

pH Value Effects in Shear Rheology of Concentrated Alumina Suspensions*

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1 INTRODUCTION

The suspensions employed in ceramic processing are highly concentrated. These suspensions are normally known as slip or slurry in materials science and engineering. It is of great interest that concentrated suspension exhibit many of the phenomena of very dilute colloidal suspensions^[1]. This is probably because both the suspension systems have charged particles, so that the principles of colloid chemistry can be applied for them.

Wiese and Healy^[2] reported the zeta (ζ) potential of alumina as function of pH at different electrolyte concentration. Zeng and Rand^[1,3] showed the variations of ζ -potential of alumina with pH at a constant ionic strength (I) of 10^{-3} mol·L⁻¹. Large absolute values of ζ -potential are found to be at both ends of the pH scale. The nominal isoelectric point (IEP) is over the range of pH 7—9, which is termed as pH_{IEP}. The graph of ζ -potential versus pH is roughly symmetrical about the nominal pH_{IEP}. In an acid medium the absolute values of ζ -potential consistently remain comparatively high over the wide range of pH 3.5—7. Scales and his co-workers reported that the absolute values of ζ -potential decreased with the solid particle volume fractions (Φ_p , up to 0.3) of alumina suspensions^[4].

When fine powders are dispersed in water, small clusters of particles (plus enclosed water) are often formed in the suspensions, which are commonly called flocs^[5]. They are classified into soft agglomerate. Michaels and Bolger^[5] introduced the flocs structure indicator (C_{FP}) for very dilute suspensions: $C_{FP} = \Phi_F/\Phi_p$, where Φ_F is flocs volume fraction. The value of C_{FP} reflects the amount of trapped liquid in the floc or the openness of the floc structure, and thus can be

related to the floc size (r_F).

Michaels and Bolger^[5] showed that the basic flow units in a flocculated suspension were the flocs rather than the primary particles. Firth^[6] indicated that the basic shear diagram, shear stress versus shear rate ($\tau-\dot{\gamma}$), for the concentrated suspensions was plastic-pseudoplastic. Firth^[6] found that for the suspension with Φ_p up to 0.2, C_{FP} and Bingham shear yield stress decreased linearly with the increase in $1/r_F$, and they were inversely proportional to ζ^2 (the strength of interparticle force). Scales and his co-workers^[4] have recently developed a new model to study the relation of shear yield stress with ζ^2 for suspensions including $\Phi_p = 0.3$. Lange^[7] has pointed out that for a given alumina-water system, the apparent viscosity (η_A , at which the linear portion of the flow curve begins) is dependent mainly upon two factors: the ζ -potential and the Φ_p .

An ideal circumstance would be one in which the rheological properties of a given system could be accurately determined from the measurement of its electrokinetic and particle size characteristics, or vice versa. Unfortunately, despite the attentions of a number of workers in recent years, the quantification of the colloid chemistry-rheology association has remained largely unresolved^[4]. Most significant rheological parameters have had to be obtained experimentally until now. These rheological properties are critical, for example, in the optimization of ceramic wet processing^[7,8]. The concentrated suspensions can only be examined, however, qualitatively or at best semi-quantitatively at the present in most cases.

2 EXPERIMENTAL

Commercial Alcoa A16 alumina powder was used in

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the present work. It had a specific surface area of $9.2 \times 10^3 \text{ m}^2 \cdot \text{kg}^{-1}$, a calculated mean primary particle diameter of $1.6 \times 10^{-7} \text{ m}$; and a median particle size (D_{50}) of $4.6 \times 10^{-7} \text{ m}$ ^[1]. Alumina suspensions of $\Phi_p = 0.27$ with different pH values were prepared. A certain quantity of distilled water was mixed with different quantities and concentrations of either aqueous HNO_3 (GP grade) or ammonia (Analar) solution. The alumina powder was made into a paste with the diluted solution and then the paste was further thinned. The suspensions were rolled in 50 ml polyethylene jars overnight, using a grinding ball to powder weight ratio of 1:1, and then the pH values were measured. Counter acid or base was not used to adjust the pH to a given value, because this would lead to an increase in I and buffer effect in the suspensions.

The Haake RV2 Viscometer (NSE, Fisons, Germany) sheared a suspension between a cone-plate system. The viscometer was calibrated with the data measured by Carri-Med CSL 500 Rheometer (UK). The quantity of the concentrated suspension put on the plate was carefully controlled. The temperature of the suspensions between the cone and the plate was maintained at 294 K using the Haake RV2 Viscometer constant temperature bath. The η_A , the plastic viscosity (η_p), the extrapolated shear yield stress (τ_{EY}) and the apparent shear yield stress (τ_{AY}) were determined from the first single curve of the pseudoplastic, near Bingham flow curve, which was shown in the previous work^[1]. Barnes^[9] indicated that Bingham equation could only be applied over approximately a one-decade range of τ . In the present work, τ_{EY} was therefore extrapolated from the first part of the initial linear portion of the flow curve. τ_{EY} and η_p were chosen in this work to study rheological behaviour of the suspensions. These two parameters are experimentally more stable than τ_{AY} and η_A respectively, and therefore more precise results can be obtained.

3 RESULTS AND DISCUSSION

3.1 Variation of shear stress-shear rate curves with pH

Fig. 1 shows the variations of the τ - $\dot{\gamma}$ curves with the pH between 4.2 and 7.4. As the pH decreases from 7.4 down to 4.2, the slope of the η_p - $\dot{\gamma}$ curve generally decreases, which implies a corresponding fall in the η_p . There are strong repulsive interparticle forces when pH is low. A large ζ^2 corresponding to a small C_{FP} , results in a small τ_F . The τ_F is related with the ratio of the mass of particles to the amount of freely movable liquid in the system. With a decrease in this ratio, the effective separation among particles increases, and the decreased interference among par-

ticles causes a decrease in the η_p . A large ζ^2 and a small τ_F result in a low η_p , and vice versa. As the pH is away from the IEP, the ζ -potential increases, while the C_{FP} , the τ_F and the η_p decrease.

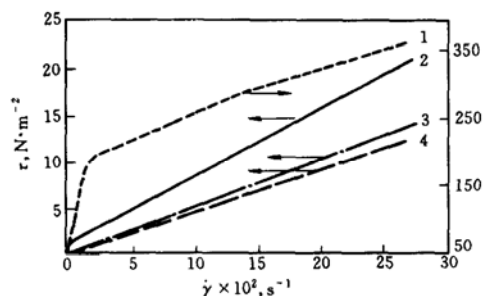


Figure 1 Shear stress-shear rate curves for Alcoa A16 alumina suspensions of $\Phi_p = 0.27$ with pH 4.2–7.4 pH: 1—7.4; 2—6.1; 3—4.8; 4—4.2

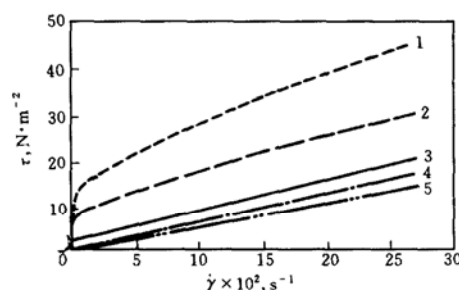


Figure 2 Shear stress-shear rate curves for Alcoa A16 alumina suspensions of $\Phi_p = 0.27$ with pH 1.3–3.8 pH: 1—1.3; 2—1.6; 3—3.4; 4—4.2; 5—3.8

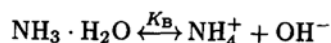
Fig. 2 shows the variations of the τ - $\dot{\gamma}$ curves with the pH from 3.8 down to 1.3. The η_p reaches a minimum at the pH around 4 and then increases with the pH being away from 4. The addition of either the acid or the basic electrolyte (HNO_3 or ammonia) to the alumina suspension results in two opposing effects on the absolute value of ζ -potential, i.e., an increase of the absolute value of ζ -potential caused by an increased surface potential resulting from higher H^+ or OH^- adsorption, and a decrease by reducing the thickness of double layer (κ^{-1}) under the higher I , according to the Debye-Hückel and Gouy-Chapman models^[10]. Beyond the points of full deflocculation, the ζ -potential must have failed with the increase in electrolyte concentration, thus, resulting in an observed increase in η_p . The results obtained from pH 9.3 to pH 11.6 are analogous to those shown in Figs. 1 and 2.

The fully deflocculated samples exhibit Newtonian characteristics, whereas most samples show pseudoplastic, near Bingham flow behaviour. Rheological data around the IEP within the pH 7.4–9.3 are difficult to obtain using the Haake RV2 Viscometer. The cone and plate of the Haake RV2 Viscometer must be

just off contact before the suspension is loaded into the space between them. The concentrated alumina suspensions at the pH about pH_{IEP} , however, are very sticky and difficult to spread on the plate of the viscometer. An over loaded concentrated suspension may force the cone upwards. This causes an increase in the pressure on the suspension, and consequently a change in rheological behaviour. A large experimental deviation might arise and the rheology measurements around the pH_{IEP} were not pursued further. The concentrated suspensions at the pH around the pH_{IEP} show a very complex rheological behaviour, while they have very high η_A and τ_{AY} .

3.2 The plastic viscosity versus pH

The η_p -pH curves for the concentrated suspensions are summarized in Fig. 3. The suspensions with the pH near the IEP have very high viscosity. As the degree of deflocculation increases, the η_p decreases and reaches the minima around pH 4 and 10 respectively. Outside these two minima, the η_p increases again. Moreover, the values of the η_p are lower in the acid medium than in the basic one. This variation of the η_p with the pH can be explained by the fact that the addition of nitric acid, a strong electrolyte, leads to low ionic strength, whereas the addition of ammonia, a weak electrolyte, results in high ionic strength. It can be calculated that $I \approx 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ at pH=4 in HNO_3 solution, and $I \approx 2.31 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ at pH=10.2 in ammonia solution. In this investigation, 2 ml ammonia with concentration of $5 \text{ mol}\cdot\text{L}^{-1}$ is added to 19.9 ml deionized water, and then 32.2 g alumina powder is dispersed into the solution, thus, making 30 ml suspension of $\Phi_p = 0.27$ at pH=10.2. The initial $[\text{OH}^-]$ is $1.58 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$. For ammonia, the $\text{p}K_B = -\lg K_B = 4.75$ at 298 K^[11], where K_B is the equilibrium constant. Therefore, the K_B is given as 1.78×10^{-5} at 294 K. The equilibrium of ammonia can be expressed as



In equilibrium state, assuming $[\text{NH}_4^+] = x$, then $[\text{NH}_3 \cdot \text{H}_2\text{O}] = [(5 \times 2/21.9) - x] = 0.457 - x$, and $[\text{OH}^-] = 1.58 \times 10^{-4}$, then the value of x is determined as $4.62 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$. Thus, $I \approx 2.31 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$. The higher I results in the larger Debye-Hückel parameter κ ^[10] and a smaller absolute value of ζ -potential. Therefore, a higher value of the η_p exists in the base alumina suspensions.

3.3 The extrapolated shear yield stress versus pH

The τ_{EY} values obtained from pH 3.1 to pH 11.2 are also summarized in Fig. 3. As expected, the τ_{EY}

decreases as the deflocculation level increases. This correlates to the increase in ζ -potential and the decrease in τ_{F} .

Two different Y-axes are used in Fig. 3 to represent the τ_{EY} and the η_p respectively. However, the changes of τ_{EY} with the pH are much larger than that of η_p . This suggests that τ_{EY} is more sensitive than η_p to the rheological properties of concentrated suspensions, though the value of the latter is experimentally more stable than that of the former.

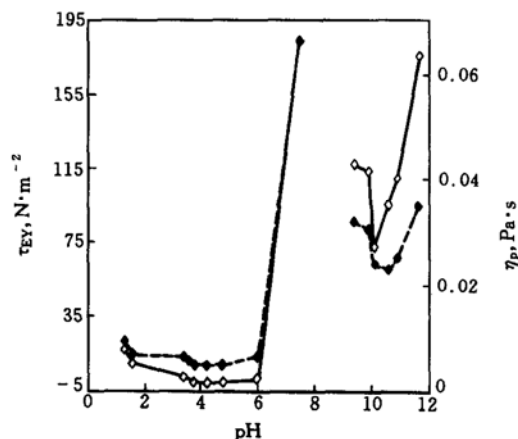


Figure 3 Effects of pH on extrapolated shear yield stress and the plastic viscosity of the concentrated suspension $\diamond \tau_{\text{EY}}$; $\blacklozenge \eta_p$

4 CONCLUSIONS

Most suspensions of Alcoa A16 alumina with $\Phi_p = 0.27$ at various pH exhibit pseudoplastic, near Bingham flow behaviour. The fully deflocculated suspensions show Newtonian flow behaviour, whereas the fully flocculated ones have very complex rheological behaviour with very high viscosity and shear yield stress. The fully flocculated suspensions are obtained between pH 8 and pH 9; while the minima of the η_p and the τ_{EY} are obtained at about pH 4 and pH 10 respectively. These indicate the strong dependence of rheological behaviour on ζ -potential. Beyond the two minima, the η_p and the τ_{EY} of the suspensions increase again. This results from the extra high ionic strength. The η_p and the τ_{EY} of concentrated suspension in basic medium (ammonia) are higher than that in acid one (HNO_3). It has been demonstrated that τ_{EY} is much more sensitive than η_p to the pH.

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NOMENCLATURE

C_{FP}	floc structure indicator
I	ionic strength, mol·L ⁻¹
K_B	equilibrium constant
r_F	floc size, m
$\dot{\gamma}$	shear rate, s ⁻¹
ζ	zeta potential, V
ζ^2	strength of interparticle force, V ²
η_A	apparent viscosity, Pa·s
η_P	plastic viscosity, Pa·s
κ	Debye-Hückel parameter, m ⁻¹
κ^{-1}	thickness of double layer, m
τ	shear stress, N·m ⁻²
τ_{AY}	apparent shear yield stress, N·m ⁻²
τ_{EY}	extrapolated shear yield stress, N·m ⁻²
Φ_F	flocs volume fraction
Φ_P	solid particle volume fraction

Subscripts

IEP	isoelectric point
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