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The application of contact angle measurement as a method for flotation collector evaluation

S.G.E. de Jager[1], J.H.P. van Heerden[1], F.W. Petersen[2,*]

[1] *SASTECH, P.O. Box 1, Sasolburg, 1947, South Africa*
[2] *Anglo Platinum Corp. Ltd., P.O. Box 62179, Marshalltown, South Africa*

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ABSTRACT

Contact angle measurement of flotation reagents (called collectors) on coal is used for screening suitable collectors that will enhance flotation performance of coal. The application of this method is associated with uncertainties due to the hysteresis that is associated with contact angle measurements.

Three coal samples namely Waterberg, Witbank seam 2, and Witbank seam 4 coal were evaluated for flotation purposes. A range of characterisation techniques, were used and included contact angle measurements. Contact angle measurements are used, as a screening tool to predict which reagent would be suitable for froth flotation. Two methods of contact angle measurements were evaluated. The first method included contact angle measurement on acid treated or demineralised (mixture of hydrochloric acid and hydrofluoric acid) coal. In the second method the selectivity of the reagent on the coal was tested during contact angle determinations on density separated coal. During the selectivity contact angle determinations the coal was separated into coal-rich (density < $1.6 g/cm^3$) and mineral-rich fractions (density >$1.6 g/cm^3$). The contact angle results showed that there is an increase in flotation yield percentage as well as ash content with increasing contact angles. The reagent resulting in optimum flotation was a substituted alcohol, and was suitable as reagent for all three South African coals used in this study.

Keywords: Contact angles; South African coal; Demineralised; Density separation; Hysteresis

1. INTRODUCTION

The selection of collectors for fine coal flotation (<150μm) is often done on a trial and error basis or previous experience. Evaluation of reagents on plant scale is done with caution and if the trial run was not successful, the issue of handling the off spec products arises. The characteristics of a coal, such as the degree of surface oxidation and maceral type, determine the reagents that will be used to float the coal.

On plant-scale, it is all about production and cost. Production should be maximized and cost should be minimized. Proper evaluation of the collector is crucial to save both time and money. Contact angle measurements are used as an evaluation or screening method and the value and usefulness of this technique may be under estimated (Sarikaya and Ozbayoglu, 1994). A probable reason for being underestimated is the hysteresis that is associated with contact angle measurements.

Due to the heterogeneity of coal, it is known that contact angle measurements are not accurate and only provide information regarding the part under investigation and not the complete sample (Fuerstenau, *et al.,* 1987; Holysz, 1996).

A common example hysteresis that occurs during contact angle measurements is the effect of gravity on the drop size formed on the planar solid surface. If the solid plane is inclined, the bubble might tilt to one side (similar to being "top heavy"). Another example of hysteresis effects that occur during contact angle measurement is surface roughness and absorption effects that occur between the coal and collector (Leja, 1982; Drelich *et al.,* 1997). Contact angle measurements were used over a number of years as a method to determine the wettability of a coal surface with a reagent (Van Nierop, 1988; Orumwense, 1998; Subrahimanyam *et al.,* 1999; Orumwense, 2000).

* Corresponding author. E-mail: FPetersen@angloplat.com

The contact angle is defined as the angle formed between an air bubble or a liquid bubble and a solid surface (Allum and Whelan, 1954; Fuerstenau, 1982). The degree to which the liquid or air bubble can displace water from the coal surface is measured and is an indication of the wettability of the coal surface with a particular liquid (Holysz, 1996). Coal that is naturally hydrophobic, results in a large (above 90°) angle between the oil drop and the coal sample in a water medium (Brown, 1962).

Gutierrez-Rodrigues *et al.* (1984) investigated the contact angles of different rank coals and concluded that contact angle measurements are not accurate (cannot be measured) on coals with a fixed carbon (dry ash free) content of less than 61%.

The aim of the study is to verify the use of contact angle measurements as a "screening" tool for predicting coal flotation collectors. In order to obtain this, it is necessary to perform contact angle measurements on coal samples and to test the results against batch scale flotation performance.

2. EXPERIMENTAL

2.1. Sample preparation

Representative coal samples were obtained from the Waterberg coal field (South Africa) and seam 2 and seam 4 coal from the Witbank coal field (South Africa).

The samples were dried and crushed to 95% below 2mm using a Retsch jaw crusher. The samples were split into representative 1kg samples (the representiveness of the samples was confirmed using the ash content of each sample) using a 20 slot ¼ inch riffler. The samples were stored in a nitrogen atmosphere to prevent the coal samples from oxidation. The bulk of the coal samples were stored under water to prevent the coal from excessive oxidation.

2.2. Particle size distribution

A one kilogram sample of coal was added to a rod mill together with 613g of water to obtain a slurry density of 62%. The following rods were used in the mill: two rods with a diameter of 35mm and weight of 2450g each, six rods with a diameter of 25mm and a weight of 1215g each and six rods with a diameter of 20mm and a weight of 795g each. The sample was milled for 30, 60, 90 and 120 minutes respectively to determine the time of milling to obtain a particle size distribution of 95% below 150µm. A Retsch crystalsizer was used to determine the particle size distribution of each milled sample. The same procedure was used for all three coal samples used in this investigation. This was done to ensure a particle size distribution that is more or less the same for all three coal samples.

2.3. Contact angle measurements

Chemical demineralisation treatment was done on the prepared coal samples described above in order to minimise the influence of the minerals on the surface properties of the coal. 10g of dry coal was added in a polythene bottle together with 500cm^3 of a 1:1 mixture of hydrofluoric acid and hydrochloric acid (5 mole concentration of each). The mixture was stirred over a period of 48 hours where after it was filtered and the coal fraction again soaked in distilled water. Filtration and soaking was repeated until all traces of acid were removed. The coal was filtered and dried in an oven (with nitrogen flow) over a period of 6 hours.

The dried coal was pressed into a coal tablet using vacuum and applying pressure of 300g/cm^2. The sessile drop test procedure was followed for measuring the contact angle of the reagents on the coal. This method is preferred over the captive bubble method which is used for higher rank coal (Gutierrez-Rodrigues *et al.,* 1984). The contact angle (θ) is measured on both sides of the droplet using a contact angle meter. All measurements were conducted four times on 2 different coal tablets at times and the average angle was obtained.

The collectors were also tested for selectivity on each coal sample by pressing coal tablets from density separated (density of 1.6g/cm^3) coal and measuring the contact angle between the coal and the collector on both separated fractions (the two fractions obtained is a coal rich fraction with a density below 1.6g/cm^3 and a mineral rich fraction with a density above 1.6g/cm^3).

2.4. Flotation tests

A 3L mechanical Leeds cell was used for the batch scale flotation tests and the parameters that were used are listed in Table 1. After flotation the residual tailings that remained in the float cell were drained and the concentrate and tail samples were filtered and dried in an oven over night under nitrogen atmosphere. Both samples were weighed and submitted for ash content analysis. The flotation tests were done in duplicate.

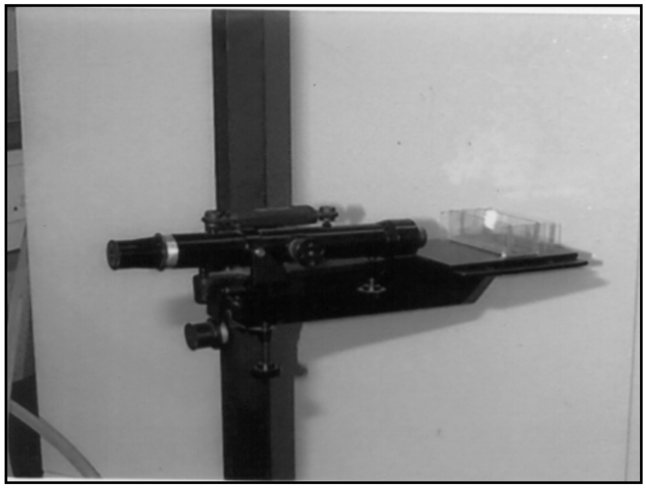

Figure 1. Contact angle meter

Table 1
Flotation parameters for ultra fine coal flotation

Parameter		Additional information
Solids content (m/m)	5%	
Air flow	3L/min	
Speed	1200rpm	
Collector dosage	3L/t	Conditioned for 5 min.
Frother dosage	20g/t	Conditioned for 30 sec.
Duration of froth collection	5min	

3. RESULTS AND DISCUSSION

The proximate analyses shown in Table 2 indicate that the Waterberg coal has the highest volatile matter content (30.1%) followed by Witbank seam 2 (27.6% volatiles) and Witbank seam 4 coal with 25.2% respectively.

Table 2
Proximate analyses on South African coal types

	Proximate analysis			
Sample	Moisture (%) (as received)	Volatiles (%) (dry ash free)	Fixed C (%) (dry ash free)	Ash content (%) (as received)
Waterberg	1.8	43.75	56.25	29.4
Witbank seam 2	2.4	34.07	65.93	16.6
Witbank seam 4	2	37.85	62.15	33.8

The fixed carbon content for the different coal types varied from Witbank seam 2 (65.93%), Witbank seam 4 (62.15%), and the lowest fixed carbon content being Waterberg coal (62.15%). Analysis conducted on these coal samples showed that the Witbank coals is mostly inertinite rich coal (>50%) and the Waterberg coal is vitrinite rich in nature (68% Vitrinite).

Based on the ash content, it is expected that Witbank seam 2 coal will be the easiest to float since this coal has the highest fixed carbon content and lowest ash content of all three coal types. The ash contents of the coals varies from 16.6% for Witbank seam 2 coal to 33,8% for the Witbank seam 4 coal. The beneficiation of Witbank seam 4 coal using flotation as beneficiation method may therefore be difficult (ash content below 12% is required for thermal grade export coal).

The contact angle results obtained for Waterberg coal are graphically depicted in Fig. 2 and are compared to flotation yield percentage obtained for the concentrate samples. Fig. 2 indicates that the flotation yield increases with increasing contact angle. This is observed for both demineralised coal and density separated coal ($\rho < 1.6 g/cm^3$). The peak that is observed in the curve at a contact angle of 180° (visually observed as absorption) is ascribed to the hysteresis effects normally associated with contact angle measurements. The collector that was used in this case was o-cresol, known for the swelling properties it has on coal.

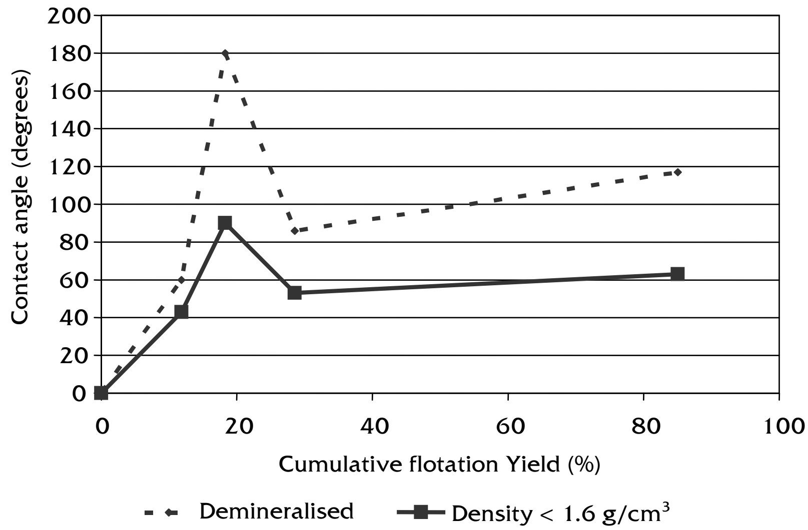

Figure 2. Contact angle versus cumulative flotation yield for Waterberg coal

In Fig. 3 the results from the contact angle measurements on Witbank seam 2 coal is shown and again it is noted that the flotation yield increases with increasing contact angle. The curve trend for the contact angles on demineralised and density separated coal is similar. The sharp peak observed at a contact angle of 180° is again ascribed to the hysteresis effect of absorption caused by o-cresol. By omitting the contact angle data obtained by using o-cresol (causing hysteresis), the increase in flotation ield with increasing contact angle can be seen more clearly (finely dotted line).

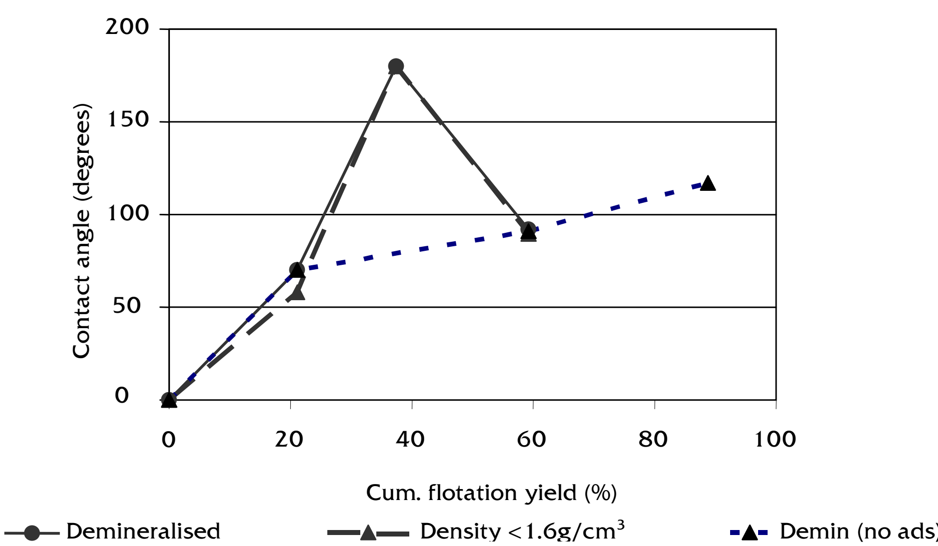

Figure 3. Contact angle versus cumulative flotation yield for Witbank seam 2 coal

The results of the Witbank seam 4 coal, shown in Fig. 4, showed an increase in flotation yield with increasing contact angle as with the Waterberg coal and Witbank seam 2 coal. The hysteresis point caused by the o-cresol reagent is again observed as a sharp peak.

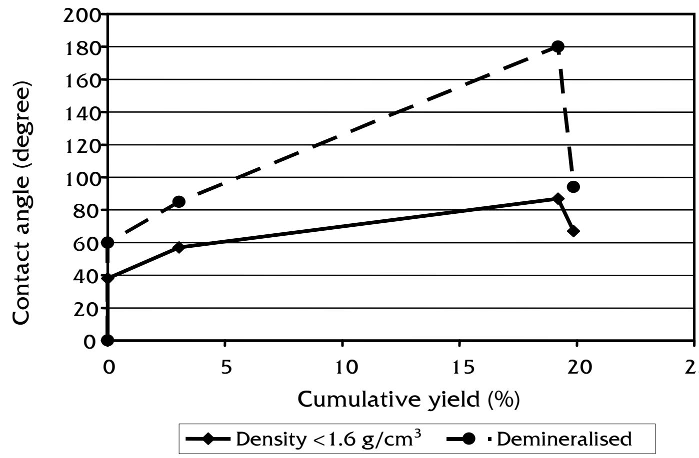

Figure 4. Contact angle versus cumulative flotation yield for Witbank seam 4 coal

Fig. 5 shows the contact angle values on density separated ($\rho < 1.6 g/cm^3$) coal of all 3 coal types. The flotation yield increases as the contact angle increases if the absorption angle obtained for o-cresol is omitted. A plateau is reached where the contact angle is more or less constant with increasing yield. The maximum contact angle was different for each coal. For Witbank seam 2 the maximum contact angle obtained was 103°, for Witbank seam 4 and for Waterberg the contact angle was the same at 63°. The latter may be linked to the fixed carbon content or ash content of Waterberg and Witbank seam 4 coal that is almost the same. The higher contact angle resulted in higher flotation yield. Similar contact angles did not produce similar flotation yields due to differences in coal properties.

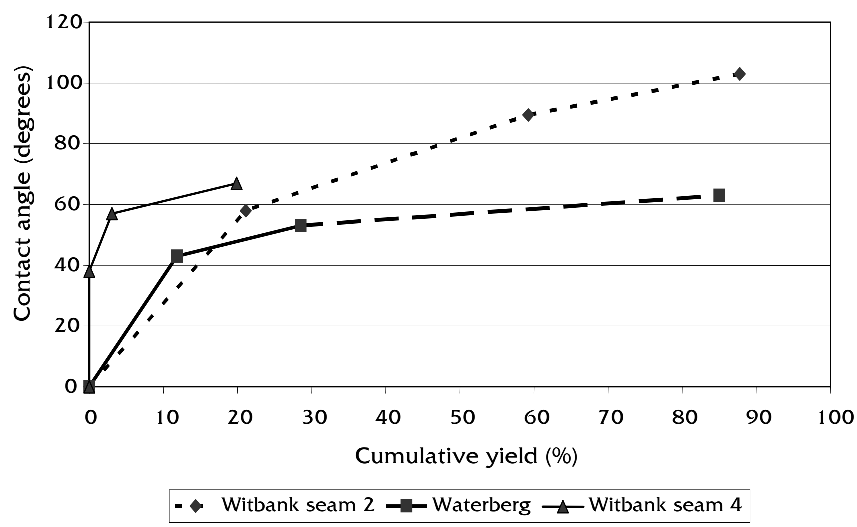

Figure 5. Comparison of contact angle versus cumulative flotation yield for different coal samples ($\rho < 1.6 g/cm^3$)

Fig. 6 shows an increase in ash content for all 3 coals as the contact angle increases. The exception is the Witbank seam 2 coal that seem to have a lower contact angle at higher ash contents. The lowest ash content that was obtained for the Witbank seam 2 coal was 9.85% at a product yield of 87.77% using isomerised alcohol as collector. The lowest ash content obtained for Witbank seam 4 coal was also with isomerised alcohol as collector. This may be due to the maceral composition of the coals that differ. Witbank coal being Inertinite rich (aromatic structures), compared to the more Vitrinite rich (more aliphatic structure) Waterberg coal that showed increasing yield but an ash content of 22% with isomerised alcohol as collector. As was predicted the Witbank seam 4 coal was difficult to float and resulted in lower yields during flotation tests.

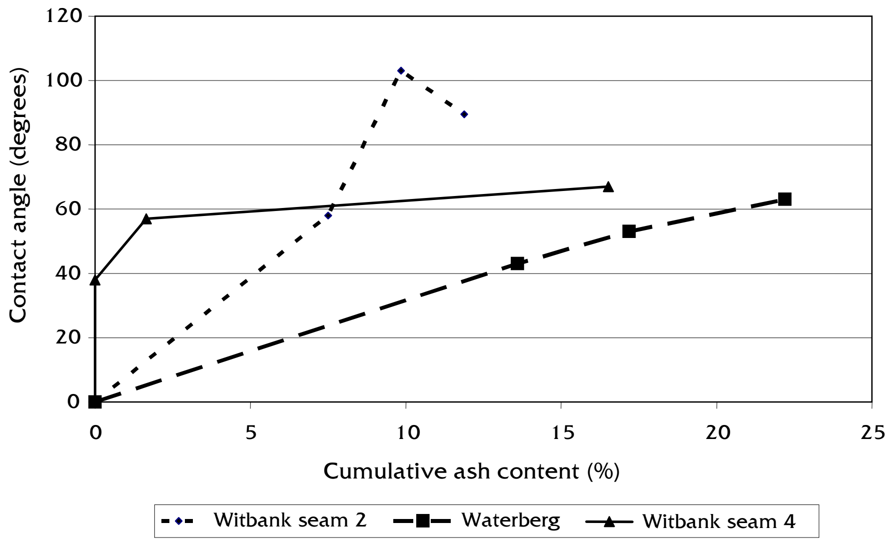

Figure 6. Comparison of contact angle versus ash content for different coal samples ($\rho < 1.6 g/cm^3$)

4. CONCLUSIONS

For the flotation of vitrinite rich Waterberg coal and inertinite rich Witbank seam 2 and seam 4 coal it is determined that there is a correlation between the contact angle and flotation data when using different reagents as collectors. When no contact angle is obtained, no flotation is obtained.

During the contact angle determination of the reagent on the coal samples, density separation and acid treatment that are done prior to determination do not show any effect on the trends that are observed. In either method, an increase in flotation yield is observed with increasing contact angle. This increase in flotation yield with increase in contact angle was observed for all three coal samples.

The effect of absorption, obtained from using o-cresol as collector during flotation, causes hysteresis resulting in errors during the prediction of reagents and as this effect is observed for all 3 coal samples, the effect is ascribed to the reagent rather than the coal.

The optimum flotation yield is obtained at contact angle values of 60° for al 3 coal samples. The flotation yield that is obtained for Witbank seam 2 coal, which has a lower ash content than seam 4 and even lower ash content than Waterberg coal, indicates that the ash content of the coal also has an influence on the contact angle of the reagent on the coal.

From this study it is clear that contact angle measurements should only be used as a screening tool for qualitative analysis.

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