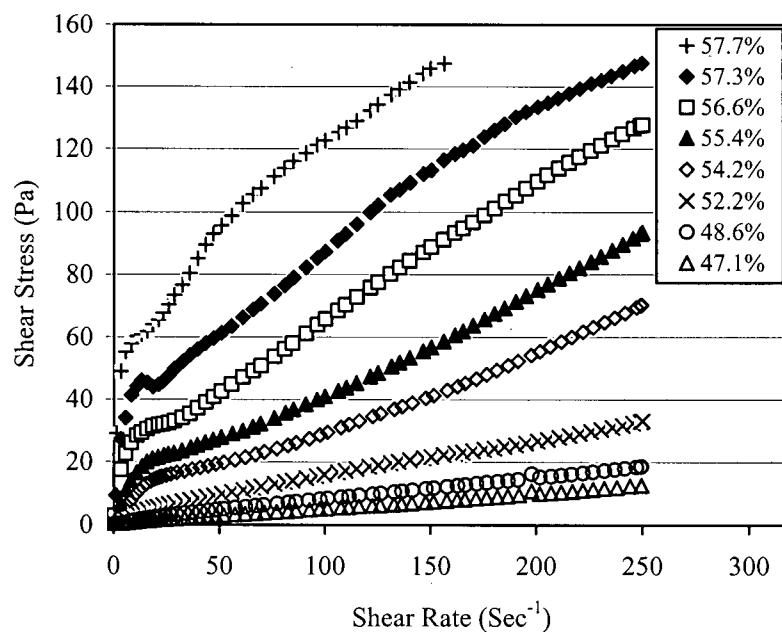
Figure 12.4 Flow curves for suspensions prepared from
the reverse flotation concentrate in water at various coal
contents (weight % solids in suspension).
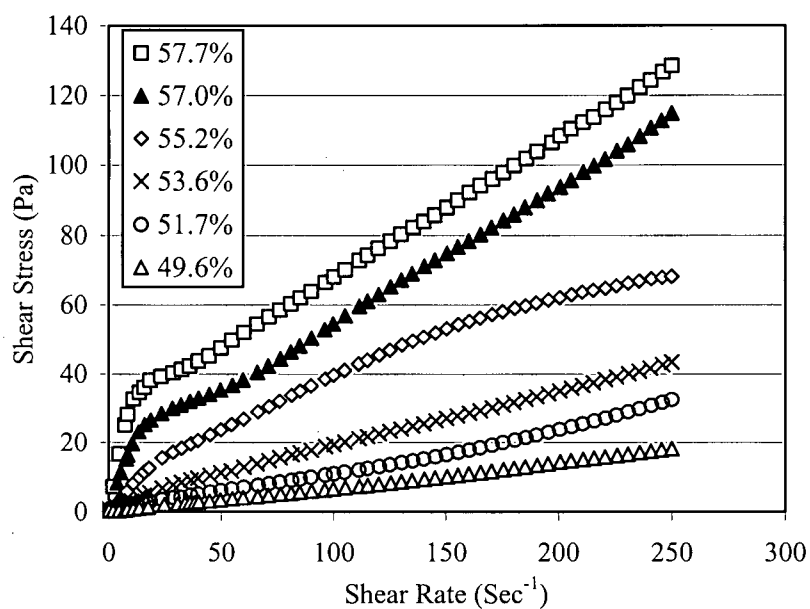
Figure 12.5   Flow curves for suspensions prepared from the reverse flotation concentrate in the presence of 0.5 % of PSS10 at various coal contents (weight % solids in suspension).
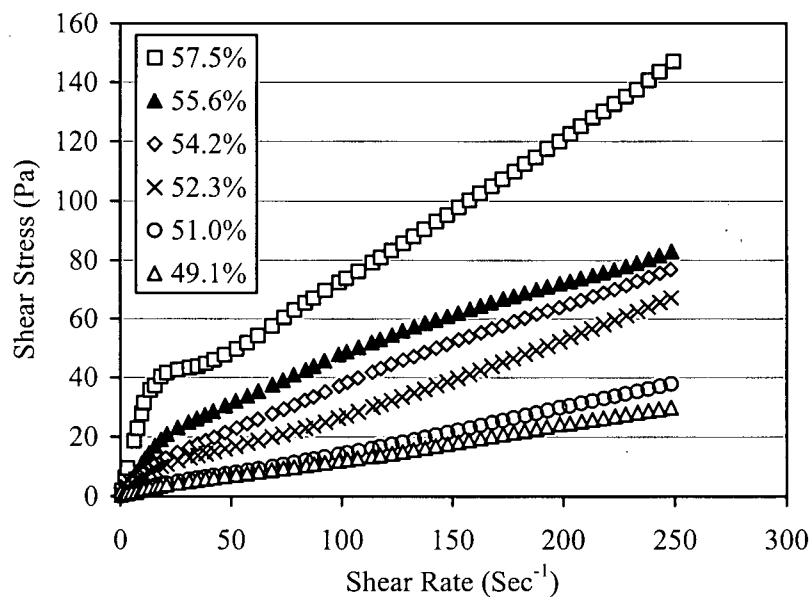
Figure 12.6   Flow curves for suspensions prepared from the reverse flotation concentrate in the presence of 1 % of PSS10 at various coal contents (weight % solids in suspension).
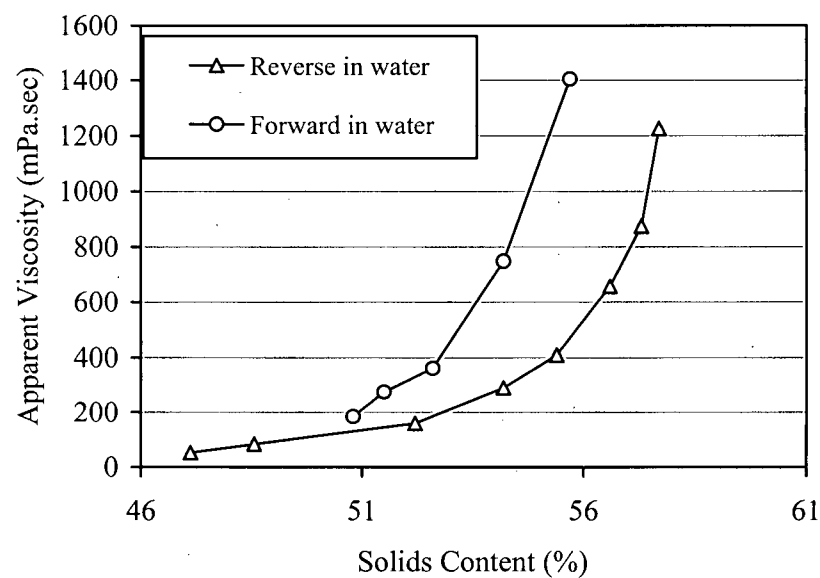
Figure 12.7 Comparison of the apparent viscosity of the coal-water slurries prepared from different flotation concentrates (calculated at a shear rate of 100 sec^{-1}).
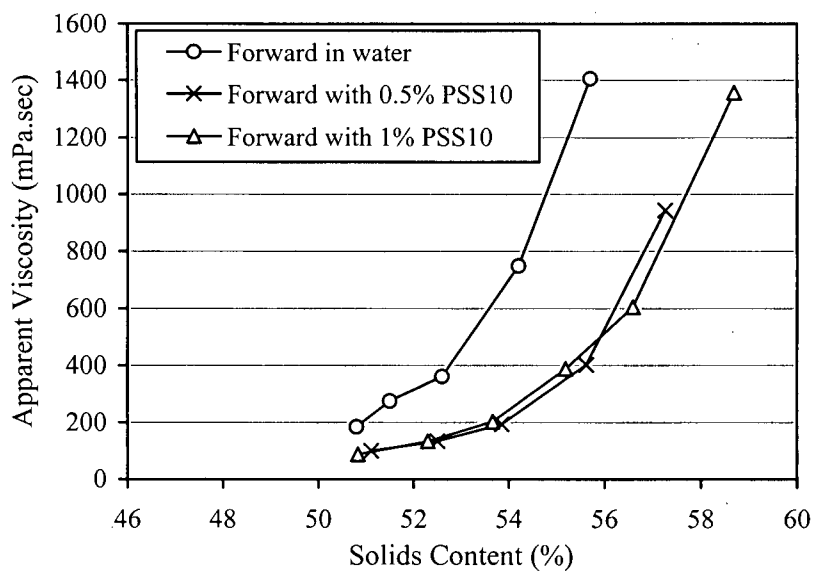
Figure 12.8   Effect of PSS10 dispersant on apparent viscosity of slurries prepared from forward flotation concentrates (calculated at a shear rate of 100 sec^{-1}).
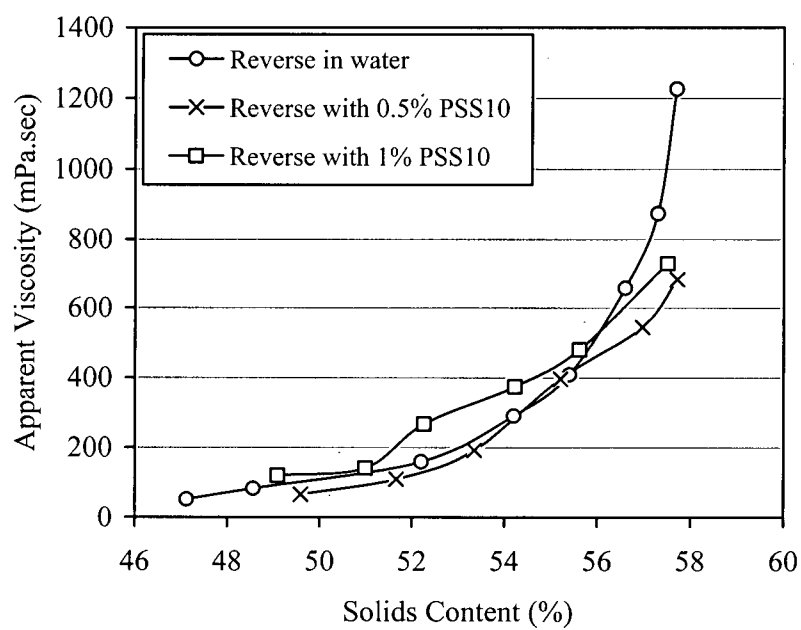
Figure 12.9 Effect of PSS10 dispersant on apparent viscosity of slurries prepared from reverse flotation concentrate (calculated at a shear rate of 100 sec^{-1}).

CHAPTER 13   DISCUSSION AND CONCLUSIONS

13.1   Discussion

13.1.1 Effect of zero conditioning with DTAC on reverse coal flotation

The hypothesis in this thesis is that the amine collector can be transported to the surfaces of gangue minerals through bubbles. Reducing conditioning time should thus result in lower collector adsorption onto the coal surface during reverse coal flotation and should improve gangue flotation.

According to the thermodynamic treatment (Chapter 3), to improve the probability of particle-to-bubble attachment in flotation, the bubbles should carry as much of flotation agents as possible to increase adsorption at the solid/gas interface, or conditioning time should be kept short to reduce adsorption at the solid/liquid interface. This approach called in this thesis "the zero conditioning time method". The process can be carried out either without any conditioning step prior to flotation, or, for better results, with the agent introduced into the flotation system with a stream of bubbles (aerosol).

Advantages of the aerosol addition of frother (MIBC) or oil to the flotation systems were already demonstrated (Wada et al., 1968; Misra and Anazia, 1987; Flint et al., 1988; Nott and Manlapig, 1994; Pokrajcic et al., 2005). The use of reagents in the form of aerosol was shown to lead to reduced reagent consumption.

The zero conditioning time flotation concept might be even more important in reverse coal flotation because of the high adsorption of amine onto coal. This technique, when applied along with A100 flocculant, was used in this thesis to conduct the reverse flotation of coal and the results of flotation and adsorption tests confirm the hypothesis proposed above.

The tested LS20 raw coal contained a large amount of fines (33.1 % of -38 μm, Table 4.4). This is further confirmed by its extremely high specific surface area, compared to the same coal pre-concentrated using a shaking table (Table 4.6). The specific surface area of the raw coal was 6.75 m²/g which is more than 6 times larger than that of the cleaned coal (0.98 m²/g). The large specific surface area made amine adsorption onto the coal extremely high (Figures 9.1 and 9.2). This unavoidably resulted in a high consumption

of amine in reverse flotation. The flotation tests showed that only 22.7 % yield of the froth product was obtained at a consumption of 6.25 kg/t DTAC (Figure 7.1, curve 3). This is consistent with the results published by Pawlik and Laskowski (2003a and 2003b) who found that the adsorption of amine onto low rank hydrophilic/oxidized coals is very high.

The yield of the froth product increased considerably from 24.4 % to 58.8 % with the application of the zero conditioning time method at a DTAC dosage of 5 kg/t (Figure 7.1, curve 1 and Figure 7.5, curve 1). This became even more apparent with the use of the A100 polyacrylamide. A froth yield of 30.5 % is obtained with 500 g/t of the PAM using conventional reverse flotation at a DTAC consumption of 3 kg/t (Figure 7.1, curve 2); the yield sharply increases to 84.8 % with the application of the zero conditioning time method at a DTAC dosage of only 1.375 kg/t (Figure 7.5, curve 2). The yield of the froth product decreases with increasing conditioning time of amine, as shown in Figure 7.17. This agrees well with the adsorption tests (Figure 9.3). Increasing the conditioning time with DTAC significantly increases its adsorption on coal.

These results confirmed that reducing conditioning time with DTAC significantly decreased its adsorption on coal and promoted gangue flotation. The adsorption results also indicated that more amine can be brought to the mineral surfaces by air bubbles. A higher amine adsorption density was measured on silica surfaces in the presence of air (Figure 9.13). However, the presence of air did not improve amine adsorption on coal (Figure 9.12).

The thermodynamic analysis presented here applies to a single solid-gas system, e.g. silica in aqueous solution. It is, however, reasonable to expect that for mixed systems, the different affinities of the same reagent towards different surfaces (e.g., coal and silica) will result in different adsorption densities at the interfaces. In the case of the coal-gangue-solution system, the surface that shows a higher affinity towards the amine will preferentially adsorb the surfactant at the expense of the other surface. As the adsorption results show, the adsorption density of DTAC at the LS20 coal-solution interface is much higher than the adsorption density at the silica-solution interface. Therefore, the idea behind the zero conditioning time concept is to minimize the exposure time of the strongly adsorbing of coal to amine molecules, and to allow the cationic surfactant to adsorb on silica as well.

The high adsorption of DTAC onto a hydrophilic coal surface, such as that of the LS20 coal, is of chemical type while the lower adsorption on the silica surface is of weak electrostatic/physical nature, and these two processes are clearly in competition in the coal-silica mixture. Moreover, the adsorption of DTAC on the coal surface can be expected to be irreversible while the adsorption of cationic surfactants on silica-type of surfaces is known to be reversible. Therefore, any direct comparisons between these two adsorption modes based purely on equilibrium thermodynamics cannot accurately describe the adsorption processes taking place in a mixture. For example, the effect of air bubbles on adsorption in Figure 9.12 shows that the chemical adsorption of DTAC on the LS20 coal surface cannot be improved by redistributing the surfactant at the different interfaces using air bubbles-the high affinity of the coal surface towards the amine basically defines the preferred adsorption interface. However, the physical adsorption of DTAC at the silica surface can be influenced by the presence of air bubbles whose surfaces also physically interact with the amine and an equilibrium between these two processes can actually be established.

13.1.2 Effect of polyacrylamide on reverse coal flotation

As the results indicate, the amine consumption was greatly reduced with the addition of A100 polyacrylamide. The effect of the A100 on the froth product yield became even more significant with the application of the zero conditioning time method (Figures 7.1 and 7.5, curves 2 and 4). The yield increased with increasing A100 dosage up to 400-500 g/t of A100 at which a maximum yield of the froth product of around 50 % was obtained (compared to only 3 % without the addition of A100, at a DTAC consumption of 1.375 kg/t, Figure 7.13). High molecular weight polyacrylamides are also used in processing potash ores in which a selective flocculation-flotation method is employed to remove the slimes as discussed in Chapter 1 (Chan et al., 1982). The addition of PAM was observed to promote sylvite (KCl) flotation. Arsentiev et al.(1988) also showed that the amine (ODA) consumption decreased considerably with the addition of PAM in potash ore flotation. The reverse flotation results discussed in this thesis indicate that the addition of

A100 polyacrylamide significantly improves gangue flotation (Chapter 7), but selective flocculation was not observed with this polymer in the standard flocculation tests (Chapter 10). As Chapter 8 indicates, not all PAMs could be used to promote gangue flotation and only those with a 7 % degree of anionicity or lower worked well. The flocculation tests (Chapter 10) also showed that different polyacrylamides respond quite differently to hydrodynamic conditions in the flocculation tests. Thus the effect of PAM and hydrodynamic conditions on reverse coal flotation merits further discussion.

It is generally accepted that all high molecular weight polyacylamides are effective flocculants in destabilizing pre-coagulated system (Hogg, 1999). Those with a degree of anionicity in the range from 10 % to 30 % are claimed to be the most efficient in thickening tailings (Xu and Cymerman, 1999). This is confirmed in this thesis by the flocculation of LS20 coal (Figures 10.1-10.6). As can been seen from the results, the flocculation ability increased with increasing degree of anionicity, but in general, these polymers are all very efficient flocculants and total flocculation of the material occurs at low dosages in standard flocculation tests. The addition of such flocculants to flotation systems should be detrimental.

The flotation results indicated that very good selectivity is obtained in the reverse flotation of coal with the addition of A100 (Figures 7.10 and 7.14). The concentrate ash content was as low as 16 % (with 10 % inherent ash). Thus, the hydrodynamic conditions created in the flotation cell must be responsible for selective flotation and convert the totally flocculated material into selectively segregated one. If this is true, then the flotation and selectivity of the totally flocculated material should depend on the intensity of conditioning. Without proper conditioning, selective separation is impossible. With sufficiently intense conditioning, the selectivity should improve. Therefore, the use of column flotation should require intense mixing in the conditioning tank prior to feeding the material into the column. This assumption is experimentally confirmed by the column flotation results shown in Tables 11.1 and 11.2. The ash contents of the concentrate and reject are practically the same (around 33 %) under low intensity conditioning (400 r.p.m.), but the selectivity improves significantly at high intensity conditioning (1500 r.p.m.) with a concentrate and reject ash of around 17 % and 53 %, respectively.

Therefore, the mode of action of A100 polyacrylamide in the reverse coal flotation can be interpreted as follows: the hydrodynamic conditions created in a flotation cell lead to rearrangement of the totally flocculated material into selectively flocculated smaller flocs which reformed and consolidated during conditioning. Those smaller flocs consisted of selectively flocculated coal and gangue particles. Thus, the surface area of the material is significantly reduced and this saves the amine consumption and promotes gangue flotation.

The proposed mechanism of A100 action in reverse coal flotation is also supported by the flocculation tests carried out immediately after the conditioning of a coal suspension with A100 in a flotation cell at 1500 rpm for 5 minutes (Figure 10.16). The flocculation ability of A100 decreased significantly due to the intense conditioning, but increasing A100 dosage could still improve the flocculation of slimes and led to a gradual decrease in turbidity. This flocculation behavior corresponds to a gradual increase in the yield of the froth product in flotation (Figure 7.13, curve 1), indicating that the flocculation of dispersed fines improved gangue flotation and greatly decreased the amine consumption. These results demonstrate that the high amine consumption is due to the dispersed fines, flocculation of which eliminates the effect of fines on flotation and sharply decreases the amine consumption. This also implies that the flocculated material consisted of separate flocs of coal and gangue.

This finding opens a new area for selective flocculation-flotation research since traditionally it is thought that selective flocculation can only be achieved through selective adsorption of a flocculant onto targeted minerals while the effect of hydrodynamics of the system on selective flocculation-flotation is entirely neglected. But, the flocculation and adsorption of the polymer are coupled processes, they take place simultaneously and the final outcome depends on both.

It is generally accepted that the application of excessive shear to long chain high molecular weight polymers during the preparation of flocculant solutions can lead to chain rupture, substantially reducing the capacity for bridging particles. There were also many investigations reported on the hydrodynamics of the floc breakage (Abdel-Alim and Hamielec, 1973; Nagashiro and Tsunoda, 1977; Nakano and Minoura, 1978; Ray and Hogg, 1987; Henderson and Wheatley, 1987; Scott et al., 1996). Those studies focused

more on hydrodynamic conditions rather than flocculant type. As Hogg (1999) pointed out, floc breakage depends on a number of factors and is quite complicated. The general relationships between floc breakage and floc size, agitation intensity, polymer type and content, etc., have yet to be developed. The flocculation tests (Chapter 10) indicate that different flocculants respond differently to the hydrodynamic conditions and this can explain why not all effective flocculants could promote gangue flotation in the reverse coal flotation process.

Of the tested polyacrylamides, only nonionic and slightly hydrolyzed anionic polyacrylamides such as N100, N300 and A100 worked well in the reverse flotation process. The most effective flocculants, A130 and A150, did not provide satisfactory flotation results. These polyacrylamides differed only in their degree of anionicity. It should be noted that the standard flocculation tests were carried out with polymer solutions added into a gently agitated suspension. Flotation tests, especially in mechanical flotation cells, are carried out under intense conditioning environment. This seems to indicate that polyacrylamides, depending on their composition, respond differently to the intensity of conditioning. This was confirmed by the settling tests in which coal-polymer suspensions were first conditioned for 5 minutes at 1500 rpm in a flotation cell and then were transferred to the cylinder to conduct settling tests as shown in Figures 10.14-10.18.

For A100 polyacrylamide, the intense conditioning resulted in a significant decrease in the settling rate, but complete flocculation still occurred when its dosage reached 400 g/t (maximum froth product yield was obtained in the flotation tests at this dosage of A100).

For A130 polyacrylamide, after intense conditioning, complete flocculation was not observed and with increasing dosage of A130, more fines were left dispersed. (Figure 10.16). The reverse flotation tests showed that this polymer does not promote gangue flotation.

These results again imply that the high amine consumption in coal reverse flotation is caused by a high surface area of fine particles. Flocculation of these fine fractions significantly reduced their surface area and in turn reduced amine consumption. Of course, this is only possible if flocculation is selective and the results demonstrate that selective

flotation was achieved by subjecting the flocculated system to intense conditioning that leads to the formation of separately flocculated smaller flocs of coal and gangue.

It can be speculated that since A130 is a more effective flocculant than A100, a different formation/breakage mechanism is followed when A130 is added and subjected to intense conditioning of the suspensions in a cell. The large flocs obtained with A130 broke into well dispersed fines. In the case of A100, intense conditioning leads to the release of the non-selectively flocculated material into smaller but selective flocs. The different responses (of the flocs obtained using A100 and A130) to intense conditioning apparently resulted from differences in the structure of the flocs, but this aspect was not further studied in this thesis.

13.1.3 Effect of pH on reverse coal flotation

As can be seen from Figure 7.15, a change in pH from 8.3 to 8.8 resulted in a sharp decrease in the yield of the froth product upon the addition of A100 (DTAC dosage is 1.375 kg/t). The yield dropped from 47.9 % to 8 %. More alkaline pH values resulted in even further decrease in the yield. This result has to be explained in terms of the effect of pH on the flocculation behavior of coal with A100. As already discussed, the high consumption of DTAC in the reverse flotation of coal is caused by a large surface area of the fines. The flocculation of fines with the addition of A100 greatly reduces the amine consumption. However, the flocculation of the LS20 coal strongly depends on pH (Figure 10.19). An increase in pH from 8.6 to 9.2 resulted in a sharp increase in the yield of dispersed fines from 3.7 % to 46.4 %, and the fines obviously abstracted a large amount of amine. As a result, the yield of the froth product also decreased significantly when only 1.375 kg/t DTAC was used.

As Figures 10.8 and 10.9 indicate, total flocculation occurred in a neutral to slightly alkaline pH range. As the pH increased, the quality of the supernatant was very poor. It became even worse after conditioning the PAM-coal suspension in a flotation cell at 1500 rpm (Figures 10.19 and 10.20).

Pradip and Fuerstenau (1986) suggested that at alkaline pH values the coal surface becomes more negative, the hydrophobic attraction of PAM macromolecule to the coal

surface is more than compensated by the electrostatic repulsion between the similarly charged functional groups of the hydrolyzed PAM and the coal surface. Therefore, flocculation and adsorption decrease with increasing pH. This is confirmed in this thesis. However, a decrease in flocculation and adsorption of hydrolyzed anionic polyacrylamides in the alkaline pH range may also result from the hydrolysis of the polyacrylamides. In the alkaline environment, more $-CONH_2$ groups are replaced by $-COOH$ groups because of the hydrolysis of polyacrylamides. The number of linkages between the polymer segments and particles thus significantly decreases, and the repulsive forces between the negatively charged particle surfaces and $-COOH$ groups increase. Therefore, flocculation and adsorption decrease. Kuzkin et al. (1964) reported a significant increase of the $-COOH$ group content for non ionic polyacrylamides in an alkaline solution.

13.1.4 Effect of dextrin on reverse coal flotation

The addition of dextrin improves the clean coal quality (Figures 7.2, 7.4, 7.6, 7.8, 7.10). The flotation tests revealed that dextrin is necessary in the reverse coal flotation process. About 85 % of the feed is floated at a DTAC dosage of 1.375 kg/t without the addition of dextrin (500 g/t of A100). The yield decreased to about 45 % with the addition of dextrin (Figure 7.5). This is consistent with the observation made by Pawlik and Laskowski (2003 a, b) who demonstrated that amine alone could not depress coal. Dextrin apparently acts as a depressant. The reject ash increased significantly with the addition of dextrin (Figures 7.2 and 7.6). The addition of tannic acid also improved the clean coal quality by a few percent (Figures 7.9, 7.10, 7.12).

13.1.5 Effect of reverse flotation on the rheology of coal water slurries and column carrying capacity

In conventional forward flotation, the coal surface is made hydrophobic and these hydrophobic particles tend to spontaneously aggregate. The aggregated coal particles in suspension develop a high yield stress and increased viscosity (Pawlik et al., 2004). Viscosity reducing additives are required in such cases (Laskowski, 1999).

It was expected that the coal-water slurries prepared from the reverse flotation concentrate should have a lower viscosity and yield stress than those produced from the forward flotation concentrate since the hydrophilic product (the clean coal) is utilized in such a case. This assumption was experimentally confirmed by the rheological measurements of the two types of coal-water slurries (Figures 12.1-12.9). As seen from Figure 12.7, if the two slurries obtained using either the forward or reverse coal flotation products are compared, then it is seen that at an apparent viscosity of 1000 mPa·sec the achievable solids content is around 54.5% for the forward flotation product, while in the case of the reverse flotation product the solids content can be as high as 57.5% at the same viscosity. Addition of a dispersant (PSS10) to the reverse flotation concentrate did not change its apparent viscosity much, indicating that the coal surface was already hydrophilic. However, the addition of PSS10 to the forward flotation concentrate system significantly reduced its apparent viscosity (Figures 12.8 and 12.9).

These results prove that viscosity reducing agents are necessary for the preparation of coal-water-slurries from the forward flotation products, but are not needed for coal-water-slurries prepared from the reverse flotation products. The reverse flotation also results in an increased column carrying capacity (Figure 11.1) and may lead to the broader application of flotation columns in the coal industry.

13. 2   Conclusions

Several conclusions are evident from the data:

1. Due to a high adsorption density of amine on fine particles, a very high dosage of amine is needed in the reverse flotation of coal. The application of the zero conditioning time method along with the use of A100 polyacrylamide significantly reduces the amine consumption from over 6 kg/t down to 1.375 kg/t in this process.

2. Although high-molecular weight polyacrylamides with up to 50 % degree of anionicity are effective flocculants of fine coal as revealed by standard flocculation tests, these flocculants respond quite differently to intense mixing conditions. While conditioning with polyacrylamides of a lower degree of anionicity initially results in total flocculation of the coal and gangue particles, it may eventually lead

to rearrangement of the large flocs into selectively flocculated, separate, smaller flocs of coal and gangue particles. The flocculation of fines reduces their surface area and this in turn reduces the consumption of amine used in the coal reverse flotation.

3. The column flotation tests clearly indicate that with the use of a polyacrylamide blinder the separation depends on the conditioning time/intensity, and the clean coal quality improves significantly with increasing conditioning intensity. However, intense conditioning with polyacrylamides of a higher degree of anionicity causes redispersion of the totally flocculated material, and this does not promote the gangue flotation.

4. It was found that the development of a bimodal size distribution consisting of some flocs and well dispersed primary fines depends on both polymer type (degree of anionicity) and hydrodynamic conditions.

5. pH has a strong effect on the reverse flotation of coal. The best flotation is obtained over a pH range from about 7.5 to 8.4 and gangue flotation is significantly depressed when pH is over 8.8. A high pH values generates more dispersed fines and leads to increased amine consumption.

6. Dextrin is necessary to depress coal in the reverse flotation process and the addition of tannic acid improves further the clean coal quality by a few percent.

7. Coal-water slurries prepared from the products of the reverse flotation have a lower apparent viscosity than those prepared from the forward flotation concentrate, and do not seem to require the use of viscosity modifiers.

8. The column carrying capacity significantly increases with the application of the reverse flotation process because of the reduced amount of the froth product.

13. 3   Future work

The direct flotation tests with/without PAM and with/without the zero conditioning demonstrate the role of PAM and the role of conditioning under which PAM is applied in reverse flotation. A series of new tests is needed to follow better, on the molecular level, the changes that lead to the phenomena observed in the flotation tests.

While adsorption and flocculation are two coupled sub-processes it is the adsorption that has attracted a lot of attention in past projects on selective flocculation. This thesis revealed the importance of conditioning and demonstrated that in some cases flocculation may become selective under properly selected hydrodynamic conditions. This opens up a new area for research. The same applies to the zero conditioning time concept, which when adopted in other flotation applications may lead to quite a significant process improvement.

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Appendix

APPENDIX A   Calibration curves for amines

Figure A.1   Calibration curve for Dodecyl-Trimethyl Ammonium Chloride (DTAC).
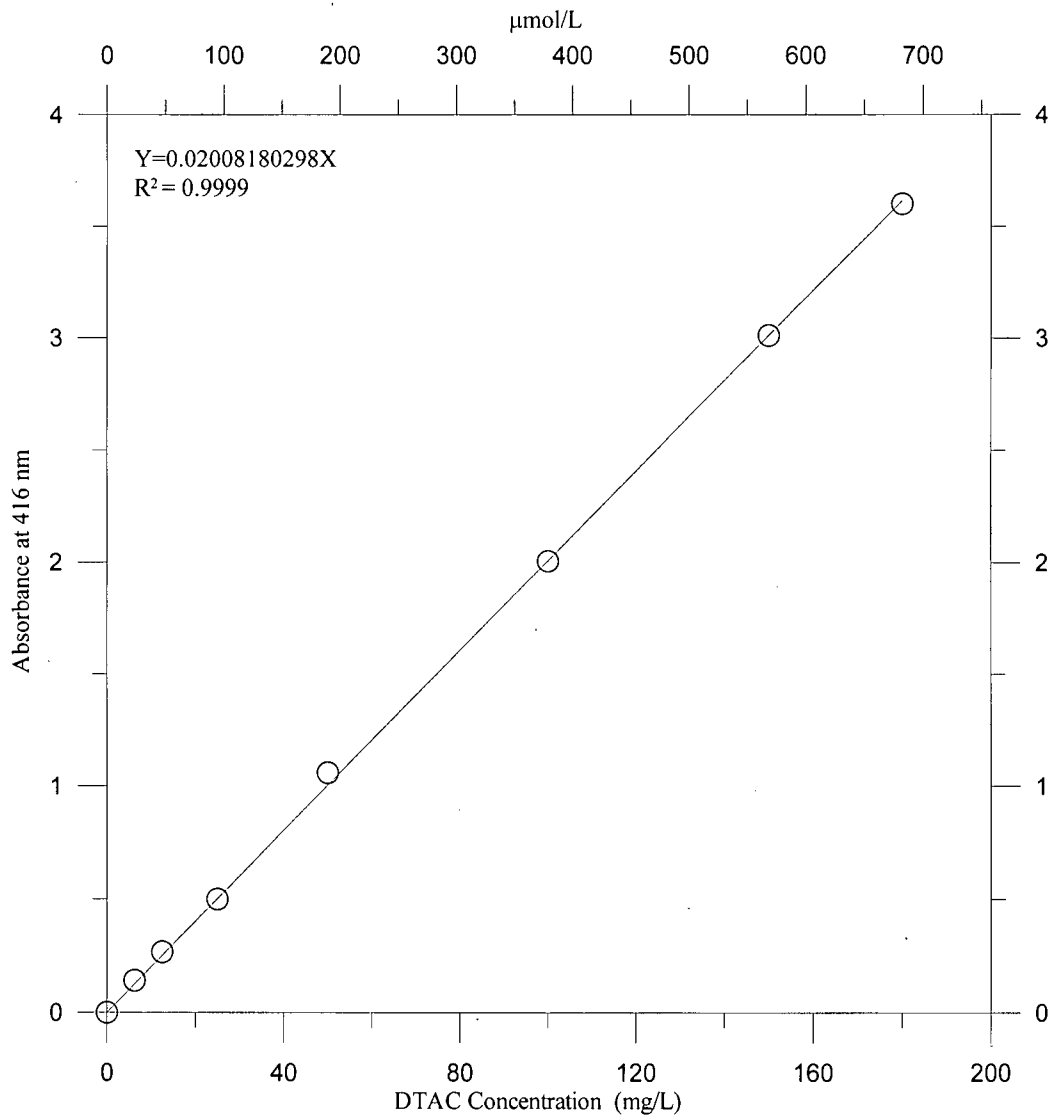
Conditions:
20 mL of 0.01 mol/L HCl
1 mL of 0.05 mol/L HCl
5 mL of 1.5 g/L BPB (Na salt)
4 mL DTAC in distilled water
20 mL Chloroform
or 30 mL of the aqueous phase + 20 mL of the organic phase

Figure A.2   Calibration curve for Dodecyl-Trimethyl Ammonium Bromide (DTAB).
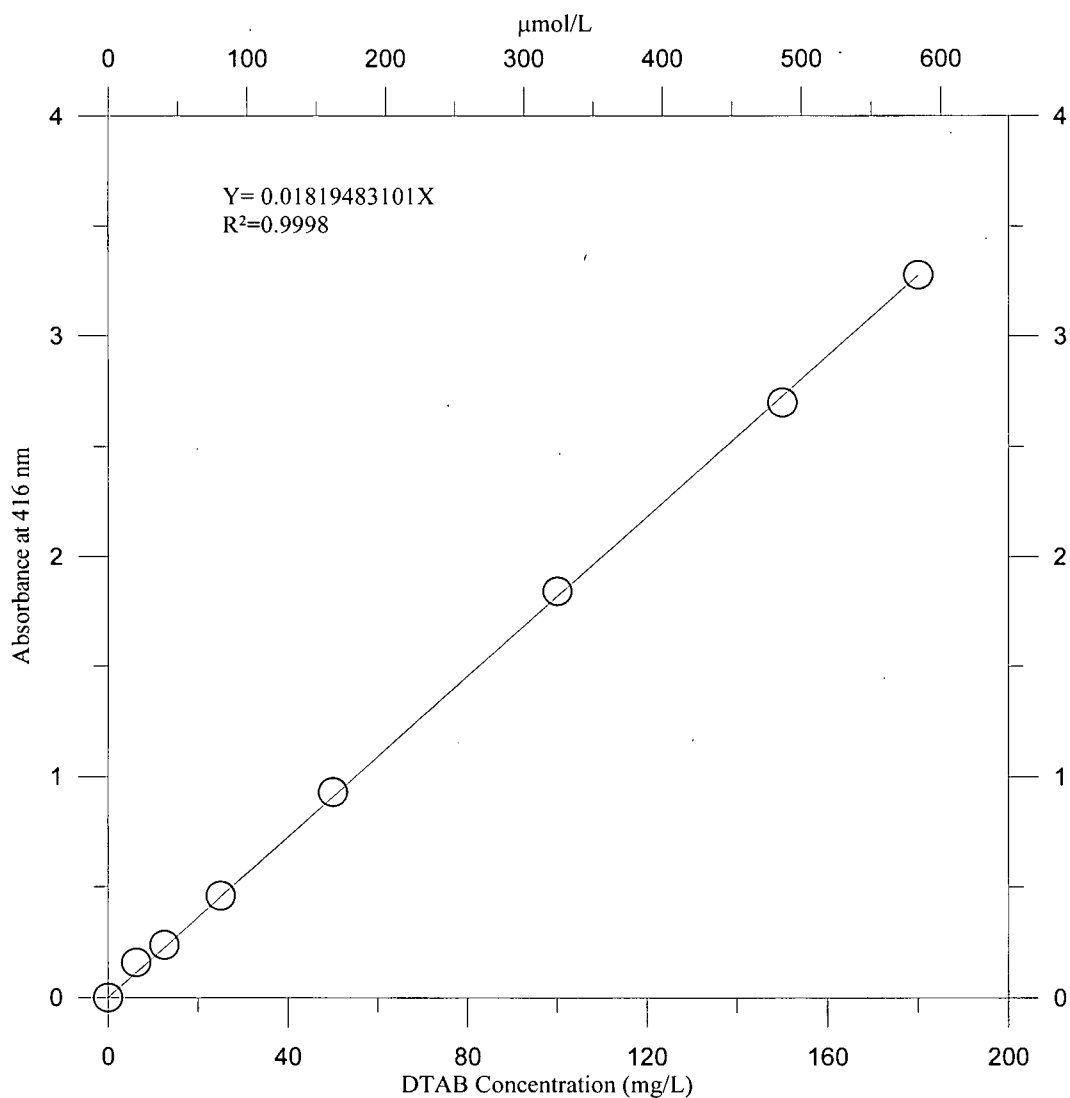
Conditions:
20 mL of 0.01 mol/L HCl
1 mL of 0.05 mol/L HCl
5 mL of 1.5 g/L BPB (Na salt)
4 mL DTAB in distilled water
20 mL Chloroform
or 30 mL of the aqueous phase + 20 mL of the organic phase

APPENDIX B   BET surface area measurement data

Figure B.1   Adsorption isotherms for LS20 raw coal (-0.216 mm).

Date: 05/11/2006

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows®

Sample ID	KDLS20-R				
Description	Raw LS20 Coal				
Comments	-0.216 mm				
Sample Weight	0.3750 g				
Adsorbate	NITROGEN	Outgas Temp	23.0 °C	Operator	SF
Cross-Sec Area	16.2 Å²/molecule	Outgas Time	44.0 hrs	Analysis Time	1044.1 min
NonIdeality	6.580E-05	P/Po Toler	0	End of Run	03/31/2006 01:32
Molecular Wt	28.0134 g/mol	Equil Time	3	File Name	KDLS20-R.RAW
Station #	1	Bath Temp.	77.35	PC SW Version	1.27

Final data -- temperature compensated.

A   ——●—— BF   ————

BET Plot

Relative Pressure, P/Po   Area 6.75
                                                    (m²/g)

200

Figure B.2   Adsorption isotherms for LS20 clean coal (-0.150 mm).

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows®

Sample ID	KDLS20-C					
Description	LS20 Shaking table concentrate					
Comments	-150 micros					
Sample Weight	0.2758 g					
Adsorbate	NITROGEN	Outgas Temp	23.0 °C	Operator	SF	
Cross-Sec Area	16.2 Å²/molecule	Outgas Time	96.0 hrs	Analysis Time	572.5 min	
NonIdeality	6.580E-05	P/Po Toler	0	End of Run	04/03/2006 17:09	
Molecular Wt	28.0134 g/mol	Equil Time	3	File Name	KDLS20-C.RAW	
Station #	1	Bath Temp.	77.35	PC SW Version	1.27	

Final data -- temperature compensated.

BET Plot

A   —●—   BF   ——

$1/[W((Po/P)-1)]$

Relative Pressure, P/Po

Area 0.96
(m²/g)

Figure B.3   Adsorption isotherms for fine calcite (-74 μm).

Sample ID	KD-calcite					
Description	Fine calcite					
Comments	-74 micros					
Sample Weight	3.4978 g					
Adsorbate	NITROGEN	Outgas Temp	85.0 °C	Operator	KD/SF	
Cross-Sec Area	16.2 Å²/molecule	Outgas Time	2.0 hrs	Analysis Time	88.5 min	
NonIdeality	6.580E-05	P/Po Toler	0	End of Run	07/23/2004 13:47	
Molecular Wt	28.0134 g/mol	Equil Time	3	File Name	KD-CAL1.RAW	
Station #	1	Bath Temp.	77.35	PC SW Version	1.27	

Final data -- temperature compensated.

A   —●— BF   ——

BET Plot

Relative Pressure, P/Po

Area 1.07
(m²/g)

202

Figure B.4 Adsorption isotherms for fine dolomite (-74 μm).

Date: 05/11/2006

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows®

Sample ID	KD-Dolomite				
Description	Fine dolomite				
Comments	-74 micros				
Sample Weight	3.5166 g				
Adsorbate	NITROGEN	Outgas Temp	85.0 °C	Operator	KD/SF
Cross-Sec Area	16.2 Å²/molecule	Outgas Time	2.0 hrs	Analysis Time	61.1 min
NonIdeality	6.580E-05	P/Po Toler	0	End of Run	07/20/2004 11:13
Molecular Wt	28.0134 g/mol	Equil Time	3	File Name	KD-DOL1.RAW
Station #	1	Bath Temp.	77.35	PC SW Version	1.27

Final data -- temperature compensated.

A ——●—— BF ————

BET Plot

Relative Pressure, P/Po   Area 1.52
                                            (m²/g)

203

Figure B.5   Adsorption isotherms for fine silica (-74 μm).

Date: 05/11/2006

Quantachrome Corporation
Quantachrome Autosorb Automated Gas Sorption System Report
Autosorb for Windows®

Sample ID	KD-Silica				
Description	Fine silica				
Comments	-74 micros				
Sample Weight	3.1846 g				
Adsorbate	NITROGEN	Outgas Temp	85.0 °C	Operator	SF
Cross-Sec Area	16.2 Å²/molecule	Outgas Time	2.0 hrs	Analysis Time	96.8 min
NonIdeality	6.580E-05	P/Po Toler	0	End of Run	07/23/2004 10:19
Molecular Wt	28.0134 g/mol	Equil Time	3	File Name	KD-SIL1.RAW
Station #	1	Bath Temp.	77.35	PC SW Version	1.27

Final data -- temperature compensated.

A   ●— BF   ——

BET Plot

$1/[W((Po/P)-1)]$

Relative Pressure, P/Po

Area 1.34
(m²/g)

204

APPENDIX C   Infra-red spectra of polyacrylamides

Figure C.1   Infra-red spectrum of an anionic polyacrylamide. Molecular weight 200,000
Daltons; degree of anionicity 10 %.

205
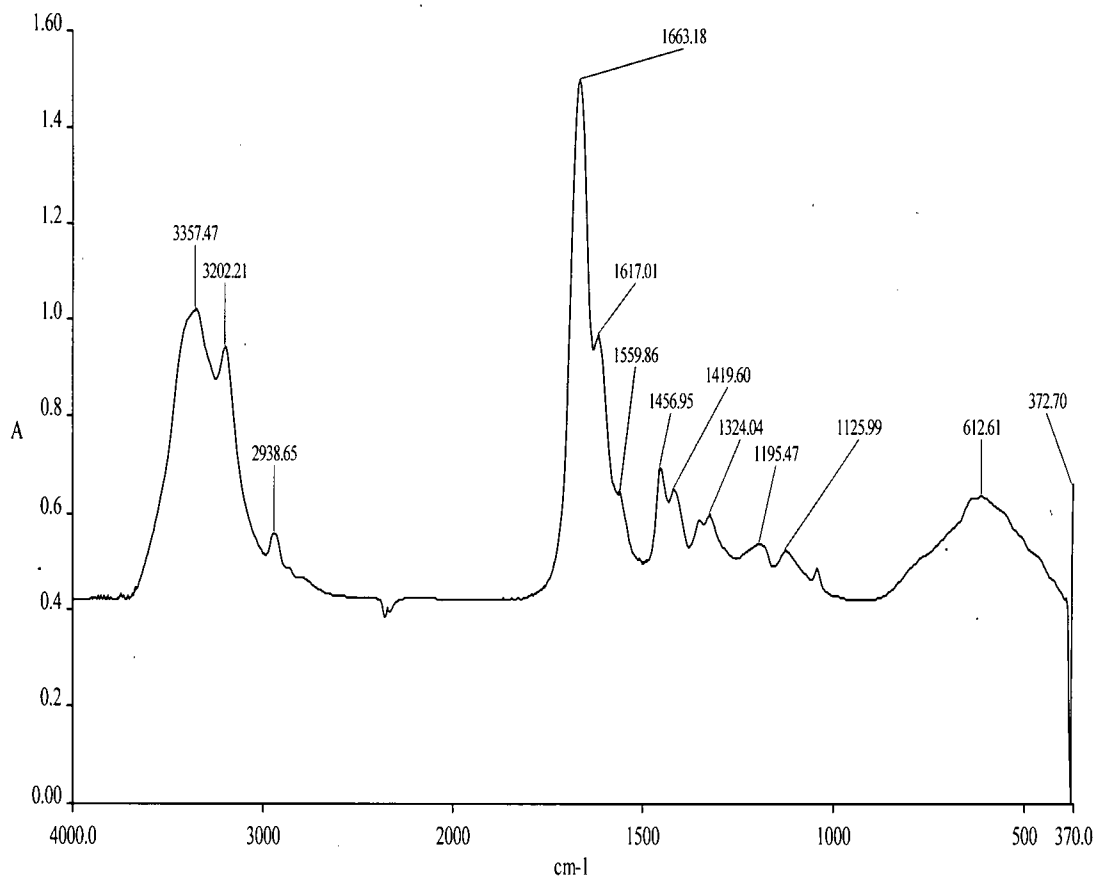
Figure C.2   Infra-red spectrum of an anionic polyacrylamide. Molecular weight 200,000 Daltons; degree of anionicity 70 %.
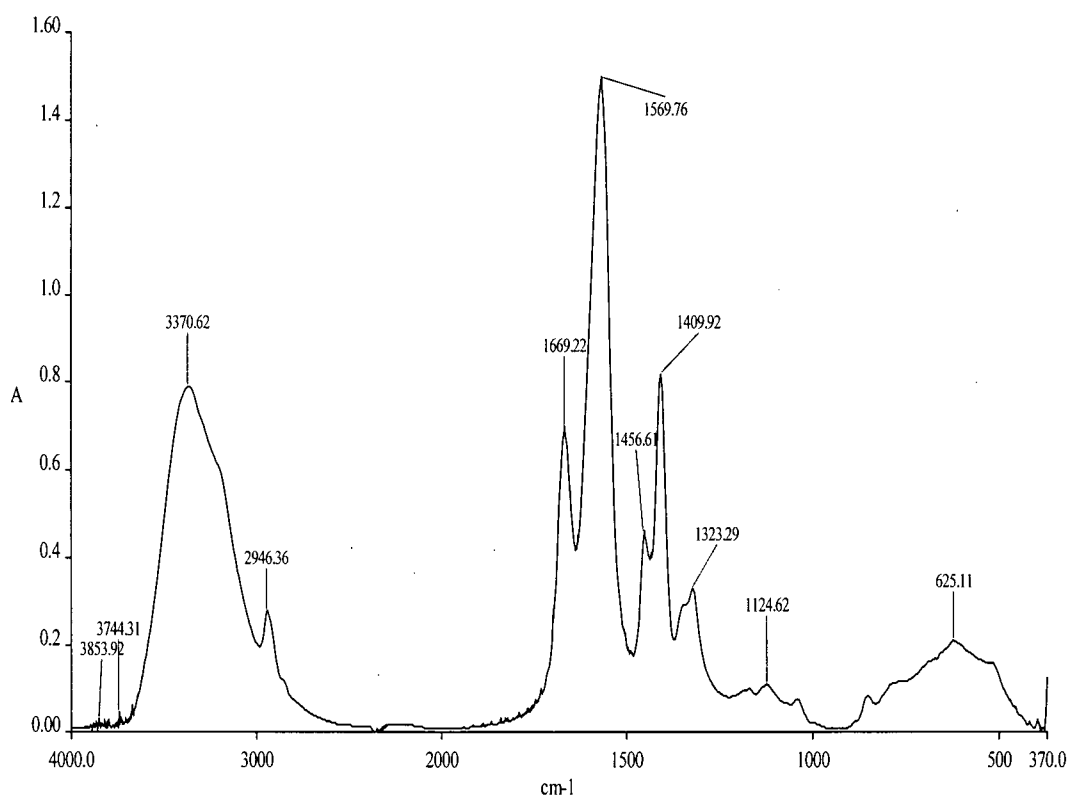
Figure C.3   Infra-red spectrum of an anionic polyacrylamide. Molecular weight >10,000,000 Daltons; degree of anionicity 40 %.
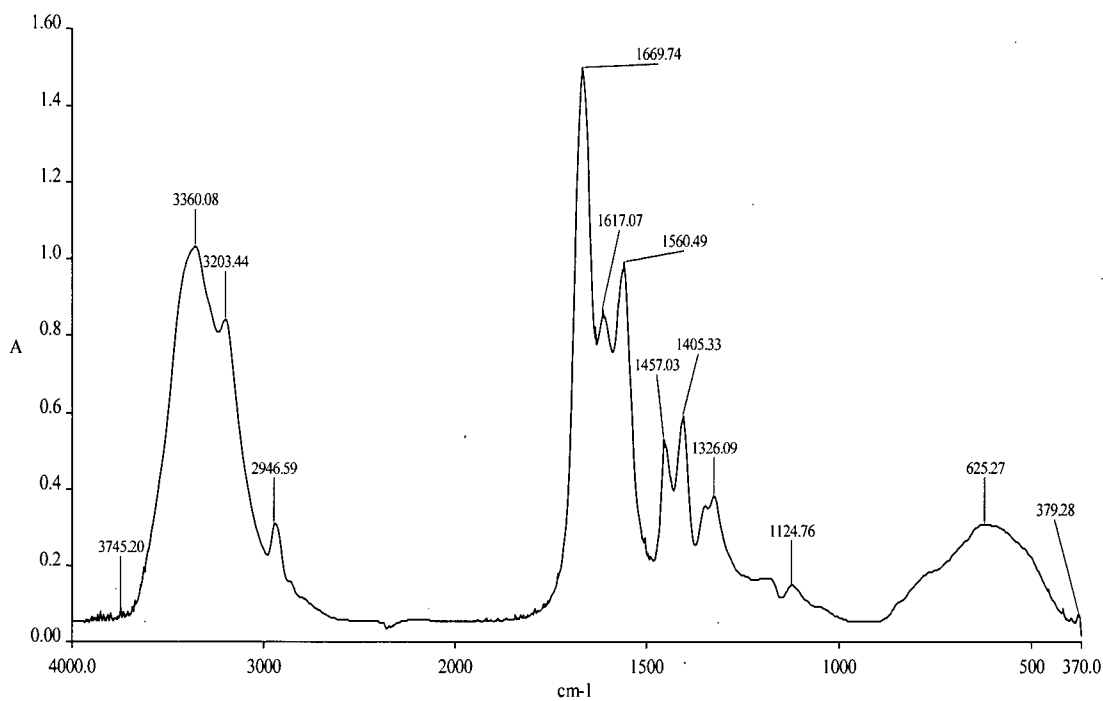
Figure C.4   Infra-red spectrum of N100 polyacrylamide. Molecular weight 15,000,000
Daltons; degree of anionicity < 2 %.
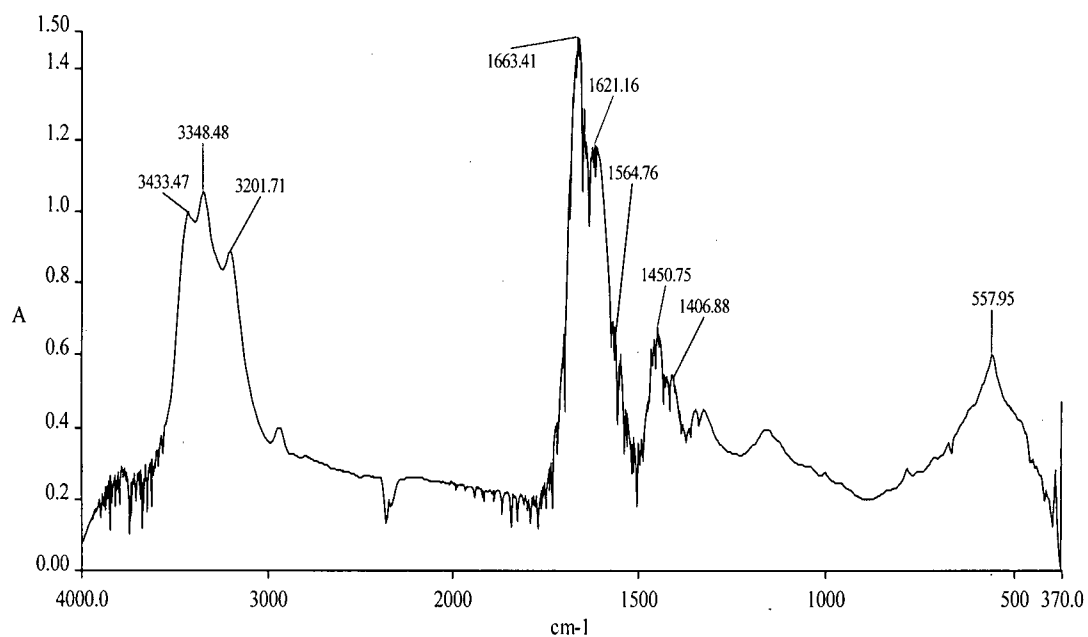
Figure C.5   Infra-red spectrum of a non-anionic polyacrylamide after hydrolysis.
Molecular weight 5,000,000-6,000,000 Daltons; 0.5 % PAM 25 mL +1 % NaOH 25mL,
0.5 hour at 25 °C.
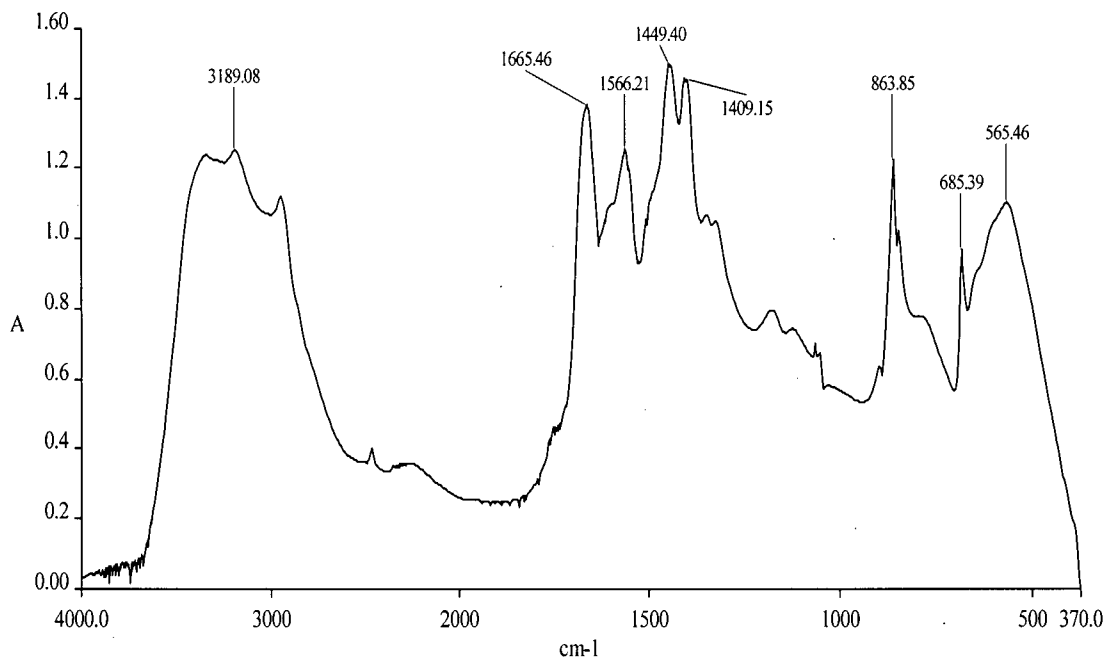
Figure C.6   Infra-red spectrum of a non-anionic polyacrylamide after hydrolysis.
Molecular weight 5,000,000-6,000,000 Daltons; 0.5 % PAM 25 mL +1 % NaOH 25mL,
0.5 hour at 100°C.
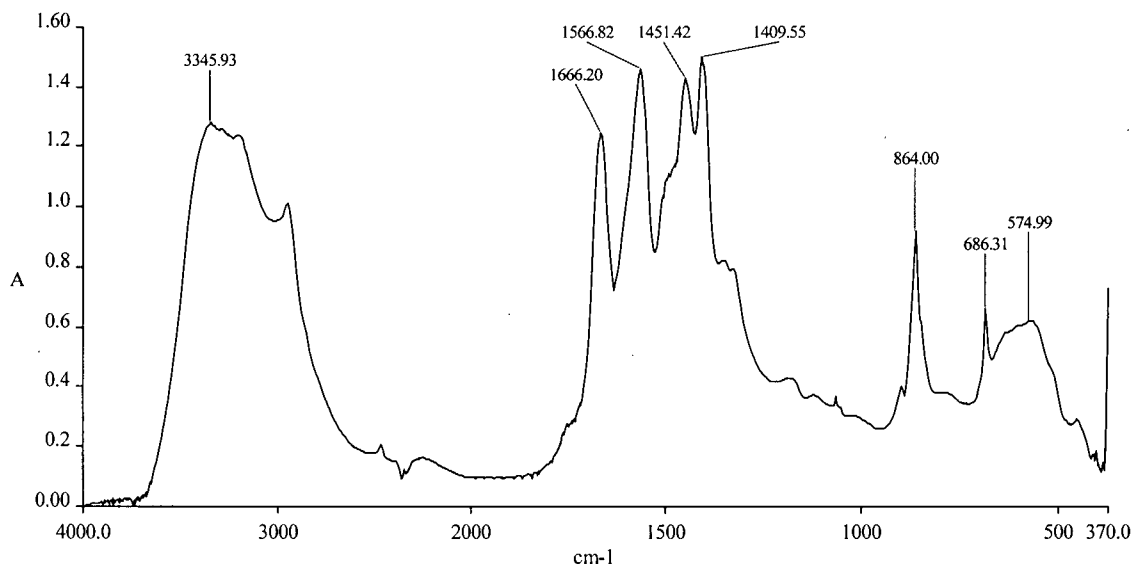
Figure C.7   Infra-red spectrum of a non-anionic polyacrylamide after hydrolysis.
Molecular weight 5,000,000-6,000,000 Daltons; 0.5 % PAM 25 mL +1 % NaOH 25mL, 1
hour at 100°C.
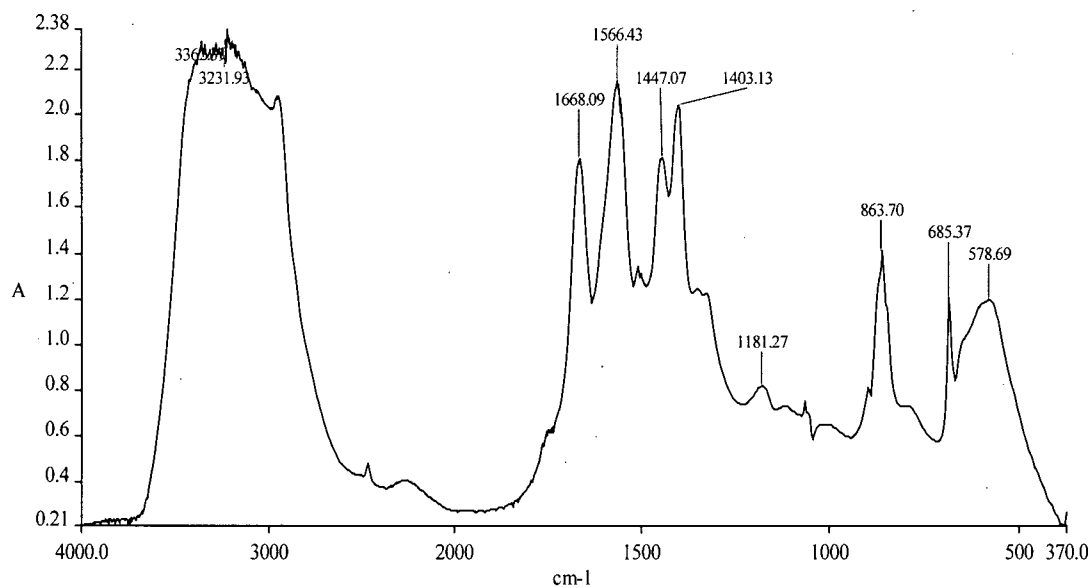
APPENDIX D   **Size analysis**

Figure D.1   Size analysis for fine calcite (-74 μm)

MASTERSIZER 2000

Result Analysis Report

Sample Name: calcite - Average	**SOP Name:**	**Measured:** Wednesday, June 30, 2004 3:58:01 PM
Sample Source & type: Supplier	**Measured by:** contract	**Analysed:** Wednesday, June 30, 2004 3:58:02 PM

Particle Name: CaCO3 (calcite)	**Accessory Name:** Hydro 2000S (A)	**Analysis model:** General purpose	**Sensitivity:** Enhanced
Particle RI: 1.572	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 13.26 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 0.943 %	**Result Emulation:** Off

Concentration: 0.0104 %Vol	**Span :** 3.603	**Uniformity:** 1.15	**Result units:** Volume
Specific Surface Area: 1.18 m²/g	**Surface Weighted Mean D[3,2]:** 5.065 um	**Vol. Weighted Mean D[4,3]:** 22.480 um	
d(0.1): 2.137 um	d(0.5): 14.255 um		d(0.9): 53.491 um

Particle Size Distribution

calcite - Average, Wednesday, June 30, 2004 3:58:01 PM

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.020	0.00	0.126	0.00	0.792	3.26	4.983	22.67	31.357	76.10	197.312	99.98
0.022	0.00	0.140	0.00	0.882	3.90	5.553	24.88	34.940	79.36	219.859	100.00
0.025	0.00	0.156	0.00	0.983	4.54	6.187	27.21	38.932	82.42	244.982	100.00
0.028	0.00	0.174	0.00	1.096	5.17	6.894	29.68	43.381	85.26	272.975	100.00
0.031	0.00	0.194	0.00	1.221	5.81	7.682	32.28	48.338	87.83	304.168	100.00
0.034	0.00	0.216	0.00	1.360	6.47	8.560	35.03	53.861	90.14	338.925	100.00
0.038	0.00	0.241	0.00	1.516	7.17	9.538	37.94	60.016	92.17	377.653	100.00
0.043	0.00	0.268	0.00	1.689	7.95	10.628	40.99	66.874	93.91	420.806	100.00
0.048	0.00	0.299	0.00	1.882	8.83	11.842	44.20	74.516	95.38	468.891	100.00
0.053	0.00	0.333	0.00	2.097	9.81	13.195	47.54	83.030	96.59	522.471	100.00
0.059	0.00	0.371	0.02	2.337	10.93	14.703	51.00	92.518	97.56	582.172	100.00
0.066	0.00	0.414	0.21	2.604	12.19	16.383	54.56	103.090	98.32	648.696	100.00
0.073	0.00	0.461	0.52	2.901	13.59	18.255	58.18	114.870	98.89	722.821	100.00
0.082	0.00	0.514	0.94	3.233	15.13	20.341	61.84	127.996	99.30	805.417	100.00
0.091	0.00	0.572	1.44	3.602	16.82	22.665	65.50	142.622	99.59	897.450	100.00
0.101	0.00	0.638	2.01	4.014	18.64	25.255	69.13	158.919	99.78	1000.000	100.00
0.113	0.00	0.711	2.63	4.472	20.59	28.141	72.67	177.078	99.90		

Figure D.2   Size analysis for fine dolomite (-74 μm)

MASTERSIZER 2000

Result Analysis Report

Sample Name: dolomite - Average	**SOP Name:**	**Measured:** Wednesday, June 30, 2004 4:14:41 PM
Sample Source & type: Supplier	**Measured by:** contract	**Analysed:** Wednesday, June 30, 2004 4:14:42 PM

Particle Name: Dolomite (ave)	**Accessory Name:** Hydro 2000S (A)	**Analysis model:** General purpose	**Sensitivity:** Enhanced
Particle RI: 1.592	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 12.42 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 1.091 %	**Result Emulation:** Off

Concentration: 0.0065 %Vol	**Span :** 4.649	**Uniformity:** 1.49	**Result units:** Volume
Specific Surface Area: 1.68 m²/g	**Surface Weighted Mean D[3,2]:** 3.579 um	**Vol. Weighted Mean D[4,3]:** 16.859 um	

d(0.1):   1.302   um   d(0.5):   8.871   um   d(0.9):   42.545   um

Particle Size Distribution

dolomite - Average, Wednesday, June 30, 2004 4:14:41 PM

Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %
0.020	0.00	0.126	0.00	0.792	4.54	4.983	35.49	31.357	84.22	197.312	100.00
0.022	0.00	0.140	0.00	0.882	5.62	5.553	38.10	34.940	86.45	219.859	100.00
0.025	0.00	0.156	0.00	0.983	6.76	6.187	40.74	38.932	88.48	244.982	100.00
0.028	0.00	0.174	0.00	1.096	7.96	6.894	43.44	43.381	90.32	272.975	100.00
0.031	0.00	0.194	0.00	1.221	9.21	7.682	46.20	48.338	91.96	304.168	100.00
0.034	0.00	0.216	0.00	1.360	10.55	8.560	49.04	53.861	93.43	338.925	100.00
0.038	0.00	0.241	0.00	1.516	11.98	9.538	51.97	60.016	94.73	377.653	100.00
0.043	0.00	0.268	0.00	1.689	13.52	10.628	54.98	66.874	95.85	420.806	100.00
0.048	0.00	0.299	0.00	1.882	15.19	11.842	58.06	74.516	96.83	468.891	100.00
0.053	0.00	0.333	0.00	2.097	17.00	13.195	61.19	83.030	97.65	522.471	100.00
0.059	0.00	0.371	0.02	2.337	18.95	14.703	64.34	92.518	98.32	582.172	100.00
0.066	0.00	0.414	0.23	2.604	21.03	16.383	67.48	103.090	98.86	648.696	100.00
0.073	0.00	0.461	0.59	2.901	23.24	18.255	70.56	114.870	99.27	722.821	100.00
0.082	0.00	0.514	1.12	3.233	25.54	20.341	73.57	127.996	99.57	805.417	100.00
0.091	0.00	0.572	1.80	3.602	27.94	22.665	76.46	142.622	99.78	897.450	100.00
0.101	0.00	0.638	2.61	4.014	30.41	25.255	79.21	158.919	99.90	1000.000	100.00
0.113	0.00	0.711	3.53	4.472	32.93	28.141	81.81	177.078	99.98		

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Figure D.3   Size analysis for fine silica (-74 μm)

MASTERSIZER 2000

Result Analysis Report

Sample Name: silica - Average	SOP Name:	Measured: Wednesday, June 30, 2004 4:44:22 PM	
Sample Source & type: Supplier	Measured by: contract	Analysed: Wednesday, June 30, 2004 4:44:23 PM	

Particle Name: silicasand	Accessory Name: Hydro 2000S (A)	Analysis model: General purpose	Sensitivity: Enhanced
Particle RI: 1.500	Absorption: 0.1	Size range: 0.020 to 2000.000 um	Obscuration: 14.52 %
Dispersant Name: Water	Dispersant RI: 1.330	Weighted Residual: 1.578 %	Result Emulation: Off

Concentration: 0.0095 %Vol	Span : 3.435	Uniformity: 1.17	Result units: Volume
Specific Surface Area: 1.59 m²/g	Surface Weighted Mean D[3,2]: 3.775 um	Vol. Weighted Mean D[4,3]: 16.061 um	

d(0.1): 1.314 um   d(0.5): 10.154 um   d(0.9): 36.189 um

Particle Size Distribution

silica - Average, Wednesday, June 30, 2004 4:44:22 PM

Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %
0.020	0.00	0.126	0.00	0.792	4.31	4.983	31.67	31.357	86.92	197.312	99.94
0.022	0.00	0.140	0.00	0.882	5.44	5.553	34.01	34.940	89.30	219.859	99.98
0.025	0.00	0.156	0.00	0.983	6.62	6.187	36.47	38.932	91.34	244.982	100.00
0.028	0.00	0.174	0.00	1.096	7.85	6.894	39.08	43.381	93.04	272.975	100.00
0.031	0.00	0.194	0.00	1.221	9.11	7.682	41.86	48.338	94.45	304.168	100.00
0.034	0.00	0.216	0.00	1.360	10.42	8.560	44.85	53.861	95.60	338.925	100.00
0.038	0.00	0.241	0.00	1.516	11.77	9.538	48.05	60.016	96.52	377.653	100.00
0.043	0.00	0.268	0.00	1.689	13.18	10.628	51.46	66.874	97.27	420.806	100.00
0.048	0.00	0.299	0.00	1.882	14.66	11.842	55.07	74.516	97.87	468.891	100.00
0.053	0.00	0.333	0.00	2.097	16.22	13.195	58.84	83.030	98.36	522.471	100.00
0.059	0.00	0.371	0.02	2.337	17.86	14.703	62.70	92.518	98.75	582.172	100.00
0.066	0.00	0.414	0.13	2.604	19.58	16.383	66.61	103.090	99.06	648.696	100.00
0.073	0.00	0.461	0.41	2.901	21.39	18.255	70.47	114.870	99.32	722.821	100.00
0.082	0.00	0.514	0.89	3.233	23.28	20.341	74.23	127.996	99.52	805.417	100.00
0.091	0.00	0.572	1.54	3.602	25.25	22.665	77.81	142.622	99.68	897.450	100.00
0.101	0.00	0.638	2.34	4.014	27.31	25.255	81.15	158.919	99.80	1000.000	100.00
0.113	0.00	0.711	3.27	4.472	29.45	28.141	84.20	177.078	99.88		

Figure D.4   Size analysis for LS20 raw coal (-0. 216 mm)

MASTERSIZER 2000

Result Analysis Report

Sample Name: LS20 coal(for flotation)	**SOP Name:** Coal	**Measured:** Friday, November 18, 2005 11:24:05 AM	
Sample Source & type: Supplier = Unknown	**Measured by:** contract	**Analysed:** Friday, November 18, 2005 11:24:06 AM	

Particle Name: Carbon	**Accessory Name:** Hydro 2000S (A)	**Analysis model:** General purpose	**Sensitivity:** Enhanced
Particle RI: 2.420	**Absorption:** 1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 12.04 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 0.373 %	**Result Emulation:** Off

Concentration: 0.0238 %Vol	**Span :** 3.131	**Uniformity:** 1.03	**Result units:** Volume
Specific Surface Area: 0.397 m²/g	**Surface Weighted Mean D[3,2]:** 15.121 um	**Vol. Weighted Mean D[4,3]:** 108.085 um	

d(0.1):   6.977   um   d(0.5):   76.507   um   d(0.9):   246.484   um

Particle Size Distribution

LS20 coal(for flotation), Friday, November 18, 2005 11:24:05 AM

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.020	0.00	0.142	0.00	1.002	0.92	7.096	10.14	50.238	38.85	355.656	96.17
0.022	0.00	0.159	0.00	1.125	1.12	7.962	11.15	56.368	41.57	399.052	97.26
0.025	0.00	0.178	0.00	1.262	1.35	8.934	12.24	63.246	44.52	447.744	98.08
0.028	0.00	0.200	0.00	1.416	1.61	10.024	13.40	70.963	47.74	502.377	98.68
0.032	0.00	0.224	0.00	1.589	1.91	11.247	14.64	79.621	51.25	563.677	99.13
0.036	0.00	0.252	0.00	1.783	2.25	12.619	15.97	89.337	55.04	632.456	99.47
0.040	0.00	0.283	0.00	2.000	2.63	14.159	17.38	100.237	59.10	709.627	99.72
0.045	0.00	0.317	0.00	2.244	3.06	15.887	18.88	112.468	63.35	796.214	99.88
0.050	0.00	0.356	0.00	2.518	3.54	17.825	20.46	126.191	67.74	893.367	99.97
0.056	0.00	0.399	0.04	2.825	4.07	20.000	22.13	141.589	72.14	1002.374	100.00
0.063	0.00	0.448	0.10	3.170	4.65	22.440	23.88	158.866	76.45	1124.683	100.00
0.071	0.00	0.502	0.17	3.557	5.28	25.179	25.73	178.250	80.54	1261.915	100.00
0.080	0.00	0.564	0.26	3.991	5.96	28.251	27.65	200.000	84.29	1415.892	100.00
0.089	0.00	0.632	0.36	4.477	6.69	31.698	29.66	224.404	87.63	1588.656	100.00
0.100	0.00	0.710	0.47	5.024	7.48	35.566	31.77	251.785	90.49	1782.502	100.00
0.112	0.00	0.796	0.60	5.637	8.31	39.905	33.99	282.508	92.84	2000.000	100.00
0.126	0.00	0.893	0.75	6.325	9.20	44.774	36.34	316.979	94.72		

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Figure D.5 Size analysis for LS20 raw coal (-74 µm)

MASTERSIZER 2000

Result Analysis Report

Sample Name: LS20 coal -74 microns - Average	**SOP Name:**	**Measured:** Thursday, January 12, 2006 12:22:38 PM
Sample Source & type:	**Measured by:** contract	**Analysed:** Thursday, January 12, 2006 12:22:40 PM

Particle Name: Carbon (mixed with min.)	**Accessory Name:** Hydro 2000S (A)	**Analysis model:** General purpose	**Sensitivity:** Enhanced
Particle RI: 1.800	**Absorption:** 0.8	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 13.81 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 0.278 %	**Result Emulation:** Off

Concentration: 0.0137 %Vol	**Span :** 2.884	**Uniformity:** 0.917	**Result units:** Volume
Specific Surface Area: 0.577 m²/g	**Surface Weighted Mean D[3,2]:** 7.422 um	**Vol. Weighted Mean D[4,3]:** 38.749 um	

d(0.1): 2.995 um   d(0.5): 29.737 um   d(0.9): 88.768 um

Particle Size Distribution
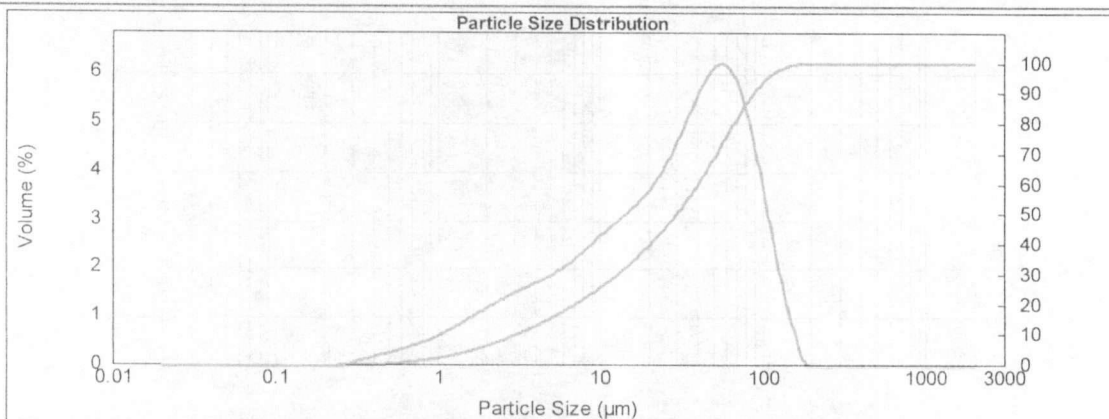
LS20 coal -74 microns - Average, Thursday, January 12, 2006 12:22:38 PM

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.020	0.00	0.112	0.00	0.626	1.03	3.499	11.58	19.572	39.13	109.466	95.38
0.022	0.00	0.124	0.00	0.692	1.28	3.872	12.66	21.658	41.53	121.132	97.20
0.024	0.00	0.137	0.00	0.766	1.56	4.285	13.79	23.966	44.06	134.041	98.51
0.027	0.00	0.152	0.00	0.848	1.87	4.742	14.97	26.520	46.74	148.326	99.36
0.030	0.00	0.168	0.00	0.938	2.23	5.247	16.19	29.346	49.61	164.133	99.86
0.033	0.00	0.186	0.00	1.038	2.62	5.806	17.47	32.473	52.68	181.625	100.00
0.037	0.00	0.205	0.00	1.149	3.07	6.425	18.82	35.934	55.98	200.981	100.00
0.041	0.00	0.227	0.00	1.271	3.56	7.109	20.23	39.764	59.50	222.400	100.00
0.045	0.00	0.251	0.00	1.407	4.11	7.867	21.72	44.001	63.24	246.101	100.00
0.050	0.00	0.278	0.00	1.556	4.71	8.706	23.30	48.690	67.16	272.329	100.00
0.055	0.00	0.308	0.03	1.722	5.38	9.633	24.97	53.879	71.22	301.351	100.00
0.061	0.00	0.341	0.10	1.906	6.10	10.660	26.73	59.621	75.32	333.467	100.00
0.067	0.00	0.377	0.19	2.109	6.88	11.796	28.59	65.975	79.38	369.005	100.00
0.075	0.00	0.417	0.31	2.334	7.72	13.053	30.53	73.006	83.29	408.330	100.00
0.083	0.00	0.462	0.45	2.583	8.61	14.444	32.55	80.787	86.94	451.846	100.00
0.091	0.00	0.511	0.62	2.858	9.55	15.983	34.65	89.396	90.22	500.000	100.00
0.101	0.00	0.565	0.81	3.162	10.54	17.687	36.84	98.924	93.05		

Figure D.6   Size analysis for LS20 raw coal (-45 μm)

MASTERSIZER 2000

Result Analysis Report

Sample Name: LS20coal for flocculation	**SOP Name:** Coal	**Measured:** Friday, November 18, 2005 11:29:41 AM	
Sample Source & type: Supplier = Unknown	**Measured by:** contract	**Analysed:** Friday, November 18, 2005 11:29:42 AM	

Particle Name: Carbon	**Accessory Name:** Hydro 2000S (A)	**Analysis model:** General purpose	**Sensitivity:** Enhanced
Particle RI: 2.420	**Absorption:** 1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 12.06 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 2.097 %	**Result Emulation:** Off

Concentration: 0.0085 %Vol	**Span :** 2.947	**Uniformity:** 0.932	**Result units:** Volume
Specific Surface Area: 1.08 m²/g	**Surface Weighted Mean D[3,2]:** 5.566 um	**Vol. Weighted Mean D[4,3]:** 22.971 um	
d(0.1): 2.278 um	d(0.5): 17.209 um	d(0.9): 52.985 um	

Particle Size Distribution

LS20coal for flocculation, Friday, November 18, 2005 11:29:41 AM

Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %
0.020	0.00	0.142	0.00	1.002	3.32	7.096	28.52	50.238	88.26	355.656	100.00
0.022	0.00	0.159	0.00	1.125	3.97	7.962	30.96	56.368	91.87	399.052	100.00
0.025	0.00	0.178	0.00	1.262	4.69	8.934	33.50	63.246	94.90	447.744	100.00
0.028	0.00	0.200	0.00	1.416	5.51	10.024	36.14	70.963	97.24	502.377	100.00
0.032	0.00	0.224	0.00	1.589	6.43	11.247	38.87	79.621	98.85	563.677	100.00
0.036	0.00	0.252	0.00	1.783	7.45	12.619	41.71	89.337	99.78	632.456	100.00
0.040	0.00	0.283	0.03	2.000	8.59	14.159	44.66	100.237	100.00	709.627	100.00
0.045	0.00	0.317	0.12	2.244	9.83	15.887	47.75	112.468	100.00	796.214	100.00
0.050	0.00	0.356	0.24	2.518	11.19	17.825	51.02	126.191	100.00	893.367	100.00
0.056	0.00	0.399	0.40	2.825	12.67	20.000	54.49	141.589	100.00	1002.374	100.00
0.063	0.00	0.448	0.59	3.170	14.27	22.440	58.20	158.866	100.00	1124.683	100.00
0.071	0.00	0.502	0.83	3.557	15.98	25.179	62.16	178.250	100.00	1261.915	100.00
0.080	0.00	0.564	1.11	3.991	17.81	28.251	66.37	200.000	100.00	1415.892	100.00
0.089	0.00	0.632	1.44	4.477	19.75	31.698	70.77	224.404	100.00	1588.656	100.00
0.100	0.00	0.710	1.82	5.024	21.79	35.566	75.30	251.785	100.00	1782.502	100.00
0.112	0.00	0.796	2.26	5.637	23.93	39.905	79.82	282.508	100.00	2000.000	100.00
0.126	0.00	0.893	2.75	6.325	26.18	44.774	84.19	316.979	100.00		

Figure D.7   Size analysis for LS20 shaking table concentrate (-0.15 mm)

MASTERSIZER 2000

Result Analysis Report

Sample Name: LS20 shaking table concentrate	**SOP Name:**	**Measured:** Sunday, July 04, 2004 12:51:54 PM
Sample Source & type: Supplier	**Measured by:** contract	**Analysed:** Sunday, July 04, 2004 12:51:56 PM

Particle Name: Carbon (mixed with min.)	**Accessory Name:** Hydro 2000S (A)	**Analysis model:** General purpose	**Sensitivity:** Enhanced
Particle RI: 1.850	**Absorption:** 0.8	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 11.48 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 0.451 %	**Result Emulation:** Off

Concentration: 0.0472 %Vol	**Span :** 1.730	**Uniformity:** 0.522	**Result units:** Volume
Specific Surface Area: 0.146 m²/g	**Surface Weighted Mean D[3,2]:** 29.266 um	**Vol. Weighted Mean D[4,3]:** 73.736 um	

d(0.1):   16.578   um   d(0.5):   68.695   um   d(0.9):   135.448   um

Particle Size Distribution
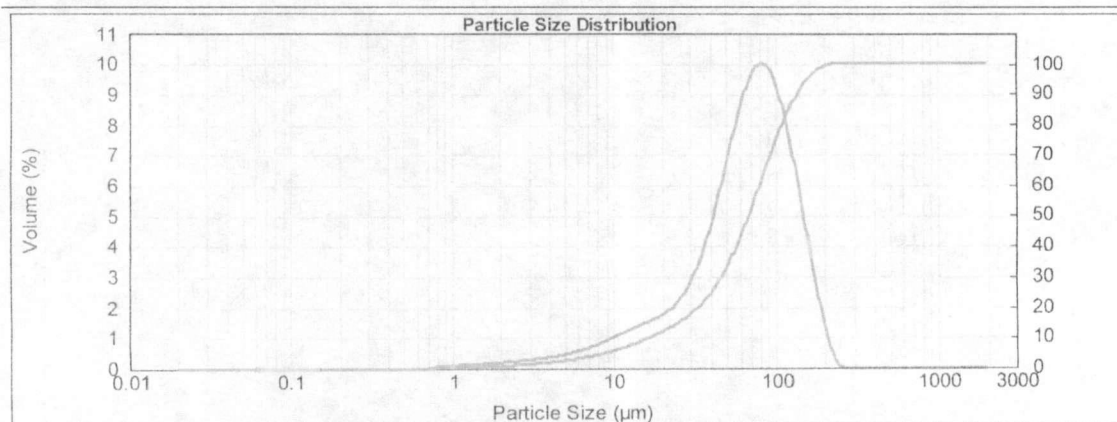
LS20 shaking table concentrate(-150 micro) - Average, Sunday, July 04, 2004 12:51:54 PM

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.020	0.00	0.126	0.00	0.792	0.01	4.983	2.58	31.357	18.59	197.312	99.14
0.022	0.00	0.140	0.00	0.882	0.06	5.553	2.92	34.940	20.95	219.859	99.84
0.025	0.00	0.156	0.00	0.983	0.12	6.187	3.30	38.932	23.82	244.982	100.00
0.028	0.00	0.174	0.00	1.096	0.19	6.894	3.73	43.381	27.30	272.975	100.00
0.031	0.00	0.194	0.00	1.221	0.26	7.682	4.23	48.338	31.46	304.168	100.00
0.034	0.00	0.216	0.00	1.360	0.35	8.560	4.80	53.861	36.40	338.925	100.00
0.038	0.00	0.241	0.00	1.516	0.45	9.538	5.44	60.016	42.05	377.653	100.00
0.043	0.00	0.268	0.00	1.689	0.56	10.628	6.17	66.874	48.35	420.806	100.00
0.048	0.00	0.299	0.00	1.882	0.68	11.842	6.98	74.516	55.14	468.891	100.00
0.053	0.00	0.333	0.00	2.097	0.82	13.195	7.87	83.030	62.20	522.471	100.00
0.059	0.00	0.371	0.00	2.337	0.97	14.703	8.84	92.518	69.26	582.172	100.00
0.066	0.00	0.414	0.00	2.604	1.14	16.383	9.88	103.090	76.02	648.696	100.00
0.073	0.00	0.461	0.00	2.901	1.32	18.255	11.00	114.870	82.20	722.821	100.00
0.082	0.00	0.514	0.00	3.233	1.53	20.341	12.19	127.996	87.57	805.417	100.00
0.091	0.00	0.572	0.00	3.602	1.76	22.665	13.50	142.622	91.97	897.450	100.00
0.101	0.00	0.638	0.00	4.014	2.00	25.255	14.96	158.919	95.34	1000.000	100.00
0.113	0.00	0.711	0.00	4.472	2.28	28.141	16.62	177.078	97.69		

Figure D.8   Size analysis for reverse coal flotation concentrate (for preparation of coal water slurries, flotation feed size -74 µm)

MASTERSIZER 2000

Result Analysis Report

Sample Name: Reverse flotation concentrate	**SOP Name:** Coal	**Measured:** Friday, November 18, 2005 11:01:24 AM
Sample Source & type: Supplier = Unknown	**Measured by:** contract	**Analysed:** Friday, November 18, 2005 11:01:25 AM

Particle Name: Carbon	**Accessory Name:** Hydro 2000S (A)	**Analysis model:** General purpose	**Sensitivity:** Enhanced
Particle RI: 2.420	**Absorption:** 1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 11.21 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 0.360 %	**Result Emulation:** Off

Concentration: 0.0201 %Vol	**Span :** 2.136	**Uniformity:** 0.666	**Result units:** Volume
Specific Surface Area: 0.437 m²/g	**Surface Weighted Mean D[3,2]:** 13.746 um	**Vol. Weighted Mean D[4,3]:** 50.214 um	

d(0.1): 7.519 um   d(0.5): 44.180 um   d(0.9): 101.884 um
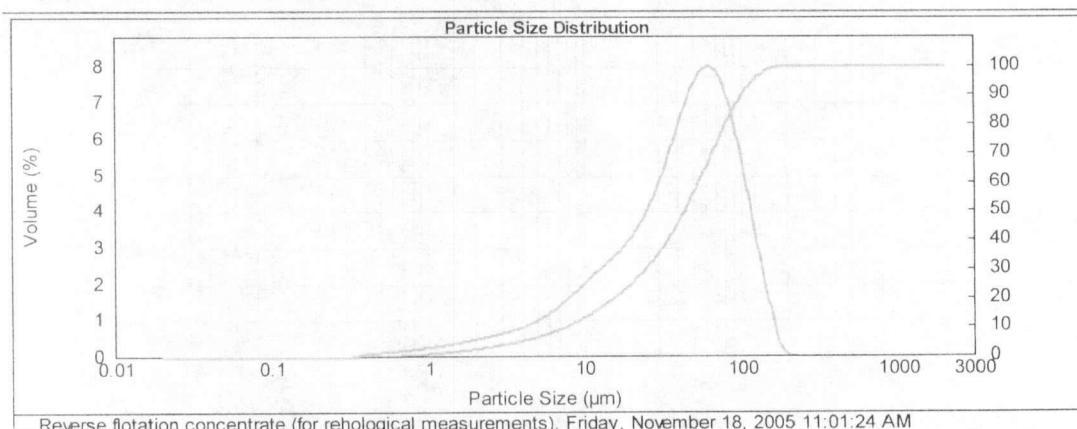
Particle Size Distribution

Reverse flotation concentrate (for rehological measurements), Friday, November 18, 2005 11:01:24 AM

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.020	0.00	0.142	0.00	1.002	1.04	7.096	9.45	50.238	56.04	355.656	100.00
0.022	0.00	0.159	0.00	1.125	1.24	7.962	10.58	56.368	61.84	399.052	100.00
0.025	0.00	0.178	0.00	1.262	1.47	8.934	11.84	63.246	67.83	447.744	100.00
0.028	0.00	0.200	0.00	1.416	1.73	10.024	13.26	70.963	73.81	502.377	100.00
0.032	0.00	0.224	0.00	1.589	2.01	11.247	14.83	79.621	79.55	563.677	100.00
0.036	0.00	0.252	0.00	1.783	2.32	12.619	16.54	89.337	84.82	632.456	100.00
0.040	0.00	0.283	0.00	2.000	2.66	14.159	18.41	100.237	89.41	709.627	100.00
0.045	0.00	0.317	0.00	2.244	3.03	15.887	20.43	112.468	93.18	796.214	100.00
0.050	0.00	0.356	0.00	2.518	3.43	17.825	22.60	126.191	96.06	893.367	100.00
0.056	0.00	0.399	0.05	2.825	3.87	20.000	24.96	141.589	98.06	1002.374	100.00
0.063	0.00	0.448	0.13	3.170	4.35	22.440	27.54	158.866	99.30	1124.683	100.00
0.071	0.00	0.502	0.21	3.557	4.88	25.179	30.38	178.250	99.87	1261.915	100.00
0.080	0.00	0.564	0.31	3.991	5.45	28.251	33.55	200.000	99.99	1415.892	100.00
0.089	0.00	0.632	0.42	4.477	6.09	31.698	37.11	224.404	100.00	1588.656	100.00
0.100	0.00	0.710	0.55	5.024	6.79	35.566	41.12	251.785	100.00	1782.502	100.00
0.112	0.00	0.796	0.69	5.637	7.57	39.905	45.61	282.508	100.00	2000.000	100.00
0.126	0.00	0.893	0.85	6.325	8.46	44.774	50.61	316.979	100.00		

Figure D.9   Size analysis for forward coal flotation concentrate (for preparation of coal water slurries, flotation feed size -74 μm)

MASTERSIZER 2000

Result Analysis Report

Sample Name: Forward flotation concentrate	**SOP Name:** Coal	**Measured:** Friday, November 18, 2005 11:16:46 AM
Sample Source & type: Supplier = Unknown	**Measured by:** contract	**Analysed:** Friday, November 18, 2005 11:16:47 AM

Particle Name: Carbon	**Accessory Name:** Hydro 2000S (A)	**Analysis model:** General purpose	**Sensitivity:** Enhanced
Particle RI: 2.420	**Absorption:** 1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 11.49 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 0.323 %	**Result Emulation:** Off

Concentration: 0.0152 %Vol	**Span :** 2.384	**Uniformity:** 0.749	**Result units:** Volume
Specific Surface Area: 0.583 m²/g	**Surface Weighted Mean D[3,2]:** 10.289 um	**Vol. Weighted Mean D[4,3]:** 44.562 um	

d(0.1): 5.024 um   d(0.5): 37.694 um   d(0.9): 94.871 um

Particle Size Distribution

Forward flotation concentrate(for rehological measurements), Friday, November 18, 2005 11:16:46 AM

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.020	0.00	0.142	0.00	1.002	1.63	7.096	13.56	50.238	62.17	355.656	100.00
0.022	0.00	0.159	0.00	1.125	1.93	7.962	14.98	56.368	67.53	399.052	100.00
0.025	0.00	0.178	0.00	1.262	2.27	8.934	16.53	63.246	72.98	447.744	100.00
0.028	0.00	0.200	0.00	1.416	2.64	10.024	18.23	70.963	78.33	502.377	100.00
0.032	0.00	0.224	0.00	1.589	3.05	11.247	20.06	79.621	83.36	563.677	100.00
0.036	0.00	0.252	0.00	1.783	3.51	12.619	22.02	89.337	87.89	632.456	100.00
0.040	0.00	0.283	0.00	2.000	4.01	14.159	24.12	100.237	91.76	709.627	100.00
0.045	0.00	0.317	0.01	2.244	4.56	15.887	26.35	112.468	94.86	796.214	100.00
0.050	0.00	0.356	0.08	2.518	5.15	17.825	28.72	126.191	97.17	893.367	100.00
0.056	0.00	0.399	0.16	2.825	5.80	20.000	31.25	141.589	98.71	1002.374	100.00
0.063	0.00	0.448	0.27	3.170	6.51	22.440	33.98	158.866	99.64	1124.683	100.00
0.071	0.00	0.502	0.40	3.557	7.27	25.179	36.95	178.250	100.00	1261.915	100.00
0.080	0.00	0.564	0.54	3.991	8.11	28.251	40.22	200.000	100.00	1415.892	100.00
0.089	0.00	0.632	0.71	4.477	9.01	31.698	43.83	224.404	100.00	1588.656	100.00
0.100	0.00	0.710	0.90	5.024	10.00	35.566	47.83	251.785	100.00	1782.502	100.00
0.112	0.00	0.796	1.11	5.637	11.08	39.905	52.23	282.508	100.00	2000.000	100.00
0.126	0.00	0.893	1.36	6.325	12.26	44.774	57.03	316.979	100.00		

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Figure D.10   Size analysis for reverse coal flotation concentrate (flotation feed size -0.216 mm)

MASTERSIZER 2000

Result Analysis Report

Sample Name: LS20 reverse flotation **concentrate**	**SOP Name:** Coal	**Measured:** Friday, November 18, 2005 11:40:41 AM	
Sample Source & type: Supplier = Unknown	**Measured by:** contract	**Analysed:** Friday, November 18, 2005 11:40:43 AM	

Particle Name: Carbon	**Accessory Name:** Hydro 2000S (A)	**Analysis model:** General purpose	**Sensitivity:** Enhanced
Particle RI: 2.420	**Absorption:** 1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 8.41 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 0.555 %	**Result Emulation:** Off

Concentration: 0.1198 %Vol	**Span :** 1.626	**Uniformity:** 0.508	**Result units:** Volume
Specific Surface Area: 0.0615 m²/g	**Surface Weighted Mean D[3,2]:** 97.501 um	**Vol. Weighted Mean D[4,3]:** 146.064 um	

d(0.1): 54.645 um   d(0.5): 127.942 um   d(0.9): 262.677 um

Particle Size Distribution

LS20 reverse flotation concentrate(19.75% ash), Friday, November 18, 2005 11:40:41 AM

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.020	0.00	0.142	0.00	1.002	0.00	7.096	0.00	50.238	8.20	355.656	97.29
0.022	0.00	0.159	0.00	1.125	0.00	7.962	0.00	56.368	10.75	399.052	98.63
0.025	0.00	0.178	0.00	1.262	0.00	8.934	0.01	63.246	13.99	447.744	99.42
0.028	0.00	0.200	0.00	1.416	0.00	10.024	0.08	70.963	17.99	502.377	99.83
0.032	0.00	0.224	0.00	1.589	0.00	11.247	0.16	79.621	22.80	563.677	99.97
0.036	0.00	0.252	0.00	1.783	0.00	12.619	0.26	89.337	28.41	632.456	100.00
0.040	0.00	0.283	0.00	2.000	0.00	14.159	0.39	100.237	34.76	709.627	100.00
0.045	0.00	0.317	0.00	2.244	0.00	15.887	0.55	112.468	41.72	796.214	100.00
0.050	0.00	0.356	0.00	2.518	0.00	17.825	0.75	126.191	49.10	893.367	100.00
0.056	0.00	0.399	0.00	2.825	0.00	20.000	0.99	141.589	56.67	1002.374	100.00
0.063	0.00	0.448	0.00	3.170	0.00	22.440	1.29	158.866	64.16	1124.683	100.00
0.071	0.00	0.502	0.00	3.557	0.00	25.179	1.67	178.250	71.31	1261.915	100.00
0.080	0.00	0.564	0.00	3.991	0.00	28.251	2.15	200.000	77.87	1415.892	100.00
0.089	0.00	0.632	0.00	4.477	0.00	31.698	2.78	224.404	83.63	1588.656	100.00
0.100	0.00	0.710	0.00	5.024	0.00	35.566	3.62	251.785	88.47	1782.502	100.00
0.112	0.00	0.796	0.00	5.637	0.00	39.905	4.74	282.508	92.32	2000.000	100.00
0.126	0.00	0.893	0.00	6.325	0.00	44.774	6.23	316.979	95.24		

Malvern Instruments Ltd
Malvern, UK
Tel := +[44] (0) 1684-892456 Fax +[44] (0) 1684-892789

Mastersizer 2000 Ver. 5.1
Serial Number : 34403-197
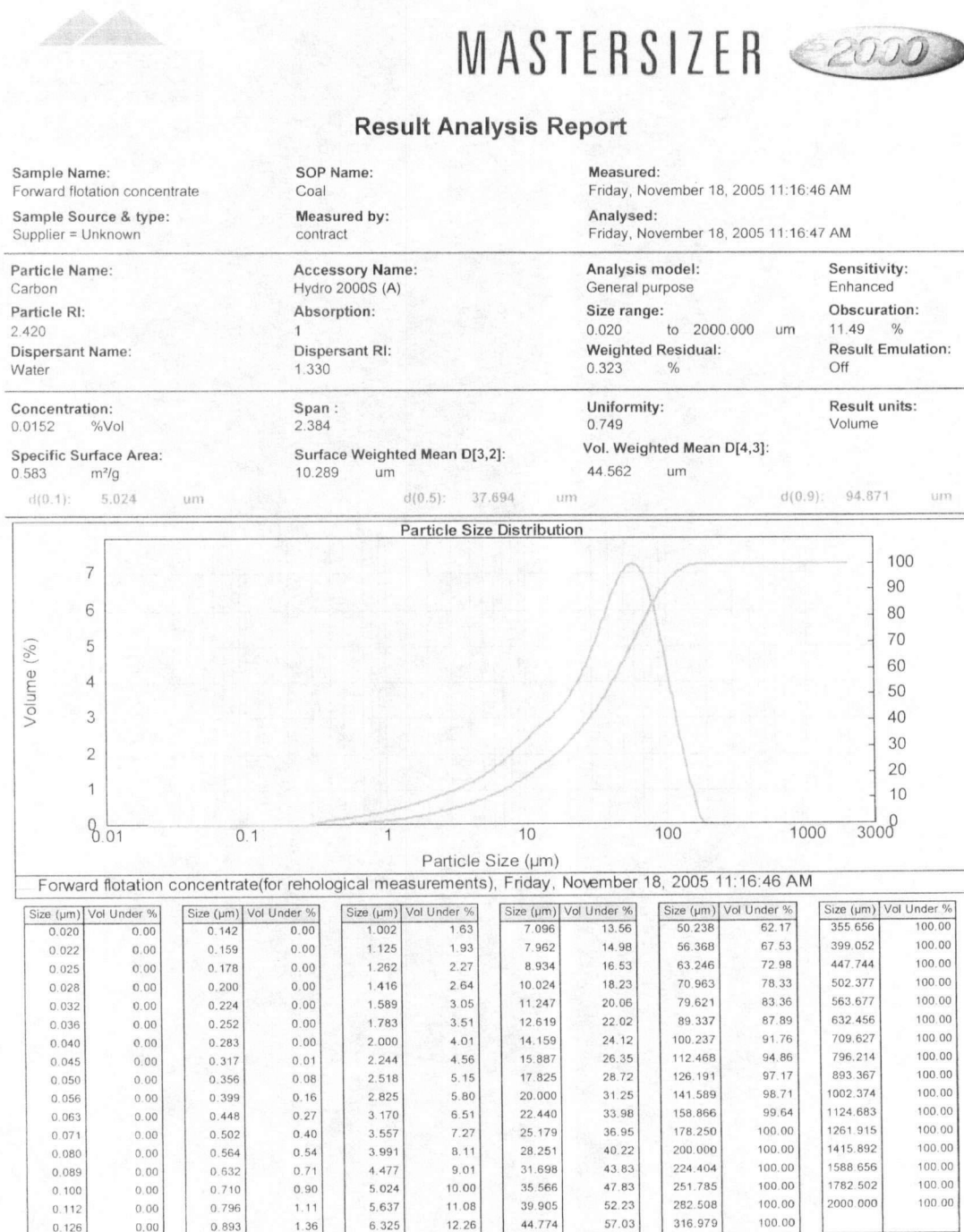
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Record Number: 22
18 Nov 2005 11:40:43 AM

221

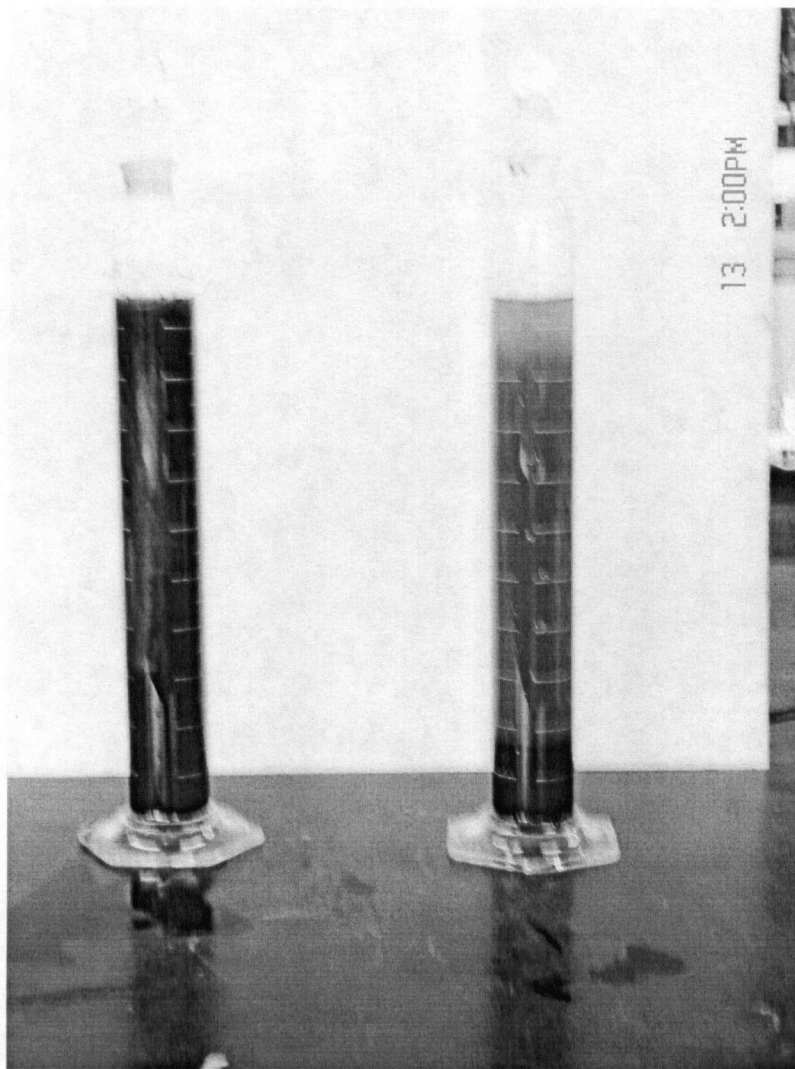Figure D.11   Size analysis for reverse coal flotation tails (flotation feed size -0.216 mm)

MASTERSIZER 2000

Result Analysis Report

Sample Name: LS20 reverse flotation tails	**SOP Name:**	**Measured:** Friday, November 18, 2005 11:56:24 AM
Sample Source & type: Works	**Measured by:** contract	**Analysed:** Friday, November 18, 2005 11:56:25 AM

Particle Name: CARBON	**Accessory Name:** Hydro 2000S (A)	**Analysis model:** General purpose	**Sensitivity:** Enhanced
Particle RI: 2.420	**Absorption:** 1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 14.97 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 0.148 %	**Result Emulation:** Off

Concentration: 0.0211 %Vol	**Span :** 2.741	**Uniformity:** 0.889	**Result units:** Volume
Specific Surface Area: 0.568 m²/g	**Surface Weighted Mean D[3,2]:** 10.557 um	**Vol. Weighted Mean D[4,3]:** 37.040 um	

d(0.1): 5.443   um   d(0.5): 26.705   um   d(0.9): 78.652   um

Particle Size Distribution

LS20 reverse flotation tails(51.66% - Average, Friday, November 18, 2005 11:56:24 AM

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.020	0.00	0.142	0.00	1.002	1.23	7.096	13.07	50.238	76.70	355.656	99.97
0.022	0.00	0.159	0.00	1.125	1.46	7.962	14.69	56.368	80.76	399.052	100.00
0.025	0.00	0.178	0.00	1.262	1.72	8.934	16.53	63.246	84.39	447.744	100.00
0.028	0.00	0.200	0.00	1.416	2.03	10.024	18.63	70.963	87.56	502.377	100.00
0.032	0.00	0.224	0.00	1.589	2.37	11.247	21.02	79.621	90.27	563.677	100.00
0.036	0.00	0.252	0.00	1.783	2.77	12.619	23.74	89.337	92.51	632.456	100.00
0.040	0.00	0.283	0.00	2.000	3.21	14.159	26.81	100.237	94.34	709.627	100.00
0.045	0.00	0.317	0.01	2.244	3.71	15.887	30.25	112.468	95.79	796.214	100.00
0.050	0.00	0.356	0.07	2.518	4.28	17.825	34.06	126.191	96.91	893.367	100.00
0.056	0.00	0.399	0.13	2.825	4.91	20.000	38.23	141.589	97.76	1002.374	100.00
0.063	0.00	0.448	0.22	3.170	5.61	22.440	42.72	158.866	98.39	1124.683	100.00
0.071	0.00	0.502	0.31	3.557	6.38	25.179	47.49	178.250	98.86	1261.915	100.00
0.080	0.00	0.564	0.42	3.991	7.24	28.251	52.44	200.000	99.21	1415.892	100.00
0.089	0.00	0.632	0.55	4.477	8.18	31.698	57.50	224.404	99.47	1588.656	100.00
0.100	0.00	0.710	0.69	5.024	9.21	35.566	62.57	251.785	99.65	1782.502	100.00
0.112	0.00	0.796	0.84	5.637	10.36	39.905	67.52	282.508	99.79	2000.000	100.00
0.126	0.00	0.893	1.02	6.325	11.64	44.774	72.26	316.979	99.90		

(a) A130   (b) A100

Conditions:

25 g of LS20 raw coal (- 45 μm) in 500 mL polymer-water solution
A100/A130 dosage: 400 g/t
The polymer-coal suspensions conditioned at 1500 r.p.m. in a flotation cell for 5 minutes
The picture taken after 5 minutes of settling