

Electrical and Rheological Properties of Colloidal Alumina Suspensions

Xu Hong Wang* and Yoshihiro Hirata

Department of Applied Chemistry and Chemical Engineering,

Kagoshima University

1 – 21 – 40 Korimoto, Kagoshima 890 – 0065, Japan

*Corresponding author : Tel (+81) 99 – 285 – 8327,

Fax (+81) 99 – 257 – 4742,

E – mail xh-wang@apc.kagoshima-u.ac.jp

Abstract

The valence (Z) of positively and negatively charged alumina particles in the dilute suspensions was analyzed with the electrical conductivity of the suspensions. The mobility of negative particles was lower than that of positive particles at a similar Z value because of the stronger effect of chemical bonding over the hydrated particle surfaces. The apparent viscosity of acidic suspensions of 1 – 40 vol % solid was lower than that of basic suspensions. This result was discussed based on the three important effects of the valence, concentration and nature of hydrated surface of alumina particles. The density of alumina compacts consolidated by filtration through gypsum molds became lower for the basic suspensions than for the acidic suspensions. This result was correlated to the properties of the colloidal alumina suspensions.

Key words : Valence, Electrophoretic mobility, Alumina suspension, Rheology, Viscosity, Chemical bonding, Green compact

1. Introduction

Colloidal processing (dispersion and consolidation of colloidal particles) with an aqueous suspension provides a well— controlled microstructure of powder compact. When a ceramic powder was put into an aqueous solution, those particles are charged positively or negatively, depending on pH and the isoelectric point of the powder. [1] The dispersion characteristics of particles in suspensions are greatly dominated by the surface potential. The individual characteristics of charged particle is evaluated by the direct measurement of electrophoretic mobility under a microscopy. On the other hand, a colloidal suspension contains a huge amount of particles and the interaction between charged particles affects the rheology of suspension and the microstructure of consolidated powder compact.

[2] The electrical conductivity of colloidal suspension (σ_s) is the summation of two kinds of conductivities of ionic motion and particle motion as expressed by Eq. (1) [3,4]

$$\sigma_s = \sigma_0(1 - v_p) + Ze \frac{3v_p}{4\pi r^3} \mu \quad (1)$$

where σ_0 is the specific conductivity of the solution added to alumina particles, v_p the volume fraction of alumina particles, Z the valence of charged one alumina particle, e the charge on the electron, r the radius of alumina particle and μ the electrophoretic mobility of charged alumina particles. This equation represents the relation of electrical characteristics between a group of colloidal particles and individual particle. It is possible to determine the Z value from the measurement of σ_s and μ value for the dilute suspensions where the interaction between colloidal particles can be ignored. However, it is difficult to measure directly the μ value in a concentrated suspension. The interaction between charged particles may be reflected in both the values of Z and μ . For a concentrated suspension, the μ value is calculated by Eq. (1) using the σ_s value measured for no overlapping of electrical double

layers. The ratio of μ / μ_0 (μ_0 : μ value for the charged particle with no interaction to another particle) is a new parameter to evaluate the magnitude of interaction between charged particles. Therefore, it is expected that the rheology affected by the interaction of charged particles may be correlated to the ratio of μ / μ_0 . In this paper, the mobility and Z value of alumina particles in the dilute suspensions (< 1 vol % solid) was calculated by Eq. (1). In addition, the rheology of the alumina suspensions was measured to correlate to the electrical properties.

2. Experimental procedure

A high purity α - alumina powder ($\text{Al}_2\text{O}_3 > 99.99$ mass %, specific surface area $10.5 \text{ m}^2 / \text{g}$, median size $0.2 \mu\text{m}$, Sumitomo Chemical Co. Ltd., Japan) was used to prepare aqueous suspensions of 1–40 vol % solid. 1N–HCl or 1N– NH_4OH solution was added to the alumina suspensions to adjust pH at 2.0–10.0. The suspensions were churned by a magnetic stirrer for 24 h and set in a bell jar to remove air bubbles by vacuum pump for 15 min. The treated dilute suspension of 1 vol % solid was poured into a cylindrical acrylic resin cell (54.5 mm width, 25.9 mm diameter) with Pt electrodes to measure the impedance and phase angle in the frequency range from 100 Hz to 1 MHz (model 4276 A, 4277 A, Yokogawa Hewlett Packard Co., Japan). The cell constant ($=d / A$, d : distance between two electrodes, A : surface area of electrode) was calibrated with the conductivity of 5×10^{-4} M and 1×10^{-3} M KCl solutions at 24 °C. The electrophoretic mobility of alumina particles in dilute suspensions (< 1 vol %) at pH 2.0–10.0 was measured under a microscopy by particle electrophoresis apparatus (Rank Mark II, Rank Brothers Ltd., UK). The shear stress of the treated suspensions of 1–40 vol % solid at pH 2.0–10.0 was measured by a cone and plate type viscometer (Visconic ED type, Tokyo Keiki., Co., Japan) in the shear rate range from 1 to 400 s^{-1} . The prepared suspensions were consolidated by the filtration through gypsum molds at room temperature. The green compacts were calcined for 1 h at 700°C (SPM 6512, Electric Furnace, Marusho Electro – Heat Co., Ltd., Hyogo, Japan.). The density of calcined compacts were measured

by the Archimedes method using distilled water.

3. Results and disussion

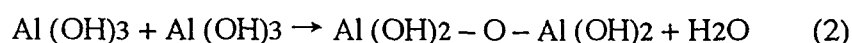
3.1 Electrical conductivity of alumina suspension

Figure 1 shows the complex impedance plots for 1 vol % suspensions at pH 2.0 – 10.0. The measured data were fitted by a straight line for the high – conductivity suspension and a semicircle for the low – conductivity suspension. This result suggests that the complex impedance plots are expressed by the series and parallel equivalent circuit of resistance and capacitance for high – and low – conductivity suspensions, respectively. The specific conductivity of suspensions (σ_s) was determined from the intercept on Z' axis at $\omega (= 2 \pi f, f : \text{frequency}) \rightarrow 0$.

Figure 2 shows σ_s and σ_0 as a function of pH, indicating that (1) σ_s is higher than σ_0 in the pH range from 2 to 10 and (2) both the values of σ_s and σ_0 show a minimum at pH 7 – 8. The change of σ_0 with pH indicates that (1) the migration of H_3O^+ and Cl^- ions added to adjust low pH dominates the σ_0 in the acidic solutions, and (2) NH_4^+ and OH^- ions control the σ_0 in the basic solutions. The increase in σ_s with alumina addition is related to the contribution of charged mobile particles. The measured σ_s and σ_0 were substituted into Eq. (1) to calculate the Z value of alumina particles. The μ values in the dilute suspensions below 1 vol % solid were measured directly under a microscopy. This value and σ_s for 1 vol % suspension were used to calculate the Z value for alumina particles with no significant interaction to another particles.

Figures 3 and 4 show the μ and Z values for the dilute suspensions, respectively. The isoelectric point of alumina particles was near pH 8.6 (Fig. 3). The mobility of positively charged particles increased with decreasing pH and approached a constant value in the pH range

3–5. Similarly, the mobility of negatively charged particles increased when pH was shifted from the isoelectric point. The Z value was sensitive to pH as seen in Fig. 4. The comparison of results shown in Figs. 3 and 4 indicates that (1) the high mobility of positively charged particles ($\text{pH} < 5$) with high Z values above 1000 was independent of Z value, (2) the mobility of positive particles with low Z values of 100 – 1000 became lower for lower Z value and (3) the mobility of negatively charged particles was lower than that of positively charged particles at a similar Z value. The Z values for negative particles at $\text{pH} 8.8 - 10.0$ were in 2000 – 10000 but the measured mobility was less than 1 / 2 of the mobility of positive particles with similar Z values. The comparison of Z values at $\text{pH} 7$ and 10 indicates that the negative particles were charged 10 times higher than the positive particles to provide a similar mobility of $\pm 3 \mu\text{m} \cdot \text{s}^{-1} \cdot \text{V}^{-1} \cdot \text{cm}$. The difference of the mobility between positive and negative particles at a similar Z value reflects the chemical bonding effect. The chemical bonding over the hydrated surface in the solution at a high pH may be another important factor controlling the mobility. [5, 6] That is, alumina particles are charged negatively in the basic suspensions but the chemical bonding over the particle surface produces the flocculated state with a low mobility. A possible reaction between hydrated surface may be expressed by Eq. (2),



3.2 Rheology of alumina suspensions

The viscosity of liquids indicates the resistance caused by the internal friction between molecules of liquids for migration. The viscosity of suspension containing solid is higher than that of solution because the solid plays as an obstacle for the migration of liquid. Figure 5 shows the shear rate – shear stress relation for 20 vol % alumina suspensions. The acidic suspensions behaved as a Newtonian fluid. On the other hand, the basic suspensions showed a pseudoplastic behavior. In the analysis of the data in Figs. 3 and 4, it was found that the valence and nature of hydrated surface (chemical bonding associated with pH) of colloidal particle are the important factors affecting the

mobility of charged particles. In the measurement of μ and σ_s at an applied electric field, neutral H₂O molecules do not contribute to the measured values. The measured values are concerned with the properties of charged species as indicated by Eq. (1). On the other hand, rheology of the suspension is related to both the motion of liquid and colloidal particles. Figure 6 shows the relation of Z value of alumina particle and apparent viscosity of the suspension at 383 s⁻¹ of shear rate. The ratio of the measured apparent viscosity (η_a) to the viscosity (1×10^{-3} Pa • s) of pure water represents the resistance of colloidal particles to the motion at a given shear stress. The η_a for 1 vol % acidic suspensions was almost independent of the Z value of positive particles, suggesting no significant interaction between colloidal particles. In the acidic suspensions of 5 – 30 vol % solid, a rapid increase of η_a started at a certain low Z value. This result is interpreted by the formation of flocculation of weakly charged particles with decreased interparticle distance. The decrease of interparticle distance (H) normalized by the particle diameter (2 r) is approximated by Eq. (3) [7] ,

$$\frac{H_1 - H_2}{2r} = \left(\frac{1}{v_1}\right)^{\frac{1}{3}} - \left(\frac{1}{v_2}\right)^{\frac{1}{3}} \quad (3)$$

where state 1 corresponds to the dilute suspension with the particle fraction v_1 and state 2 represents the concentrated suspension. Figure 7 shows the decrease of interparticle distance as a function of v_2 under the condition of $v_1 = 0.01$. The interparticle distance is very sensitive to the particle fraction below 10 vol % and decreases gradually at a higher particle fraction. The decreased interparticle distance produces the two different types of interaction between particles : flocculation and dispersion. When van der Waals attraction dominates the interaction between weakly charged particles, particles are flocculated to form the network structures. This result is observed in the high μ_a value at lower Z value in Fig.6. When the strong electrostatic repulsion dominates the interaction,

highly charged particles are dispersed with a certain distance, reducing the resistance to the migration of both the liquid and particles.

The basic suspension provided a higher η_a value than the acidic suspension at a similar solid fraction. As seen in Fig. 6, this result is not explained by the Z value and suggests that the nature of hydrated surface plays a more important role to form the flocculated state. Furthermore, the concentration effect was greater in the basic suspensions than the acidic suspensions.

Figure 8 shows the influence of pH on the η_a value at 383 s^{-1} of shear rate. Both the effects of Z value and nature of hydrated surface on the rheology of the suspensions are controlled by pH. Increase in pH in the acidic suspensions reduces the Z value effect (Fig. 4), leading to the gradual increase of η_a value. The apparent increase of η_a in the basic suspension with pH is associated with the stronger effect of nature of hydrated surface than the Z value because a higher Z value was measured at a higher pH (Fig. 4).

Figure 9 shows the relative density of calcined alumina compacts as a function of pH. This result inherited the rheological properties of the suspensions (Fig. 8). The density for the basic suspensions became lower than that for the acidic suspensions. The increased density at low pH of the suspensions is deeply correlated with the low viscosity of well – dispersed positive particles with high Z values (Fig. 4). These particles are densely packed by the elimination of aqueous solution. The gradual decrease of density with increasing pH reflects the increased particle interaction as shown in the increased viscosity (Fig. 8). This result is caused by the decrease in Z values in the acidic suspensions (Fig. 4) and by the formation of chemical bonding over the hydrated particle surfaces in the basic suspensions (Fig. 6). The slight decrease of density with increasing solid content of the suspensions is ascribed to the increased particle interaction associated with the decrease of interparticle distance (Fig. 7). That is, the formation of particle clusters reduces the efficiency of particle packing.

4. Conclusions

The electrophoretic mobility (μ) of charged alumina particles depended on the valence (Z) and the nature of hydrated surface of colloidal particles. In the dilute acidic suspensions (< 1 vol %), the mobility of positively charged particles with high Z values above 1000 was independent of Z values. The mobility of positive particles with Z values of 100 – 1000 became lower for lower Z value. In the basic suspensions, the similar effect of Z value was observed for the negatively charged particles. In addition, the chemical bonding between the hydrated particle surface affected the mobility. As a result, the mobility of negatively charged particles became lower than that of positive particles at a similar Z value. The basic suspension provided a higher apparent viscosity than the acidic suspension at a similar solid fraction. The apparent viscosity of acidic suspensions is controlled by the Z value and solid fraction (interparticle distance) which affect the formation of flocculated state. On the other hand, the rheology of the basic suspensions is dominated by solid fraction and the nature of hydrated particle surface depending on pH. The density of powder compacts consolidated by filtration was deeply correlated to the viscosity of the suspensions. The low viscosity suspension of well – dispersed positive particles provided a high packing density. The formation of particle clusters in the high viscosity basic suspensions reduced the packing density.

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Figure Caption

Fig. 1 Complex impedance plots for 1 vol % alumina suspensions.

Fig. 2 Specific conductivity of the solution and alumina suspension of 1 vol % solid.

Fig. 3 Electrophoretic mobility of alumina particles as a function of pH.

Fig. 4 Valence of charged alumina particle as a function of pH.

Fig. 5 Shear rate – shear stress relation for 20 vol % alumina suspensions.

Fig. 6 Apparent viscosity of alumina suspensions as a function of valence.

Fig. 7 Decrease of interparticle distance as a function of particle fraction, v_2 .

Fig. 8 Apparent viscosity of alumina suspensions as a function of pH.

Fig. 9 Relative density of powder compacts consolidated by filtration.

