

Effect of hydrolysed aluminium treatment on rheological characteristics of α -alumina slurries

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This paper describes the process for the hydrolysed aluminium treatment (HA) on alumina surface and its influence on the rheological characteristics of alumina slurries. Three different commercial grade aluminas were provided with the surface treatment with hydrolysed aluminium using aluminium nitrate and hexamethylenetetramine (HMTA) under controlled conditions. The HA treatment increased the concentration of Al-OH surface sites resulting in higher H⁺ adsorption on the alumina surface. A highly concentrated (>55 vol%) electrostatically stabilized alumina slurry was prepared from HA treated alumina powders. The rheology of such slurry was studied and the results on the viscosity and yield stress are presented. The alumina slurries followed the Casson Model flow behaviour. The 'wet' and 'flow' behaviour of the alumina with and without HA treatment was also studied and the results are compared. The surface treatment showed the advantage of maintaining low viscosity and yield stress of alumina slurries even at higher solids loading (>55 vol%) that are prepared in the acidic aqueous medium. The results on viscosity and yield stress were compared with that of the polyelectrolyte dispersed system. © 2001 Kluwer Academic Publishers

1. Introduction

In ceramics processing, green body formation plays a critical role, otherwise the inhomogeneities present in the green ceramic lead to defects in the microstructure of the sintered ceramic [1]. Colloidal methods, in particular slip casting and gel casting have been recognized as a preferred way for producing defect free, reliable, high quality, near-net shape ceramic components [2–5]. However, in these processes control over slip properties with respect to concentration, viscosity and yield stress are very essential. One of the criteria is to have highly concentrated slurries with low viscosity and yield stress, so that the slurry flows into all parts of the intricate shape of the mould. In the case of alumina, highly concentrated dispersions are prepared either using polyelectrolyte dispersants (polyacrylates) or by adjusting pH, far away from the isoelectric point [6–9]. The stability of the alumina slurries prepared by pH adjustment using mineral acids is governed by the long range electrostatic repulsion between positive charges developed on particle surfaces due to the protonation of the Al-OH surface sites. In polyacrylate dispersed systems the particles are stabilized by both electrostatic and steric (short range) mechanisms.

The flow behaviour of slurry depends on particle size, size distribution, shape, surface area and surface

charge density of the powder [10–12]. The slurry prepared from the powder that are having lower particle size and surface charge density, but higher surface area showed an increased tendency for the formation of reversible flocs resulting in higher viscosity and 'shear thinning flow' behaviour which finally resulted in high yield stress. It has been reported that the viscosity and yield stress of alumina slurries prepared by pH adjustment using mineral acids were higher than that of its counterpart prepared by polyacrylate dispersant systems [13]. In our earlier work, on preparation of concentrated alumina dispersions in aqueous acidic medium for gelcasting using urea formaldehyde, we have proposed a surface treatment of alumina particle with hydrolysed aluminium [HA] in order to obtain higher solids loading and green density [14, 15]. The treatment enhanced the polyelectrolyte nature of the alumina surface due to the adsorption of poly nuclear aluminium ions $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{OH}_2)_{12}]^{7+}$ that are produced in the pH range 3.5 to 5 [16]. In the present paper, the effect of hydrolysed aluminium treatment on the three different commercial grade alumina powders are studied. The results on the surface charge characteristics, viscosity and yield stress were presented and discussed. The results are compared with the characteristics of polyacrylate dispersed system.

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TABLE I Characteristics of alumina powders

Powder designation	Alumina content (%)	Median particle size (μm)	BET surface area (m^2/g)	Density (g/cm^3)
MR-04 ^a	98.9	0.79	6.23	3.83
AKP-15 ^b	0.34	0.63	3.70	3.94
A16SG ^c	99.8	0.34	10.4	3.91

^aIndian aluminium company, Belgaum, India.

^bSumitomo Corporation, Tokyo, Japan.

^cACC-Alcoa Limited, Calcutta, India.

2. Experimental

Three α -alumina powders, A16 SG, AKP-15 and MR-04 were used in this study. The details of particle size, surface area and purity as supplied by the manufacturers are presented in Table I. Aluminium nitrate (AR, CDH Bombay, India) hexamethylene tetramine (Puram, Fluka, Switzerland) and Darvan 811 dispersant (Average molecular weight 5000, R.T. Vanderbilt Company Inc. Norwalk), a 43% solution of sodium polyacrylate were used. The double distilled water was used for the preparation of dispersions. The detailed procedure for the surface treatment of alumina is reported elsewhere [14]. The summary of the treatment involved the tumbling of alumina 80 wt% slurry in an aqueous medium with 2.5 mg/m² of aluminium nitrate and an equivalent amount of hexamethylenetetramine as base generator for 12 h in a polyethylene container using zirconia balls. The slurry pH was adjusted to 4 at the end of 36 h and centrifugally washed three times. The procedure was repeated for alumina without aluminium nitrate and hexamethylene tetramine for comparison. In another experiment, alumina dispersions using Darvan solution was prepared at pH 9. The concentration of sodium polyacrylate was optimized as 0.3 mg/m².

A relative measure of the surface charge characteristics of as-received and HA treated alumina was determined by the titration method as reported by Whittman and Feke [17]. Accordingly, alumina 5 wt% aqueous suspension was prepared at pH 4 and was titrated against 0.01 N NaOH solution to pH 8 (pH 8 was assumed as the iso electric point of alumina). The equivalent volume of the suspension medium was taken as the reference solution. The difference between the amount of titrant necessary to produce the same pH value for the alumina suspension and the reference solution is attributed to the desorption of protons complexed with the surface sites of the particles.

The experiment on the determination of the 'wet' and 'flow' points of alumina with and without surface treatment was done using the procedure reported by H. Okamoto *et al.* [18, 19]. In a typical experiment alumina 20 g was taken and the water was added from a burette. The quantity of water required to form a lump was read as the 'wet point' and the quantity of water at which the lump starts flowing was read as the 'flow point'.

The viscosity of alumina slurries were measured at different shear rates ranging from 4.65 to 93 s⁻¹ in a Brookfield Viscometer (LVT/RVT) using SC4-21/13R

spindle. The apparent yield stress of the slurries were calculated from viscosity data by a graphical method [20].

3. Results and discussions

3.1 Surface charge characteristics

Fig. 1 shows the surface charge characteristics of all the three alumina powders in the as-received condition and also after the HA treatment in the pH range 4 to 8. In all the cases, the HA treated alumina showed a higher H⁺ adsorption capacity as well as the surface charge density compared to the untreated counterpart. The increase in surface charge density during HA treatment is more in the case of A16 SG and MR-04 alumina than in AKP-15. A16SG and MR-04 aluminas after HA treatment, showed ~50% increase in surface charge density at pH 4 and the same was only ~15% for AKP-15. The lower level of increase in surface charge density AKP-15 alumina upon HA treatment was because of its higher H⁺ adsorption capacity in the untreated form. In all the cases it was observed that the H⁺ adsorption capacity is low at pH near isoelectric point of alumina and significantly high when the pH becomes less than 5. The higher H⁺ adsorption is due to the additional Al-OH sites generated by the adsorption of [AO₄Al₁₂(OH)₂₄(OH)₁₂]⁷⁺ ions on the surface of alumina produced by the hydrolysis of aluminium nitrate.

The 'wet' and 'flow' point characteristics of alumina with and without HA treatment is presented in Table II. The surface of the HA treated aluminas gets wetting and consequently started flowing in minimum quantity of water where as the untreated one required higher amount of water for wetting and also to induce flow. The difference in wet and flow points for the treated alumina is comparatively lower than the untreated one which further indicates that the surface treatment imparts better dispersibility in minimum quantity of aqueous phase with suitable flow characteristics. It is already reported that if the difference between wet and

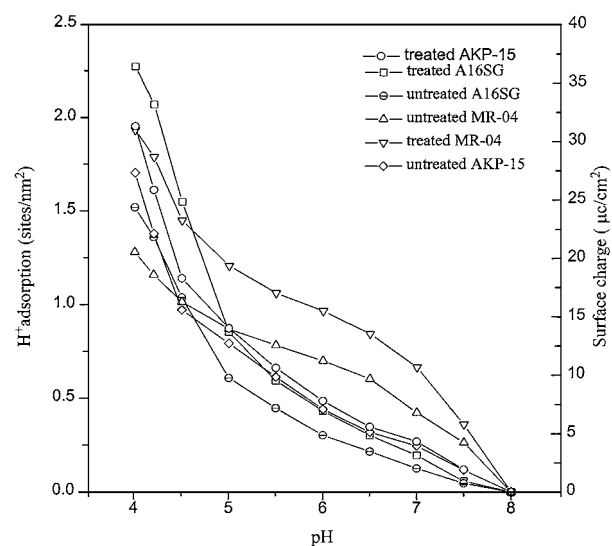


Figure 1 H⁺ adsorption and surface charge characteristics of HA treated and untreated alumina powders.

TABLE II Wet and flow characteristics of alumina powders

Sample	Wet point (ml/20 gm)	Flow point (ml/20 gm)	Difference between wet and flow points (ml/20 gm)	Thickness of water layer at the flow point (nm)
Untreated MR-04	3.2	3.7	0.5	29.69
HA treated MR-04	3	3.4	0.4	27.28
Untreated AKP-15	3	3.4	0.4	45.94
HA treated AKP-15	2.9	3.1	0.2	41.89
Untreated Al6SG	3	3.8	0.8	18.26
HA treated Al6SG	8	3.1	0.3	14.9
Al6SG using Darvan	3.1	3.6	0.5	17.3

flow point is as low as possible, then a better dispersion could be obtained [18]. The lowering of wet and flow points is due to the increased surface charge density of treated alumina powders. The thickness of the water layer at the flow point, which was calculated by dividing the volume of water required to induce flow with the total surface area of the powder, decreases with an increase in the surface area of the powders and the value is lower for HA treated powder than the untreated counterpart.

3.2 Rheological characteristics

Fig. 2a and b shows the change in viscosity of alumina with and without HA treatment at different shear rates. It was observed that the dispersed slurries containing at lower solids loading showed shear independent flow behaviour (Newtonian) which changed to ‘shear thinning’ (pseudoplastic) at higher solids loading and the same become ‘shear thickening’ (dilatant) above a certain critical concentration. In the present case, alumina slurries (>50 vol%) showed shear thinning flow behaviour and the extent of this behaviour was decreased considerably during HA treatment. Also the HA treated alumina slurry showed lower viscosity than the untreated counterpart. The transition of the slurry rheology from shear thinning to dilatant occurred at a solids loading near the flow point. Fig. 3a and b is the plot of square root of shear rate versus square root of shear stress of alumina slurries. In all the cases, alumina slurries (>50 vol%) showed Casson model flow behaviour and follow the mathematical expression [20].

$$\tau \frac{1}{2} = m\gamma \frac{1}{2} + \tau_y \frac{1}{2}$$

where τ is the shear stress, γ is the shear rate and τ_y is the yield stress of the slurries. This is a typical flow characteristic of a pseudoplastic systems. The yield stress determined from the above plot gives lower values for HA treated alumina than the untreated one.

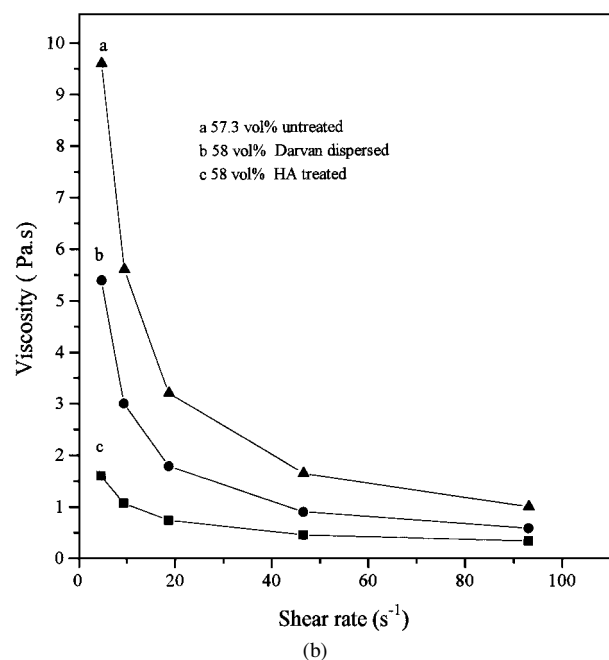
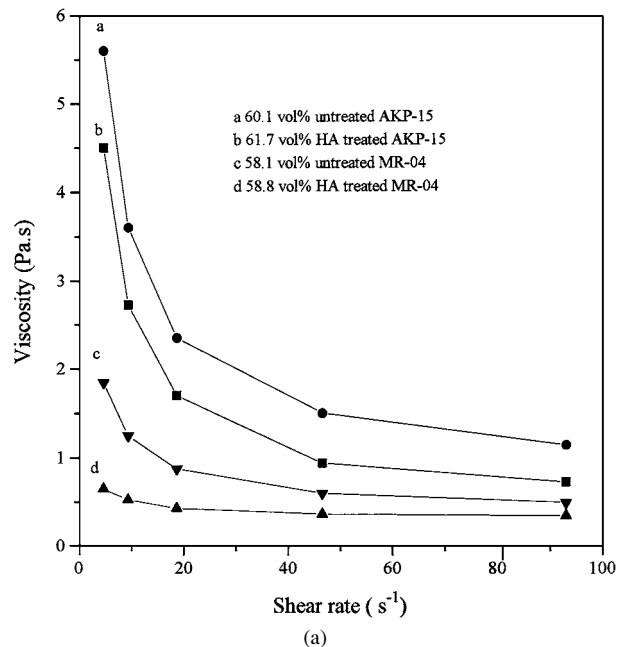


Figure 2 (a) Viscosity versus shear rate of AKP-15 and MR-04 alumina slurries. (b) Viscosity versus shear rate of Al6SG alumina slurries.

3.3 Effect of solids loading on yield stress

The dependence of yield stress values on solids loading of treated, untreated and Darvan dispersed alumina slurries are presented in Fig. 4a and b. Initially, the yield stress value increased gradually with an increase in the volume fraction of solids and above a critical fraction a rapid increase in yield stress was occurred. The critical volume fraction at which the yield stress started increasing rapidly was lower for the untreated slurries compared to the treated one. The difference in yield stress between the treated and untreated slurries is small at a lower volume fraction of solids and significantly higher at higher solid content. Al6 SG alumina slurries showed a higher value of yield stress than AKP-15 and MR-04 slurries. However, the decrease in yield stress after HA treatment was more

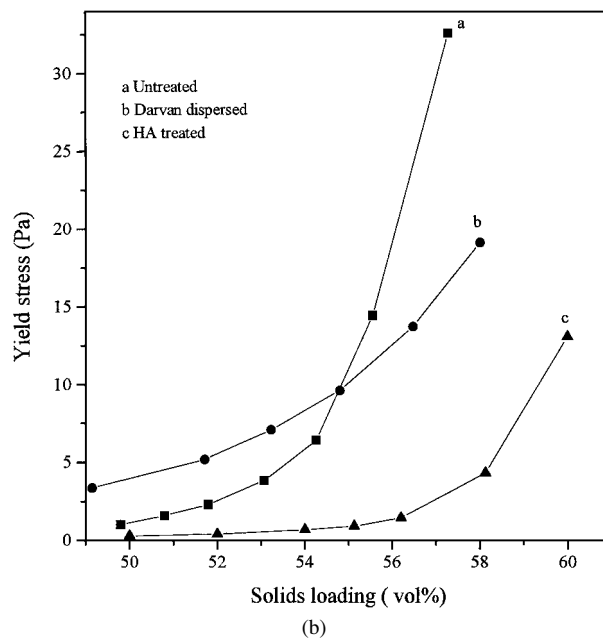
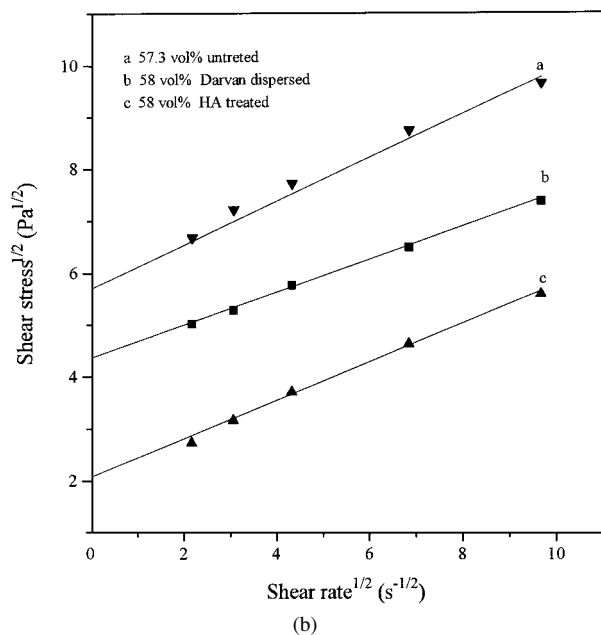
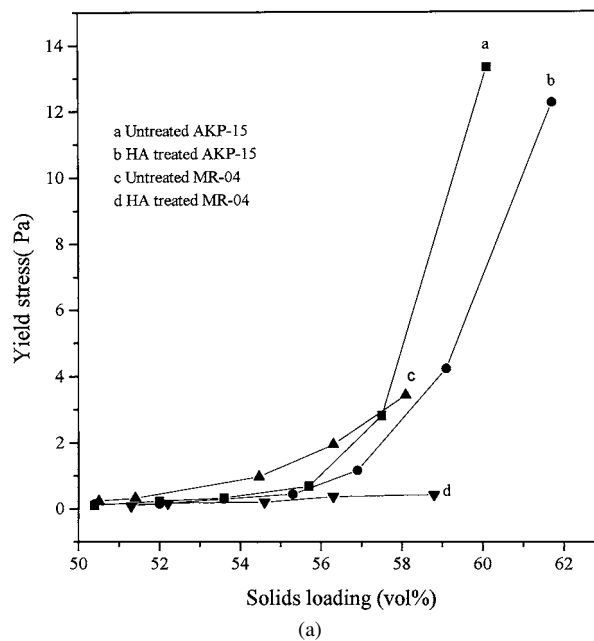
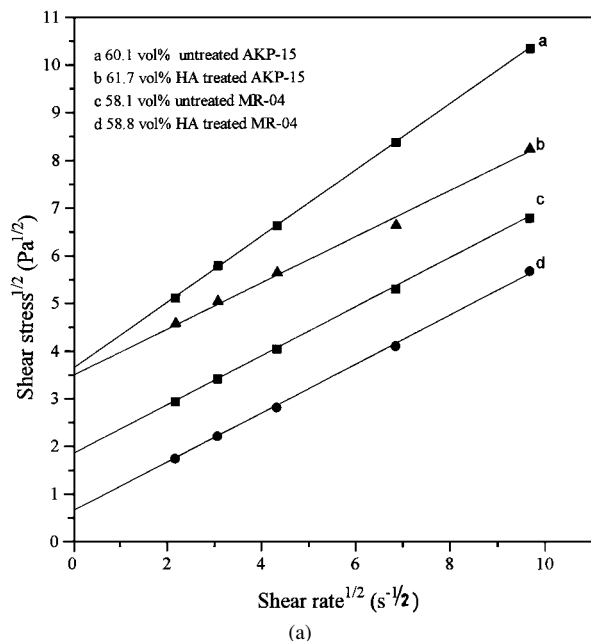


Figure 3 (a) Square root of shear rate versus square root of shear stress of AKP-15 and MR-04 alumina slurries. (b) Square root of shear rate versus square root of shear stress of Al6SG alumina slurries.

Figure 4 (a) Effect of solids loading on yield stress of AKP-15 and MR-04 alumina slurries. (b) Effect of solids loading on yield stress of Al6SG alumina slurries.

in the case of Al6SG and MR-04 aluminas, in accordance with their increase in surface charge density. The yield stress value of Al6SG and MR-04 alumina slurries showed $\sim 80\%$ decrease above 55 vol%, whereas the AKP-15 alumina slurries showed $\sim 50\%$ decrease above 59 vol% during HA treatment. P.A. Smith *et al.* reported that the repulsion barrier has definite effect on flocculation and in the case of large particle–small particle and the small particle–small particle, the repulsion barrier is much lower than the large particle–large particle repulsion barrier. Therefore tendency for flocculation is much more in the slurry systems that are having fine particles [11]. The high yield stress observed for dispersions of Al6SG alumina compared to AKP-15 and MR-04 counterparts is because of its fine nature. The decrease in yield stress, especially at higher

solids loading, during HA treatment is attributed to the increase in inter-particle potential resulting from enhanced surface charge density. The smaller difference in yield stress between treated and untreated alumina slurries at lower volume fraction of solids suggests that the surface hydroxyl groups present in as-received aluminas are sufficient for the dispersion of the powders in acidic medium at a low volume fraction of solids.

The slurry prepared from Al6SG alumina using Darvan showed lower viscosity and yield stress than the untreated slurry at solids loading above 55 vol%. However, at lower solids loading (< 55 vol%), the untreated slurry showed lower viscosity and yield stress than the Darvan dispersed system. It appears that in electrosterically stabilized slurries, the steric part of the electrosteric stabilization being short range is

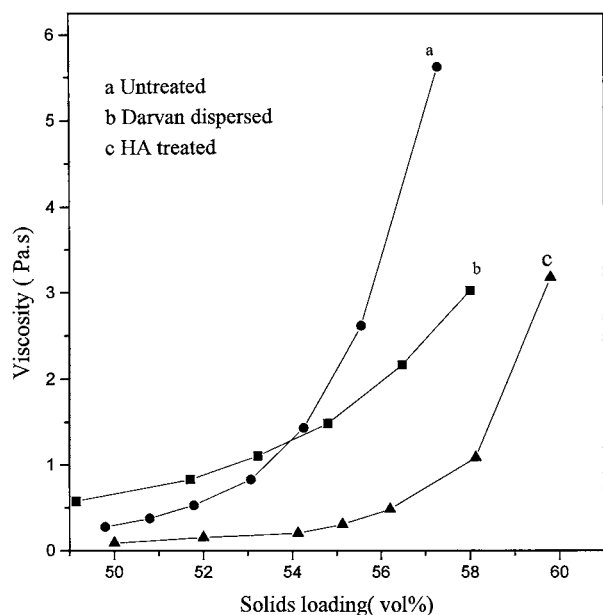


Figure 5 Effect of solids loading on viscosity of Al6SG slurries.

effective only at higher solids loading (>55 vol%), resulting in lower viscosity and yield stress than electrostatically stabilized untreated alumina slurry. Also at lower solid fraction, dispersion is achieved by the electrostatic part of the electrosteric stabilization which is less effective than electrostatic stabilization in untreated powder. However, the HA treated slurry showed a lower viscosity and yield stress than Darvan dispersed system at all solids loading. The effect of viscosity on untreated, HA treated and Darvan dispersed Al6SG alumina is shown in Fig. 5.

4. Conclusions

The effect of hydrolysed aluminium treatment on the rheological behaviour of the three submicron commercial alumina powders were reported. The hydrolysed aluminium treatment increases the surface charge density of aluminas resulting in a decrease in viscosity and yield stress of concentrated slurries prepared in acidic aqueous medium. The concentrated slurries followed the Casson model flow behaviour. Al6SG and MR-04 aluminas showed ~50% and AKP-15 alumina showed ~15% increase in surface charge density during HA treatment. The decrease in yield stress upon HA treatment was ~80% for Al6SG and MR-04 alumina slurries at a solids loading above 55 vol% and ~50% for AKP-15 alumina slurries at a solids loading above 59 vol%. The viscosity and yield stress of the Darvan dispersed

Al6SG slurry is lower than the untreated counterpart at a solids loading above 55 vol% and higher than the untreated slurry at a solids loading below 55 vol%. The HA treated Al6SG alumina slurry showed a lower viscosity and yield stress than the Darvan dispersed system at all solids loading.

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