

# Dispersion properties of alumina powders in silica sol

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## Abstract

The dispersion of alumina powders in silica sol has been investigated by zeta potential, sedimentation, and rheological measurements. Zeta potential of alumina in silica sol changes significantly in comparison with that of alumina in deionized water. This is caused by the absorption of silica colloidal particles with negative charge on the surface of alumina particles. Sol-dispersed alumina slurry shows a minimum in sedimentation volume and viscosity around pH 10. The viscosity depends strongly on the silica sol concentration and reaches a minimum in 10–15 wt.% silica sols. It is proposed that the dispersion and stabilization of alumina particles in silica sol are attributed to the electrostatic and steric effects of the colloidal particles absorption. Effects of pH, solids content and silica sol concentration on the rheological behavior of sol-dispersed alumina slurries are discussed in detail. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Al<sub>2</sub>O<sub>3</sub>; Dispersion; Rheology; Silica sol; Suspensions; SiO<sub>2</sub>

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## 1. Introduction

Recently, colloid processing has been suggested as a preferred way to produce high performance ceramic materials. The homogenization, dispersion and stabilization of ceramic particles in the liquid are of primary importance in the processing of high performance ceramics through this wet processing, because the microstructure of green bodies are greatly affected by the rheological properties of the suspensions.<sup>1,2</sup>

Fine ceramic particles (< 1 μm) usually spontaneously aggregate in the dispersion medium due to the relatively high strength of the inter-particle Van der Waals attractive forces. It is, therefore, necessary to reduce the effect of these attractive Van der Waals forces in order to impart a resistance against aggregation. In this case, organic and inorganic dispersants are widely used to disperse the ceramic particles in liquid by steric stabilization interaction via the absorption of the polymer molecules, which can form a protective layer. Ceramic suspensions can also be stabilized by electrostatic repulsion. A

combination of the above methods is mostly chosen to stabilize the suspension by using polyelectrolytes as dispersants, which can create electrostatic stabilization via a polyelectrolyte and a significant electrical double-layer repulsion.<sup>3,4</sup>

The researches that zirconium hydrogel and alumina sol can be used as effective-processing aids for various ceramic powders are reported.<sup>5–7</sup> These results show that inorganic sols can enhance the stability of alumina, silicon carbide, titania and zirconia suspensions and change the zeta potential of these ceramic particles. The zirconium hydrogel interacts with the dispersed ceramic particles to form a surface layer on each particle that provides stability of the slip.<sup>5</sup> Large AlO<sub>4</sub>Al<sub>12</sub>(OH)<sub>24</sub>(H<sub>2</sub>O)<sub>127</sub>+sol clusters that are absorbed on the surface of the ceramic particles may control the deagglomeration and stabilize the suspensions of ceramic particles in the alumina sol by steric interactions and electrostatic mechanism during wet processing.<sup>7</sup> Inorganic sol is considered as an efficient, clean dispersant for ceramic powders, because it can not only provide high bond strength for ceramics bodies due to its conversion to a solid gel at relatively low temperature, but also improve sinterability of ceramic powders.<sup>8,9</sup> However, the rheological behavior of ceramic suspensions stabilized by inorganic sol has not been reported.

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The objective of this work is to study the dispersion of alumina particles in silica sol by employing zeta potential, sedimentation, and viscosity/rheological measurements. Effects of pH, solids content and silica sol concentration on the rheological behavior of the slurry are investigated. The hypothesis that dispersion of alumina particles was improved in silica sol has been confirmed. It is believed that this investigation will be helpful in understanding the dispersion behavior of ceramic powders in silica sol in order to make full use of silica sol for ceramic and castable processing.

## 2. Experimental procedure

### 2.1. Materials

A commercial alumina powder ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, 99.16% purity, a mean particle size of 0.62  $\mu$ m, Shandong Aluminum Industry Company, PR China) and a commercial silica sol (26.2%, pH=9.5–10, Shanghai Second Reagent Plant, PR China) were used in this study.

### 2.2. Slurry preparation

Each slurry was prepared by mechanically stirring for about 10 min under 1400-rotation per minute (RPM). The pH value of the slurry was adjusted by 1 N NaOH or 1 N HCl.

### 2.3. Zeta-potential measurement

The zeta potential of alumina particles dispersed in deionized water and silica solution, as a function of pH, were measured with JS94F Micro-Electrophoretic instrument (Shanghai Zhongshen Economic Development Company, China). Zeta potential measurements can only be conducted on very dilute suspensions.

The 5 vol.% alumina suspensions using deionized water and silica sol as dispersing medium were prepared, respectively, by stirring 5 min, ultrasonicated 5 min and stirring 5 min again. These suspensions were centrifuged and the supernatant was decanted into a beaker, subsequently, a very minute amount of the sediment was remixed with the supernatant. The samples were ultrasonicated 5–10 min prior to the measurement to ensure that only the mobility of the single particles was measured. The pH value of suspensions was adjusted with 1 N HCl and 1 N NaOH.

### 2.4. Sedimentation test

The 5 vol.% alumina suspensions with different pH values ranging from 2 to 13, were put in volumetric cylinders to measure the sedimentation volume as a function of time.

### 2.5. Viscosity and rheological measurements

Viscosity measurements were done with two kinds of rotational viscometers (Model NDJ-1 and Model NDJ-7, Shanghai Balance Instrument Factory, China) by putting the prepared slurries in a beaker with its diameter not less than 70 mm.

The rheological behavior was characterized using a stress controlled Rheometrics scientific SR5 (Rheological scientific Inc, USA) with a parallel plate geometry (25 mm diameter) by stress sweep and steady shear measurements. All measurements were performed at 25°C with a bath and circulator. A thin layer of 5 cps silicon oil was applied to the sample surface to reduce drying effects during testing.

## 3. Results and discussion

### 3.1. Surface chemistry of alumina powders

Fig. 1 shows the effect of alumina concentration in deionized water on the pH of the suspension. As the concentration of alumina increases, the pH of the suspensions increases and reaches rapidly more than pH 10 at 10 wt.%. This rapid increase in pH is caused by an ion exchange reaction on the surface of the alumina between sodium and hydrogen ions in the aqueous solution, because more sodium exists on the surface of the alumina powders,<sup>1</sup> which is clearly observed from Table 1.

By putting oxide particles such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> into an aqueous solution, water molecule may be both physically and chemically adsorbed on their surface. The reactions are as follows:<sup>10</sup>

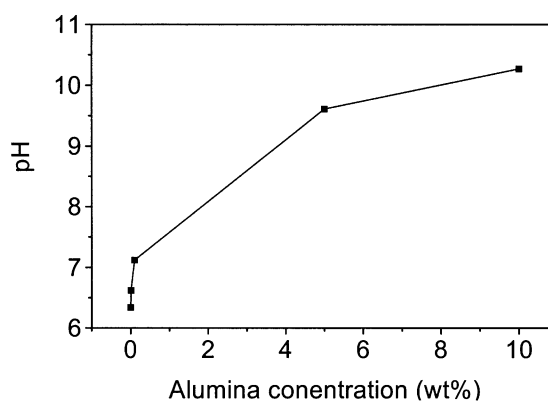
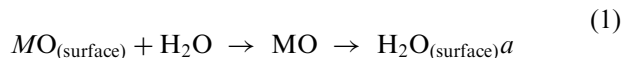


Fig. 1. pH vs alumina concentration in deionized water.

Table 1  
Impurity content of alumina powders

SiO <sub>2</sub> (wt.%)	Na <sub>2</sub> O (wt.%)	Fe <sub>2</sub> O <sub>3</sub> (wt.%)
0.07	0.5	0.08

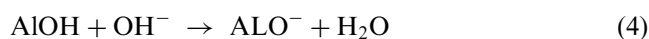
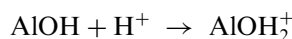
Physical adsorption



and chemical adsorption



Where M is cation and O is oxygen ion. Furthermore, the adsorption of  $H^+$  ions in acidic solution onto hydroxy groups on the surface of alumina particles forms positively charged  $AlOH_2^+$ , causing increase of pH. The pH value goes down when the combination of  $OH^-$  ions in basic solution and  $H^+$  ions from  $AlOH$  forms  $AlO^-$  sites. Such reactions are expressed by<sup>11</sup>



The zeta potential arising from net effective surface charge on the particles in the suspension directly reflects the dispersability levels of the particles in water. Zeta potentials measured as a function of pH for alumina powders in deionized water and in 5 wt.% silica sol are shown in Fig. 2. The IEP (isoelectric point) of alumina in water is about pH 6, where the site numbers  $AlOH_2^+$  and  $AlO^-$  become equal. This value is in accordance with that reported by Sun<sup>12</sup> and Yang,<sup>13</sup> while lower than other reported values (pH 7–9).<sup>14–16</sup> The difference in the IEP of alumina is probably caused by different processing techniques and impurities, and so on.

The IEP of alumina in 5 wt.% silica sol, estimated by extrapolation of the experimental curve, is obtained at pH close to 2, which is similar to that of silica suspensions.<sup>17</sup> Zeta potential of alumina in silica sol shows a great change in comparison with that of alumina in water. This is attributed to the absorption of silica colloidal particles with negative charge on the surface of

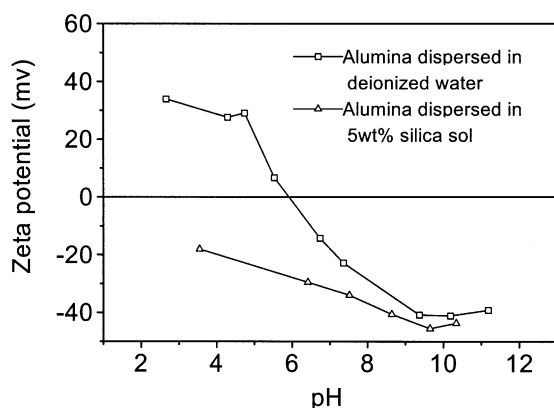
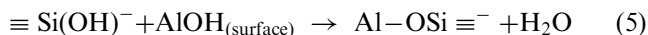


Fig. 2. Zeta potential as a function of pH for alumina powder.

the alumina particles. The chemical reaction may occur at the interface between the alumina particles and colloidal particles as follows:



### 3.2. Sedimentation studies

The sedimentation volume, a function of pH of the suspensions, is shown in Fig. 3. It is observed that the lowest sedimentation for the suspension of alumina in the deionized water occur in the pH range 2–4 after 4 months. This is indicative of good dispersion of alumina in water in the pH range 2–4, which is attributed to the higher zeta potential values of these suspensions. However, the suspensions display a very high settling volume over 4 months at  $pH > 6$ , which is the direct outcome of low values of zeta potentials for alumina particles around its isoelectric point. This result is in accordance with the other report<sup>18</sup> In comparison with the sedimentation behavior of alumina in water, the sedimentation of alumina in silica sol is quite different. The suspensions show the lowest sedimentation for  $pH = 10$ , which is indicative of the best dispersion of alumina in silica sol. The sedimentation volume increases as the pH value decreases and reaches a maximum at  $pH = 6$ , which shows very high levels of aggregation of alumina particles in silica sol around pH 6. Despite the fact that the negative charge on the particles increases, the sedimentation volume increases for the sol-suspension in the pH range from 2 to 6. This is mainly due to the combination between the silica colloid particles absorbed on the surface of alumina particles, which causes the aggregation of alumina particles. As pH decreases further, the sedimentation decreases. The sedimentation results show that the pH value of optimum dispersion of alumina powders in water and silica sol is around 3.5 and 10, respectively.

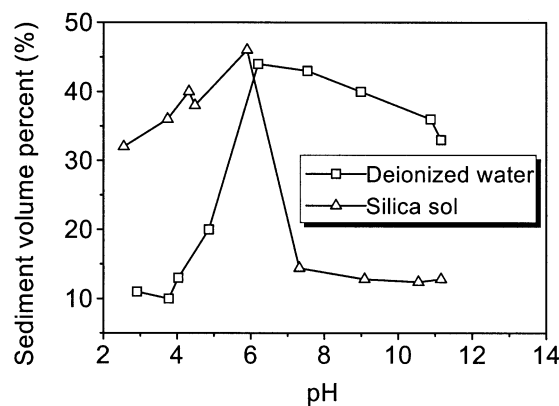


Fig. 3. Sedimentation volume as a function of pH for 5 vol.% alumina suspensions in deionized water and in 5 wt.% silica sol after four months.

### 3.3. Slurry rheological behavior

#### 3.3.1. Effect of pH

The viscosity values for 55 wt.% (percent of weight of alumina powders in the slurry, the same below) alumina slurries in deionized water and in 5 wt.% silica sol are plotted as a function of pH in Fig. 4. The slurry shows the lowest viscosity at a highly acidic condition (around pH 3) but high viscosity at neutral and alkaline condition (pH = 6–11) for water-dispersed alumina. The lowest viscosity in the pH range 3–4 is indicative of optimum dispersion of alumina powders in water. This result is in correlation with the sedimentation behavior discussed above. For sol-dispersed alumina, the viscosity is low at high acidity (around pH = 3). The viscosity keeps increasing with increasing pH and reaches a maximum value at pH 5–6. High viscosity around pH 5–6 is associated with the condensation of silanol groups around pH 5–6 as follows:<sup>19</sup>



In the pH 4–7.5 range, the combination between the silica colloid particles absorbed on the surface of alumina particles causes the aggregation of alumina particles, which results in a rapid increase in the viscosity. As the pH increases further, the viscosity decreases and reaches a minimum value at pH 10. In this pH region, silica colloidal particles are dispersed and are absorbed on the surface of large alumina particles. The absorbed colloidal particles are beneficial to dispersion of alumina particles by electrostatic repulsion. This is in good agreement with the sedimentation results. The viscosity data show that dispersion of alumina in 5 wt.% silica sol is improved significantly in comparison with that of alumina in water around pH 10.

Fig. 5(a) gives viscosity curves versus shear rate for the 60 wt.% alumina slurry in deionized water and in 5 wt.% silica sol near pH = 10, respectively. The shear-thinning behavior of water-dispersed alumina slurry indicates a flocculate structure of particles in water, which arises

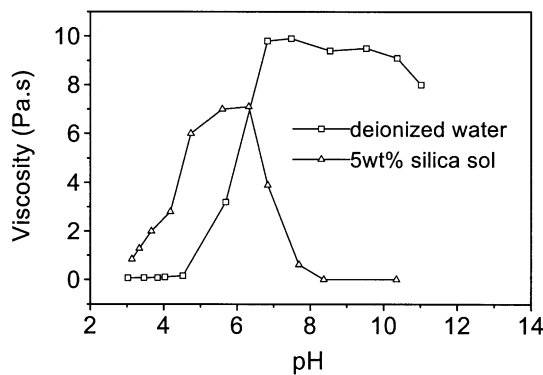


Fig. 4. Viscosity vs pH for 55 wt.% alumina slurry in deionized water and in 5 wt.% silica sol.

from the attraction between the particles. Meanwhile, sol-dispersed alumina slurry shows Newtonian behavior. Shear stress curves versus shear rate for the 60 wt.% alumina slurries in deionized water and in 5 wt.% silica sol near pH = 10 are shown in Fig. 5(b), respectively. It is interesting to see that the flowability of alumina in 5 wt.% silica sol is improved dramatically in comparison with that of alumina in water around pH 10.

Viscosity curves versus shear rate for the 60 wt.% alumina slurry in deionized water and in 5 wt.% silica sol near pH = 6.5, given in Fig. 6(a) show that, both the slurries display shear-thinning behavior near pH = 6.5. Furthermore, It is observed that sol-dispersed alumina slurry shows a very high anti-thixotropic behavior as evidenced by a large hysteresis in flow curves shown in Fig. 6(b). The thixotropic behavior is usually associated with flocculated suspensions.<sup>20</sup> This means that a strong network structure may form in the sol-dispersed slurry because of the combination of the silica colloidal particles absorbed on the surface of alumina. This structure cannot be broken at lower shear rate, but broken down with an increasing shear to overcome the attractive forces between the particles. For water-dispersed alumina, the slurry is slightly anti-thixotropic with a small hysteresis in flow curves.

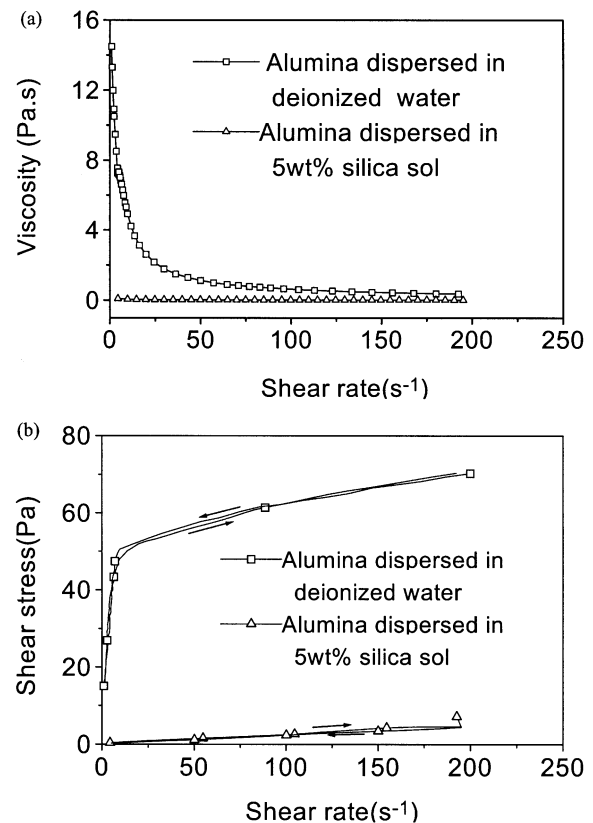


Fig. 5. (a) Viscosity and (b) shear stress vs shear rate for 60 wt.% alumina slurries in deionized water and in 5 wt.% silica sol near pH = 10.

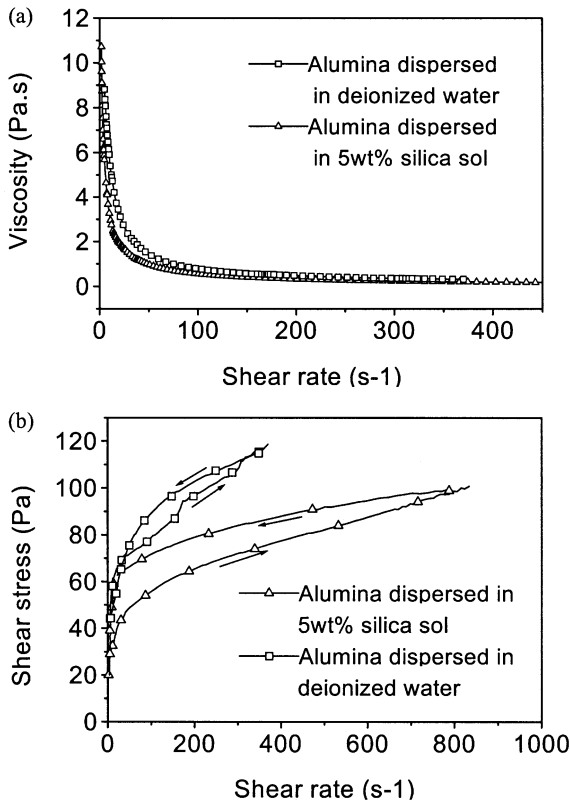


Fig. 6. (a) Viscosity and (b) shear stress vs shear rate for 60 wt.% alumina slurries in 5 wt.% silica sol and in deionized water near pH=6.5.

Fig. 7(a) gives viscosity curves versus shear rate for the 60 wt.% alumina slurry in deionized water and in 5 wt.% silica sol near pH = 3. The slurries both exhibit shear thinning behavior near pH = 3. Fig. 7(b) shows that flow behavior of sol-dispersed slurry becomes worse than that of water-dispersed slurry around pH 3. Sol-dispersed slurry shows a very high thixotropic behavior as evidenced by a large hysteresis in flow curves. But water-dispersed slurry displays a slight thixotropic behavior with a very small hysteresis in flow curves. The results show that silica sol has no contribution to dispersion of alumina in an aqueous medium around pH 3 (highly acidic condition).

### 3.3.2. Effect of solids content

Fig. 8 gives viscosity versus solids content for sol-dispersed alumina slurry near pH 10. The viscosity increases slowly with the increase of solids content when the solid content is below 68 wt.%, but increase rapidly with the increase of solids content when beyond 68 wt.%. Viscosity and shear stress curves versus shear rate for alumina slurries in 5 wt.% silica sol with various concentration near pH 10 is presented in Fig. 9. It is easily observed in Fig. 9(a) that the slurry shows almost Newtonian behavior up to 65 wt.% solids content beyond which it becomes non-Newtonian (shear-thinning)

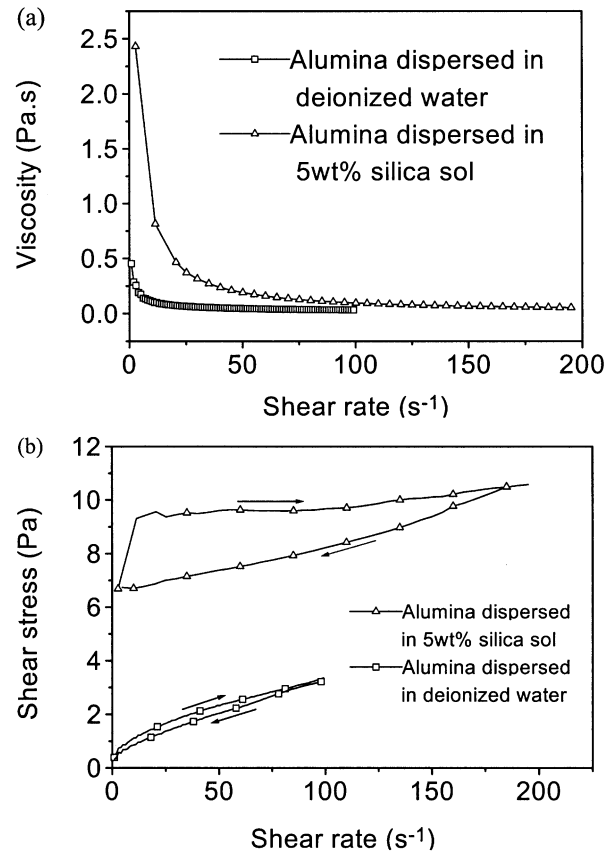


Fig. 7. (a) Viscosity and (b) shear stress vs shear rates for 60 wt.% alumina slurries in 5 wt.% silica sol and in deionized water near pH = 3.

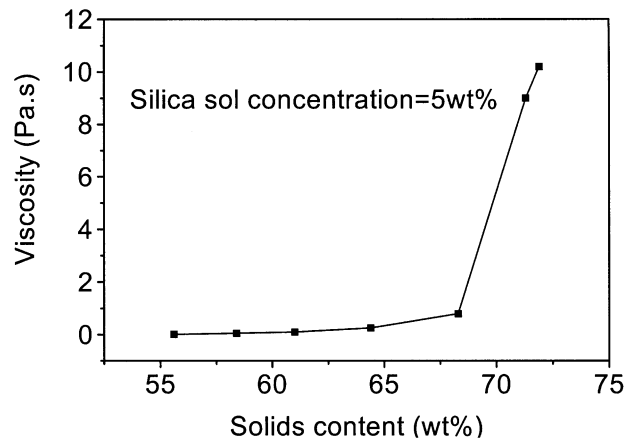


Fig. 8. Viscosity vs solids content for sol-dispersed alumina slurry around pH 10.

behavior. The slurry with 70 wt.% solid content shows a high thixotropy as evidenced by a large hysteresis in flow curves [Fig. 9(b)] as an indication of the high levels of aggregation, which results from interparticles forces.

### 3.3.3. Effect of silica sol concentration

Viscosity of silica sol itself can be expressed by Mooney's equation:<sup>21</sup>

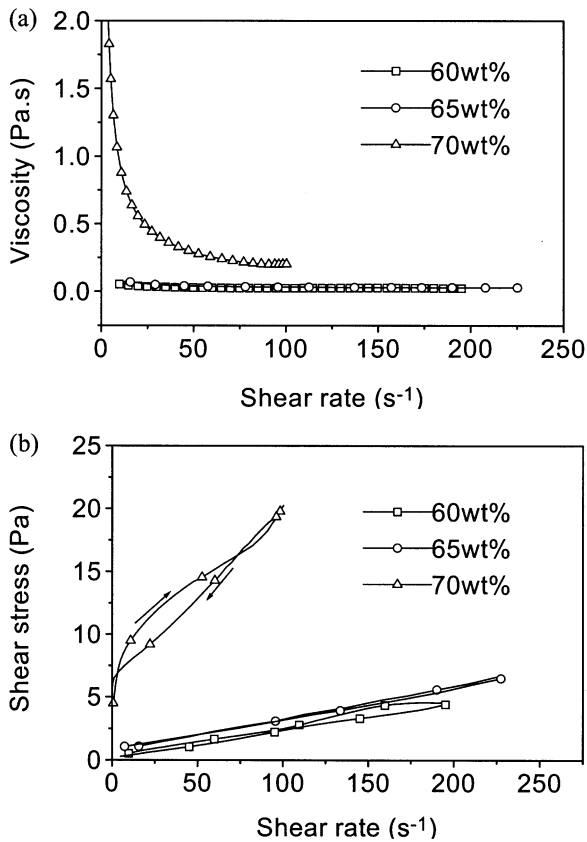


Fig. 9. (a) Viscosity and (b) shear stress vs shear rate for alumina slurries in 5 wt.% silica sol with various solids content near pH 10.

$$\log_e \eta_{\text{rel}} = \frac{2.5\phi}{1 - 1.43\phi} \quad (7)$$

Where  $\eta_{\text{rel}}$  is the relative viscosity or ratio of the viscosity of the dispersed system to that of the dispersing medium, and  $\phi$  is the volume fraction occupied by the dispersed uniform spherical particles. Eq. (7) is equivalent to the following formation:

$$\log_e \eta_{\text{rel}} = \frac{2.5}{\frac{1}{\phi} - 1.43} \quad (8)$$

According to Eq. (8), viscosity of silica sol increases as the silica sol concentration increases. But the viscosity does not show a similar change as the silica sol concentration increases when silica sol is used as dispersing medium for alumina powders, which is clearly seen in Fig. 10. It is interesting to see that slurry viscosity decreases with increasing silica sol concentration and reaches a minimum value with silica sol concentration of 10–15 wt.%. As the silica sol concentration increases further, the viscosity increases slowly. The results confirm that the silica sol concentration has an effect on the dispersion of alumina in silica sol. It is proposed that

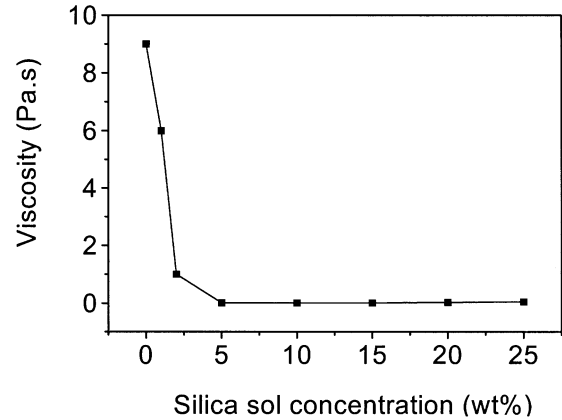


Fig. 10. Viscosity as a function of silica sol concentration for 55 wt.% alumina slurry near pH 10.

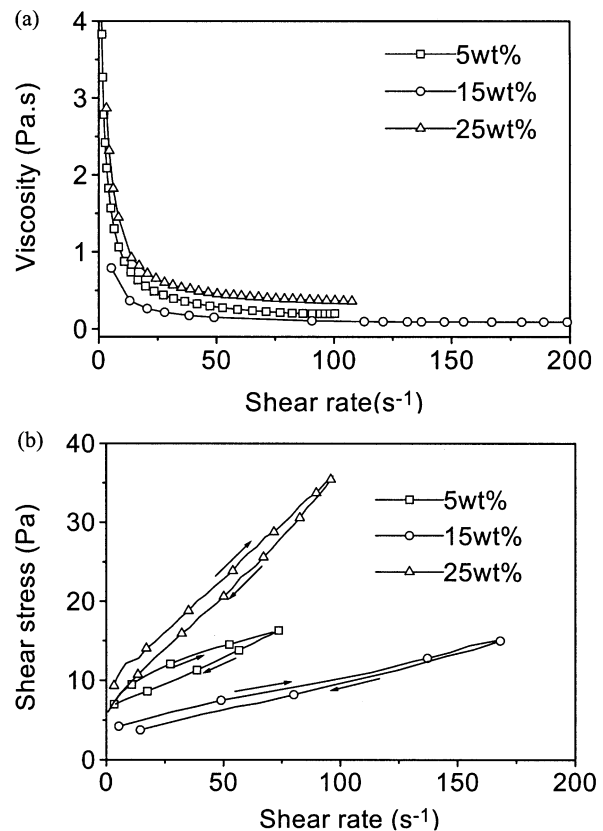


Fig. 11. (a) Viscosity and (b) shear stress vs shear rate for 70 wt.% alumina slurries in silica sol with various concentration near pH 10.

the dispersion of alumina in silica sol around pH 10 or at basic condition is dominated by electrostatic repulsion and steric interaction resulting from the absorption of colloidal particles with negative charge on the surface of large alumina particles. Viscosity curves versus shear rate for 70 wt.% alumina slurries with various silica sol concentration near pH 10, shown in Fig. 11(a), indicate

that the slurries display non-Newtonian behavior. In the meantime, shear stress curves versus shear rate for 70 wt.% alumina slurries near pH 10 with various silica sol concentration given in Fig. 11(b) show that, the slurry exhibits high thixotropy with silica sol concentration of 25 wt.%; whereas the slurry is slightly thixotropic with a very small hysteresis in flow curves with silica sol concentration of 15 wt.%. When silica sol concentration is further reduced to 5 wt.%, the slurry shows a thixotropic behavior. These results indicate that the silica sol concentration of optimum dispersion for alumina is about 15 wt.%, which is in correlation with Fig. 8.

#### 4. Conclusions

Zeta potential of alumina in silica sol changes significantly in comparison with that of alumina in deionized water. This is attributed to the absorption of silica colloidal particles with negative charge on the surface of alumina particles. Sol-dispersed alumina slurry shows a minimum in sedimentation volume and viscosity around pH 10 as an indication of optimum dispersion of alumina in silica sol; whereas it displays a very high sedimentation and viscosity at pH 5–6, which is associated with the combination between the silica colloidal particles. Meanwhile, the viscosity depends strongly on the silica sol concentration and reaches a minimum with silica sol concentration of 10–15 wt.%. It is proposed that the electrostatic and steric effects of the colloidal particles absorption help to control the dispersion and stabilize the suspensions of alumina particles in silica sol.

The 55 wt.% slurry of alumina in 5 wt.% silica sol is near Newtonian around pH 10; whereas it displays non-Newtonian with very high antithixotropy as an indication of the high levels of aggregation around pH 6.5. The slurry of alumina in 5 wt.% silica sol shows Newtonian up to 65 wt.% solids content beyond, which it becomes non-Newtonian with thixotropic behavior. The 70 wt.% slurry shows non-Newtonian with thixotropy with 5 wt.% silica sol; whereas it becomes slightly thixotropic up to 15 wt.% silica sol beyond, which it displays high thixotropic behavior.

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