



Investigations into the reduction of moisture in fine coal by plant tests with surfactants

by A. Nkolele*

†Paper written on project work carried out in partial fulfilment of B.Tech (Metallurgical Engineering) degree

Synopsis

Fine coal of the Goedehoop Colliery is dewatered by centrifuging before being sold. Full-scale plant tests were carried out to reduce residual cake moisture by the addition of surfactants. It is believed that by modifying the interface between the coal surface and the adherent surface water, as well as the water occluded in the cake voids, drainage is improved. Two anionic surfactants at concentrations up to 150 g/t were tested on coal of <0.5 mm size. The results demonstrate that quite high additions of surfactant (80 g/t) were needed to reduce moisture from 20 to about 17–18%. It was observed that when increasing surfactant additions at low levels, within a very narrow concentration range, the retained moisture first increased sharply only to decrease sharply immediately thereafter; this effect points to a critical surfactant concentration. Based on the obtained results, the use of surfactants cannot be recommended at this stage; further investigations under more controlled conditions are required.

Introduction

Coal when mined contains a certain amount of inherent or chemically bound water, which necessarily forms part of the product. In the course of upgrading or 'washing', the raw coal is crushed and a high-grade product obtained by heavy media separation; the fines are cleaned via spirals and dewatered before being admixed to the coarser product for sale. The cleaning process thus involves the contact of coal with water. The amount of this additional free moisture remaining in the dewatered product is particularly prominent for the fine coal fraction because of the high surface area to which water can adhere, and water being occluded in the inter-particle voids of the dewatered cake.

A high amount of moisture in coal is undesirable for a number of reasons: it may lead to spontaneous combustion when stored; it increases the stickiness of coal, resulting in blocked chutes and hang-ups in bunkers; it adds to storage and transportation costs, which are charged by mass; and finally, but not least, moisture reduces the heating value of coal. It has been found that reducing the

moisture by 10% increased the heat rate in a lignite-fired power station by over 4%, taking a number of factors into account¹.

Processes to reduce the free moisture of fine coal include filtration (vacuum and pressure filters), centrifuging, and warm air drying in fluidized-beds reactors¹. Bituminous coal produced at the Goedehoop Colliery typically contains 3% inherent moisture. The < 5 mm fine coal fraction is dewatered by centrifuging, resulting in 20–23% residual free moisture. The target for total moisture being 15% implies that free moisture should be reduced to some 12%.

Common methods used to lower the fine-coal cake moisture include the addition of suitable chemicals, either flocculants to produce larger coal particles, or surfactants to modify the coal surface-water interface². Various models as to the beneficial role of surfactants and the likely mechanism of improved drainage are advanced; none, however, is as yet conclusive³.

Probing tests were carried out at the Goedehoop Colliery, a division of Anglo Coal located in Witbank, to observe the effect on residual free moisture of two different surfactants that were added to the fine-coal feed to the centrifuge. The results obtained by this limited and rather unsophisticated plant-scale testwork were first presented at a student colloquium⁴. The presentation here is meant to elicit some discussion from a wider audience because of the rather interesting findings.

Coal, water and surfactants

Coal is a sedimentary rock subjected to metamorphic alteration, in the course of which its chemical composition changed: with

* Goedehoop Colliery, Witbank

† Technikon Witwatersrand, Johannesburg.

© The South African Institute of Mining and Metallurgy, 2004. SA ISSN 0038-223X/3.00 + 0.00. Paper received Jan. 2004; revised paper received Mar. 2004.

Investigations into the reduction of moisture in fine coal by plant tests with surfactants

increasing coalification, a progressive enrichment of the coal substance in carbon of organic origin occurred. The various ranks of coal are represented by materials such as peat, lignite, bituminous coal, and anthracite, with graphite being the end member of the series. The carbon content increases in this order.

While coal thus consists mainly of carbon in various forms (for example, as condensed benzene rings), it also contains various hetero-atoms and functional groups, of which hydroxyl and keto groups form easily on the surface as a result of oxidation; their presence affects to some extent the physical behaviour of the coal surface. Finally, a certain amount of mineral matter remains as part of the coal even after washing. In the case of upgraded fine coal this would be little and should not affect the surface properties to any great extent.

Other than in its degree of coalification, the organic matter in coal itself is rather inhomogeneous, consisting of various components with distinct chemical and physical properties referred to as macerals. They are the product of the parent organic matter and their definition is based on microscopic examination. Chemical and physical properties of the macerals, such as elemental composition, moisture content, hardness, density and petrographic features, differ widely and change with degree of coalification. However, the macerals are said to play only a minor role in affecting the surface properties of coal⁵.

The properties of coal, in particular the role of the coal surface, depend on the fineness of the coal particles: Fine (<0.5 mm particle size) or ultrafine (<0.1 mm) coal behaves differently from coarse coal. The aspect of the coal-water interaction is especially affected by the coal size: among others things, sufficient drainage of water from a cake made

up of fine coal, as obtained by mechanical dewatering processes, poses a problem. Here, the nature of the coal surface is believed to come into play.

Water is a good solvent and has a relatively high boiling point. These properties are based on the water molecule being strongly polar. Another property related to water is the strong internal attraction or association of molecules in the liquid, i.e., its high surface tension.

A molecule in the centre of a beaker of water is attracted to all of its immediate neighbours by short-range van der Waals forces, with an equal pull in all directions. The molecules on the surface, however, experience unbalanced attractive forces, which result in a net inward pull or surface tension. Water therefore tends to seek the minimum surface area per unit of volume, and, if not contained, forms spherical droplets. This characteristic of water makes it behave as though it were covered with an invisible elastic membrane (illustrated by a water strider walking on the water surface).

Surfactants can be briefly defined as materials that reduce the surface tension of water at low concentrations (hence also the term tensides). They achieve this because the structure of their molecules consist of a hydrophobic tail (long-chain hydrocarbons) and a highly polar, ionic hydrophilic head. Typical surfactants would thus be soaps (e.g., sodium stearate, where the head would consist of the $-\text{COO}^-$ group) or modern synthetic detergents (e.g., sodium lauryl sulphate, where the head would consist of the $-\text{SO}_4^{2-}$ group). A similar effect is achieved with NH_4^+ or pyridinium salts of longer-chain organic compounds. In the former case, one speaks of anionic, in the latter of cationic surfactants.

Surfactants function by modifying the forces at phase

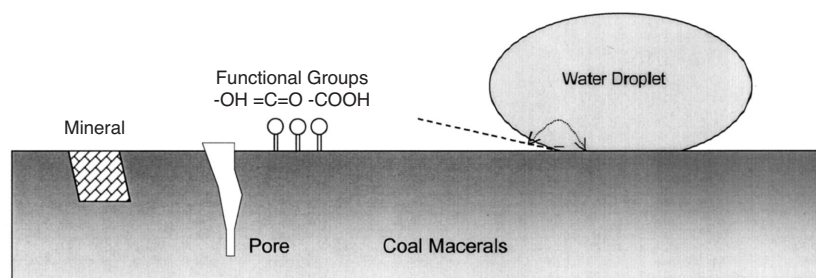


Figure 1—Schematic representation of a coal surface

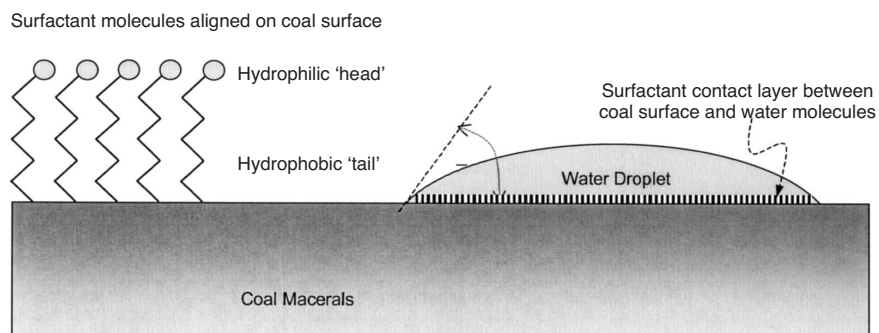


Figure 2—Surfactant on a (coal) surface

Investigations into the reduction of moisture in fine coal by plant tests with surfactants

boundaries: dissolved in water they lower the surface tension by aligning along the water–air interface, their hydrophilic heads sticking into the water phase and their hydrophobic tails into the air away from the water. In the bulk of the water they form agglomerates, so called micelles, with the tails pointing towards the centre and the heads towards the outside.

If solid surfaces are available, the surfactant molecules will adsorb on them, their orientation depending on whether the surface is hydrophilic (the heads will attach) or hydrophobic (tails attach); by doing so, surfactants change the nature of the solid surface. This can be quantified by the (receding) contact angle θ . As sketched in Figure 1, a hydrophobic surface causes a water droplet to shrink away from surface contact (non-wetting, large θ). If a surfactant is added, it turns the hydrophobic into a more hydrophilic surface, causing the water droplet to spread on the surface (wetting, small θ , see Figure 2). This effect can be easily observed by applying dish-washing liquid onto a greasy plate: instead of forming distinct spherical droplets, the water develops a smooth continuous film spread over the entire surface of the plate.

The interaction between coal and water

Quite a number of models have been advanced and are reported in literature, which describe the coal–water system, in particular trying to explain the interaction of coal surfaces with water with which they are in contact. This interaction is often modified by the addition of chemicals, such as collectors that promote the flotation behaviour of fine coal particles, flocculants that assist in thickening, and surfactants, some of which are said to enhance the drainage and therefore reduce the moisture content of the fine coal product.

While in general the physical processes that occur in the coal–water system are correctly predicted by the models, the role of surfactants in the drainage of water from fine coal is not yet fully understood and remains by and large unpredictable³. This has to do with the large number of

parameters that may influence the behaviour of the system, such as condition of the coal surface, type of surfactant, type of dewatering device, conditioning time, pH value, etc.

Since the present work deals only with rather simple plant tests, an equally simple concept was developed to help in designing the experiment and possibly interpreting its results.

Water

Free water associated with the fine-coal product after centrifuging is present (1) in cracks, and (2) as a surface film around the fine coal particles; both are dependent on the surface tension of water and increase if this is reduced. The majority of the retained water is, however, believed to reside in the interstitial voids formed between the fine coal particles after mechanical dewatering (e.g., filter cake or centrifuge product). This is illustrated by the sketch shown in Figure 3.

That this assumption is not unlikely can be shown by the following reasoning: a densest packing of (spherical) particles would leave 26% of the volume void. This is about the mass fraction of water found experimentally in most fine coal cakes and results because of the comparable densities of coal and water. Further, according to de Korte⁶, for small coal particle sizes, the voids become capillary cavities filled with water. Free drainage of the water is no longer possible since the attractive forces between the coal surface and the water become larger than the force exerted by mechanical dewatering.

Coal surface

The surface of coal is considered to be hydrophobic, i.e., water repelling⁷, notwithstanding the presence of functional groups and of the occasional embedded minerals. These are not believed to affect the coal–water interaction to any great degree⁵. A drop of water on a coal surface would thus exhibit a high receding contact angle θ , as indicated in Figure 1. Therefore, no continuous water film would develop on the surface and only a little water would be found in cracks. The water lodged in the voids between the particles would form

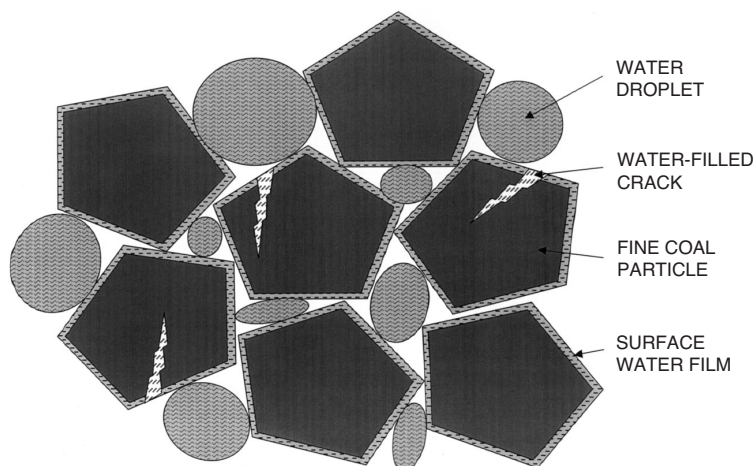


Figure 3—Schematic of dewatered fine coal cake

Investigations into the reduction of moisture in fine coal by plant tests with surfactants

rounded droplets in order to minimize contact with the coal surface and represent the bulk of the residual water after centrifuging.

Surfactants

Because of the high surface area presented to the dissolved surfactant, its molecules would first tend to become adsorbed on the coal surface. One would therefore expect that the free concentration of surfactant in water is initially low. However, once the available coal surface is covered by a (monomolecular) layer of surfactant molecules, the concentration in the water of free, i.e., non-adsorbed surfactant, will rise with the concomitant formation of micelles and a lowering of the surface tension of the water droplets. This then implies that a critical amount of surfactant must first have been added to a fine coal-water system before the surface tension of the retained water is affected.

Process description

Raw no. 4 seam coal is fed to the plant by conveyor belts at a rate of 550 t/h. This is then split by screening into >12 mm and <12 mm fractions. The larger fraction is cleaned in a Wemco drum vessel by heavy media separation, while the <12 mm is deslimed by further screening at 0.5 mm. The oversize fraction is treated in DSM cyclones; the <0.5 mm undersize fraction is directed to the fines treatment plant.

The fine coal is cleaned by spirals and the upgraded product sent to the classifying cyclones for removal of excess water and extremely fine particles. The cyclone underflow is fed to a static drains screen where unwanted oversize material is removed. The screened pulp forms the feed to the solid bowl centrifuge, which has replaced the previously used

screen bowl centrifuge. The feed to the centrifuge is some 120 m³/h of pulp at 40% solids, which calculates to some 55 t/h of solids, assuming a solid density of 1.5 t/m³.

After dewatering, the fine coal product is admixed to the coarser coal fractions for sale. The flowsheet of the fines treatment plant is depicted in Figure 4.

Experimental procedure

The test work was performed on a plant scale, with the plant operating at full capacity. Throughout the tests, which lasted one day, a steady feed rate of fine coal pulp to the centrifuge was assured. Whether the feed was also homogeneous throughout in terms of coal quality is, however, unknown.

The two surfactant samples were straw-yellow liquids supplied by Ondo-Nalco (now Impro-Chem) under the trade names Hydrogo 1 (S1) and Hydrogo 2 (S2). Despite several requests, no particulars of the surfactants were furnished by the supplier; all that is known from the accompanying Material Safety Data Sheet is that they are anionic surfactants*.

Before addition of surfactants to the feed slurry at the centrifuge inlet pipe commenced, a blank sample was taken at the discharge chute of the centrifuge to establish the base-line of water in product; this was found to be 20.1% moisture in fine coal.

The surfactants were applied with a dosing pump. Its various dosing rates were established using a measuring cylinder and converted from L/s to g/t of surfactant addition. On account of the high turbulence in the feed pipe, it is reasonable to assume that the surfactant became sufficiently mixed with the pulp before entering the centrifuge. The conditioning time is estimated to have been about 1 min.

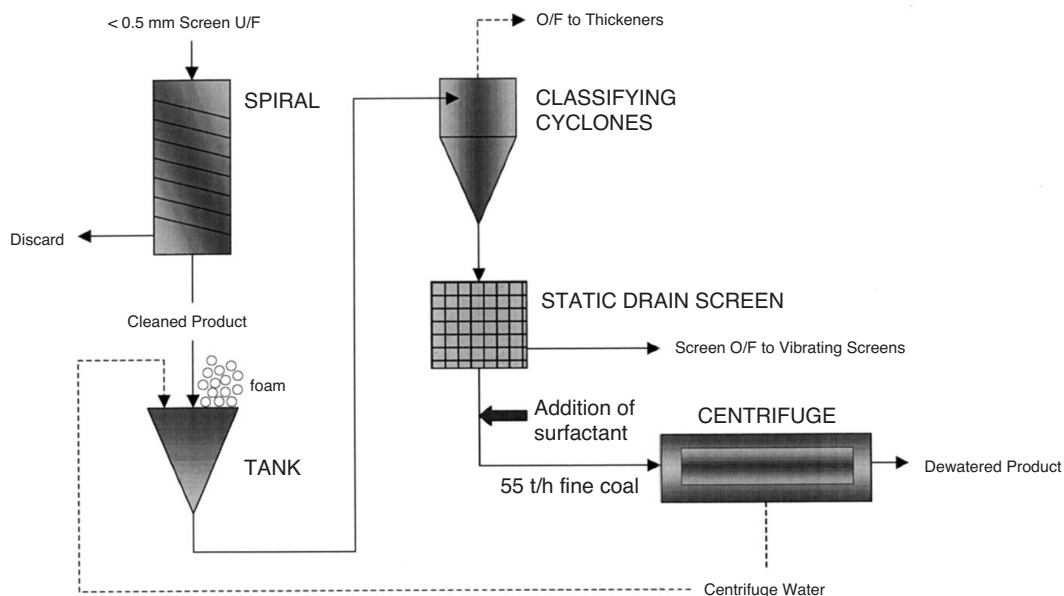


Figure 4— Flowsheet of the fines treatment plant

*Latest information indicates that these particular surfactants are no longer produced

Investigations into the reduction of moisture in fine coal by plant tests with surfactants

Surfactant addition extended over a period of 10 minutes for each chosen addition rate and surfactant type. As shown in the process flowsheet, there is a certain amount of water recycled from the centrifuge to the tank. To allow the system to clean itself of excess reagent from the preceding run, a 10-minute time interval was allowed before changing to the next surfactant addition rate. The procedure was that first surfactant S1 was added, starting with low addition rates that were then steadily increased to a maximum of 136 g/t. Once the series was completed, 20 minutes were allowed to pass before addition of surfactant S2 commenced and was subsequently carried out in the same manner.

After dewatering by centrifuging, 1-litre samples of fine coal were collected with a sampling scoop and stored in sealed containers. The moisture content of the coal samples was determined in the laboratory in the usual manner. Drying itself was carried out very carefully, viz. at a temperature not exceeding 40°C.

Results and discussion

The results of the two experimental series are presented in Figure 5, where the residual water content in the fine coal product obtained after centrifuging is plotted against the amount of surfactants S1 and S2 that were added to the centrifuge feed.

Generally, an effect could be observed that was more pronounced and more beneficial when surfactant S1 was used. Moisture in the fine coal product was significantly reduced from 20% to less than 17% at addition levels of around 80 g/t; the effect was substantially less and rather insignificant in terms of moisture reduction when surfactant S2 was used.

More interesting than this general trend, however, is the rather complicated 'fine structure' of the surfactant addition versus moisture response, which, moreover, holds for both surfactants. At low additions in the region of 15 g/t, a sudden significant increase in moisture to some 22% occurred, followed within a very narrow range of increased reagent concentration by an equally sudden decrease to below 18% moisture.

This sharp 'tooth' is followed by an extended hump of higher moisture levels when the reagent addition is further increased, only to dip down to low moisture levels of 16.5% (S1) and 18.5% (S2) at about 70–80 g/t addition of surfactant. Finally, when the reagent addition is increased to 100 g/t and beyond, the moisture content climbs up again, to eventually reach the level of the blank sample at the maximum tested addition of surfactant of 136 g/t.

This undulating response of the moisture content to increasing additions of surfactant is considered genuine, as it is closely followed in both test series, i.e., when either S1 and S2 surfactants were used, and because the respective tests were carried out at different times. That the observed effect is not spurious is further confirmed by similar 'ups and downs' of moisture reported in literature³.

Interpretation of the results is difficult. It must be remembered that these were obtained from single plant tests, which were not repeated nor followed by any further scientific investigations that could have shed light on possible mechanisms. Also, the experimental parameters were not as well defined as they would have been had the test work been carried out in a laboratory. The following attempt to make sense of the results is therefore purely speculative and based on the concept postulated above of the interaction between coal surface and water in the presence of surfactants.

If small quantities of a surfactant are added to a pulp made up of fine coal and water, the molecules will tend to distribute between the aqueous phase, in which they dissolve, and the coal surface, onto which they adsorb. Depending on the type of surfactant, adsorption of 70% and 90% onto the solid substrate surface has been reported³. According to the concept presented earlier, the tendency of surfactant molecules to become adsorbed implies that the originally hydrophobic coal surface becomes increasingly more hydrophilic. (This is in contrast to de Korte² who states that 'adsorption of the surfactant on the coal surface will render the coal more hydrophobic ...'; it is difficult to accept this. However, he continues by saying 'Should the concentration of the surfactant be increased, a point will be reached

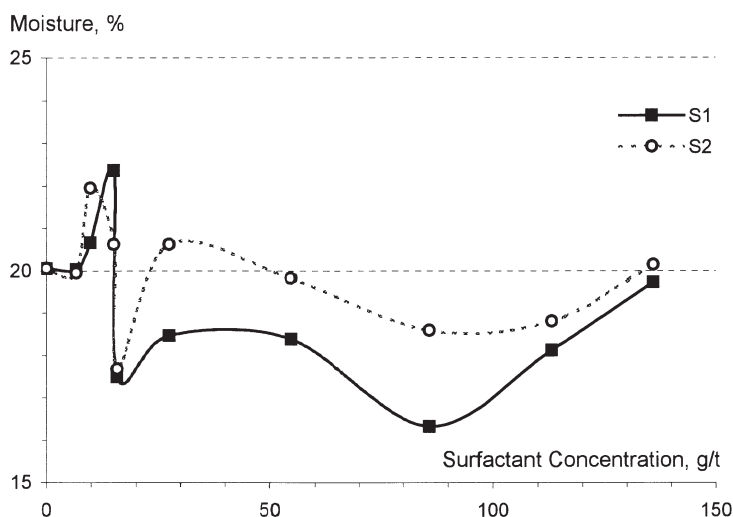


Figure 5—Residual moisture in fine coal after centrifuging as a function of surfactant addition

Investigations into the reduction of moisture in fine coal by plant tests with surfactants

where the adsorption of surfactant on the coal surface may reverse orientation. This will result in the coal surface again becoming hydrophilic.')

The result of an increased hydrophilic character is that a water film will form on and cling to the coal surface; thus, the residual moisture under conditions of low-surfactant concentration will increase by that additional amount of water. This may explain the observed initial increase in moisture up to an addition of 15 g/t surfactant.

The subsequent sudden decrease in moisture at an only slightly higher surfactant addition of 16 g/t, points to some critical value being reached that causes a dramatic change of regime. It is surmised that this may be the completion of the formation of a monomolecular layer of surfactant molecules on the available coal surface. If one assumes that initially nearly all surfactant molecules adsorb on the coal surface, this would be the moment when free surfactant becomes available to reduce the surface tension of the occluded water phase.

It was postulated earlier that the majority of moisture in the coal product is due to water droplets being retained in the inter-particle voids. Because of the high surface tension of water, the droplets are 'caged in', as it were, and drain only with difficulty. This situation would change if the surface tension is reduced by free surfactant: the droplets would form a film that drains much more readily. The effect would be similar to drying dishes: water droplets tend to tenaciously cling between the prongs of a fork; however, when some dish-washing liquid is added, the droplets change into a water film that drains immediately and leaves a near-dry fork. The water occluded between the coal particles would thus become more fluid by virtue of the reduced surface tension and be squeezed out through the narrow channels of the cavities by the gravity forces imparted by the mechanical dewatering devices.

In this picture, the cohesion between the bulk of water contained in the droplet, and the water layer attached to the hydrophilic heads of the surfactant layer (which in turn is adsorbed on the coal surface), must be ruptured. It is postulated that this is readily done and little shearing force would be needed to make the water layers slip and thus become detached from each other.

The explanation advanced here of the observed reduction in moisture upon addition of surfactants is admittedly rather primitive and not supported by measurements; it may thus be difficult to defend. It also fails to explain the undulating nature of the moisture content when more surfactant is added. Here, changing ζ -potentials or multilayer adsorption of surfactant molecules may come into play, which would change the interaction between water and coal surface. It is, however, believed that the steady increase in retained moisture at high dosages of surfactant can be satisfactorily explained by an increased viscosity of the liquid water phase that would make difficult the ready drainage of interstitial water.

On the practical side, foaming was observed during the tests after addition of surfactants to the pulp. This is indicated in Figure 4 for the cyclone feed tank. If surfactant addition had been maintained for any length of time (rather

than for only ten minutes), surely froth would also have formed downstream of the cleaning cyclone overflow. This would be undesirable as it could interfere with the smooth operation of subsequent process steps. It is not clear at present how this problem could be solved. One would be loath to redirect the water that is returned from the centrifuge or, alternatively, destroy the contained excess surfactant by adding antifoaming agents.

For want of relevant figures, no economic assessment has been attempted. It is, however, felt that surfactant additions in the order of 100 g/t may turn out not to be financially justified in view of the moderate moisture reduction achieved.

Based on the results reported here, the moisture reduction from some 20% to about 16–18% retained free water achieved with surfactant S1 must be considered as rather disappointing; surfactant S2 was not effective at all. At this stage, thus, use of either of these surfactants cannot be recommended.

On the other hand, the findings of the reported test work are regarded as sufficiently interesting to merit further investigations. These should, however, be conducted under more controlled conditions (i.e., preferably in the laboratory) and make use of physical methods such that the nature of the interaction between coal and water can be better defined.

Acknowledgements

I wish to thank the management of Goedehoop Colliery (a division of Anglo Coal) for their support and their permission to publish the results reported here.

The encouragement obtained from the staff of the Technikon Witwatersrand, Johannesburg, to publish the results of research carried out in industry is highly appreciated. In particular I wish to thank Mr Des Bell, Head of the Department of Extraction Metallurgy, Mr Malcolm Wilkinson and Dr Robert Haegele for their assistance in preparing this publication.

Very much appreciated is the professional advice received from Mr G J de Korte, Council for Scientific and Industrial Research, Pretoria.

Thanks are also due to Messrs. Foster Nkuna and Mpho Monageng of Goedehoop Colliery for their contribution.

References

1. Lehigh Energy Update 2002, vol. 20, no. 2, p. 1.
2. DE KORTE, G.J. Dewatering of fine coal—chemicals to aid the process, Literature review for the Mine Managers Association meeting, May 11, CSIR: 1990.
3. Singh, B.P. *et al.* Use of surfactants to aid the dewatering of fine clean coal, *Fuel*, vol. 77, no. 12, 1998. pp. 1349–1356.
4. SAIMM Student Colloquium, October 2003, Johannesburg.
5. BOURGEOIS, F. *et al.* Fundamentals of fine coal dewatering, Australian Coal Research Ltd., Project C3087.
6. DE KORTE, G.J. Dewatering of fine coal—Progress Report No.1, Coal Tech 2020, CSIR, Pretoria, January 2000.
7. LASKOWSKI, J.S. Flotation and Fine Coal Utilization, Seminar Notes, University of Cape Town, 2003. ◆