R & D NOTES

Role of Surface Effects in the Dewatering of Alumina Trihydrate

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INTRODUCTION

The dewatering of aqueous mineral slurries such as coal (Silverblatt and Dahlstrom, 1954; Nicol et al., 1980), clay (Wright and Kitchener, 1976; Oxford and Bromwell, 1980), iron ore (Sastry et al., 1981; Kobler and Dahlstrom, 1980), and gypsum (McCall and Tadros, 1980) has received considerable attention in the scientific literature. By contrast, less interest has been shown in the dewatering of the alumina trihydrate slurries produced in the Bayer process, despite the importance of the product and the need to dewater efficiently both to insure product purity and to reduce energy demand in the subsequent calcination step.

This note presents the results of a preliminary investigation of the factors underlying the dewatering of industrial alumina trihydrate slurries by conventional vacuum filtration. The role of humic contaminants present on the surface of slurry particles is studied and the extent to which pH and the addition of surface active agents can improve dewatering is investigated.

The experimental results obtained are evaluated in terms of surface effects and by reference to the Laplace-Young equation (Young, 1805):

$$\Delta P = \frac{2\gamma_{LA}\cos\theta}{r} LS \tag{1}$$

This equation, which relates the pressure necessary to drain a capillary to surface tension forces and a nominal capillary radius, has been used previously to quantify dewatering phenomena (Pearse and Allen, 1981).

EXPERIMENTAL

The alumina trihydrate used (SA 300 $m^2 \cdot kg^{-1}$) was typical industrial filter residue and was provided as a moist cake by Alcoa of Australia Ltd. Its screen analysis is given in Table 1.

The filtration apparatus consisted of a 0.1 m dia. Buchner funnel fitted with Whatman 41 filter paper, connected to a rotary vacuum pump, and mounted on an electronic balance. Previous workers (Henderson et al., 1957; Baker, 1976) have shown that such equipment can provide a good indication of the effect of filtration parameters, provided the solid does not sediment readily. In addition, it provides a good analog of the rotary table filter used in the alumina industry.

The experimental procedure involved reconstituting the alumina trihydrate with distilled water into a 60 wt.% solids slurry (this being typical of industrial practice) and, by the addition of hydrochloric acid or sodium hydroxide, adjusting the pH of the slurry to the desired level. The thoroughly mixed slurry was then poured onto the filter deck, the vacuum system to the flask opened, and the balance printer actuated. Permeability of the deposited cake was determined by passing 0.5 kg of pH-adjusted wash water at constant suction pressure (700 mm Hg). During this step care was taken to ensure solution coverage of the top surface of the cake. Dewatering characteristics of the cake were measured by stopping the addition of wash water and noting the rate of efflux of water from the cake over a period of 4 min from the time when the level of the solution dropped to the top surface of the cake. Residual cake moistures were determined after overnight drying at 110°C, with moisture content being expressed as:

TABLE 1. SIZE DISTRIBUTION OF ALUMINA TRIHYDRATE

Size, μm	Wt.%
+180	2.0
+ 150- 180	4.4
+ 125- 150	23.8
+ 106- 125	26.2
+ 90- 106	19.4
+ 71- 90	15.2
+ 63- 71	4.8
−63	4.2
Composite total	100.0

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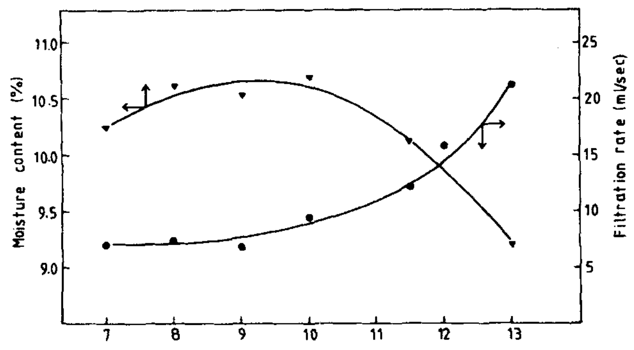

Figure 1. Moisture content of filter cake (▼) and filtration rate (●) as a function of the pH of the slurry.

$$\text{Moisture (\% wt.)} = \frac{\text{Wet weight} - \text{Dry weight}}{\text{Wet weight}}$$

A series of experiments was carried out in which the pH of the slurry was varied from 7 to 13, with the pH of the wash water held at 11, and at a constant slurry pH (=12), but with surface active agents added to both the wash water [anionic surfactant—sodium di-iso-octyl sulfosuccinate (Harcros)] and to the slurry prior to cake laydown [cationic surfactants: primary amines C_8 (Hoechst); C_{12},C_{18} (Harcros)—prelaydown agitation time 4 min]. All runs took place at 293 ± 2 K.

Zeta potentials were measured using a Micromeritics Zeta potential analyzer. For measurements in the presence of surfactant, a conditioning time of 4 min was employed as in the dewatering experiments.

RESULTS

Effect of pH

Figure 1 shows the variation in the residual moisture content in the cake and the cake permeability as a function of pH of the slurry as adjusted before cake laydown. It is apparent that increasing the pH of the slurry from 7 to 13 leads eventually to a marked reduction in the residual moisture content, which is related to an increase in cake permeability.

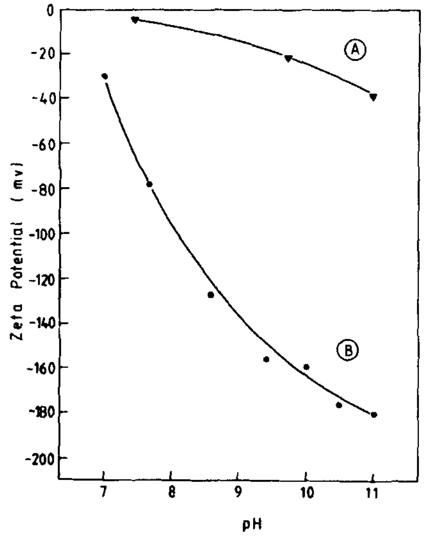

Figure 2. Zeta potentials of alumina trihydrate particles as a function of pH. ▼ Particles prewashed with methanol and hot water. ● Particles unwashed.

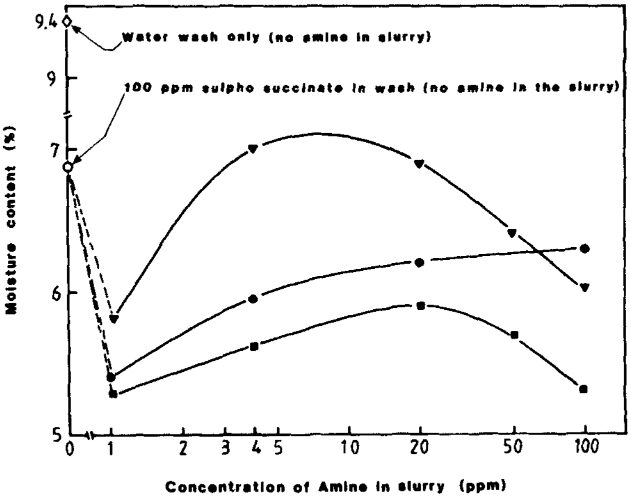

Figure 3. Moisture content of filter cake as a function of amine concentration used in slurry pretreatment for wash water containing 100 ppm di-iso octyl sulfosuccinate. ▼ C_{18}, ● C_{12}, ■ C_8 primary amines. ○ No amine pretreatment and 100 ppm di-iso octyl sulfosuccinate in wash. ◇ No amine pretreatment and no surfactant in wash.

Particle Surface Charge

Figure 2 shows the variation in surface charge (zeta potential) of both cleaned and industrial alumina trihydrate slurries with pH. Curve *A* is for a sample that had undergone a thorough hot water and hot methanol washing procedure, previously shown (Jayaweera, 1981) to be an effective method of removing adsorbed organic material from the oxide surface. An increase in pH leads to a small increase in the negative surface charge on the particles and is consonant with an adsorption of hydroxyl species onto amphoteric surface sites.

Curve *B*, by comparison, shows a strong variation in zeta potential with pH. The much higher particle charge on the industrial (unwashed) sample can be attributed to the presence of surface-adsorbed humic material. Schnitzer and Khan (1972) have shown that humic material of this type contains a number of functional groups, predominantly carboxyl, but also phenolic, alcohol, carbonyl, and methoxyl species. Above pH 5, the humic material becomes negatively charged and confers a high zeta potential. The magnitude of this charge is such that many of the chemical and physical properties of alumina trihydrate at high pH may actually be dictated by the presence of this adsorbed organic material. Firth and Nicol (1981) have made similar observations on the effect of adsorbed humics on coal slurries.

Effect of Surface Active Additives on Filter Cake Properties

In this set of experiments primary amines were added to the slurry prior to cake laydown and 0.25 L of wash water was doped with sodium di-iso-octyl sulfosuccinate (concentration = 100 ppm; solution surface tension, 29.7 mN·m^{-1} at 293 K). This volume of wash water represents approximately 0.6 L wash/kg dry solids as compared to typical industrial practice, which is 0.4 L/kg. Figure 3 shows the effect of each of these treatments plotted vs. the concentration of amine added.

With no amine in the slurry and no surfactant in the wash water, the residual moisture content was 9.4 wt.%. With the sulfosuccinate surfactant in the wash water the moisture content dropped to 6.9%.

TABLE 2. ZETA POTENTIALS OF ALUMINA TRIHYDRATE IN THE PRESENCE OF PRIMARY ALKYLAMINES (pH 12.0)

Carbon Chain Length of Amine	Concentration ppm	Zeta Potential mV
Blank	—	−180
C_8	1	−192
	50	−178
	100	−192
C_{12}	1	−181
	50	−186
	100	−174
C_{18}	1	−182
	50	−180
	100	−184

This is consistent with the lowering of the surface tension (73 to 29.7 $mN \cdot m^{-1}$) that has occurred.

Where primary amines have been added to the slurry prior to cake laydown, in nearly all cases a lower residual moisture has resulted. The most interesting region of the plots is at low concentrations (0–2 ppm) where dewatering characteristics are excellent. Further work in the region is under way. The extent of dewatering shows some dependence on amine chain length. In other experiments with shorter chain length amines, such as butylamine and methylamine, the observed minimum is found at higher added amine concentrations (about 20 ppm).

Table 2 gives zeta potentials for samples of alumina trihydrate in various concentrations of long chain alkylamines. Within the limits of experimental error (±5%) no detectable change in zeta potential is apparent.

DISCUSSION

The high zeta potential of the particles comprising industrial alumina trihydrate slurries explains the dependence of dewatering on pH. With increasing pH, particle charge and particle repulsion increase, resulting in a more open cake and hence a larger r in Eq. 1. As a consequence, cake permeability and dewatering improve. Indeed, the inherent high pH of the Bayer process exerts a beneficial effect on dewatering, as does the presence of humic surface contaminants. Any day-to-day fluctuation in the amount of adsorbed organic matter could therefore significantly alter plant dewatering characteristics.

The addition of the anionic surfactant to the wash water improves dewatering. Because of its charge, this surfactant would not be expected to adsorb significantly on the particles. The role of the sulfosuccinate is therefore primarily to alter beneficially γ_{LA} in Eq. 1.

Although the primary amines used to treat the slurry prior to cake laydown are nominally cationic, at high pH levels it is likely that these amines are undissociated and exist as RNH_2 in solution (Smith and Akhtar, 1976). Hence it is the neutral species that is adsorbed on the alumina. This is confirmed by the negligible change in zeta potential that occurs. The role of the amine is therefore to alter the surface properties such that the contact angle (θ_{LS}) is changed. The amine addition is most effective at low levels corresponding to a monolayer cover or less. At higher concentrations it is believed that the very low solubility of the amines results in a self-association or micellar type of behavior, as opposed to association with the alumina trihydrate surface.

From this initial study it would appear that the formation of a filter cake with low residual moisture content can be assisted by adjusting process filtration parameters in accordance with Eq. 1. Because of the humic contaminants present, adjustment of pH will affect moisture retention. Likewise, the addition of an anionic, surface tension lowering surfactant will improve drainage. The most important observation, and not previously reported by other workers, is that the addition of an undissociated, nominally cationic surfactant can lead to surfactant adsorption and an increase contact angle with consequent improved hydrophobicity and dewatering potential. The quantity of this surfactant required is low, and it may be possible to choose a blend of surfactants for addition to the slurry prior to cake laydown to achieve both a lowering in surface tension and an increase in contact angle simultaneously. Further work is being directed toward elucidating the nature of adsorption onto the humic-contaminated alumina surface and to measuring the resultant contact angle.

CONCLUSIONS

Adsorbed humic species play a dominant role in determining dewatering characteristics of alumina trihydrate slurries in the Bayer process. By adding small quantities of surface active agents to both the slurry prior to cake laydown and to the wash water, it is possible to improve cake dewatering markedly. These results are in agreement with Young's equation for capillary drainage. Most significant from an industrial viewpoint is the relatively small additions of surface active agent required.

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NOTATION

γ_{LA} = liquid/air surface tension

θ_{LS} = liquid/solid contact angle

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