The effects of the concentration of a polymer dispersant on apparent viscosity and sedimentation behavior of dense slurries

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Abstract

The ceramic forming process can be considered as a condensation and dehydration process, and the condensation process can be simulated by the sedimentation test under gravity or centrifugal acceleration. To investigate the condensation and compression process more fundamentally, the submicron meter alumina powders were dispersed in distilled water with polyacrylic ammonium to prepare the 20–35 vol% slurries. The following three types of slurries were prepared by changing the concentration of polyacrylic ammonium; the coagulated, well dispersed and weakly coagulated slurries. The apparent viscosity of the slurries and the depth of the clarification zone under gravity were measured. Comparing the results of the apparent viscosity and the packing volume fraction, the following are elucidated. (1) The apparent viscosity and the sediment packing volume fraction change suddenly at different dispersant concentrations. It does not mean that well-dispersed slurry changes always to well-condensed sediment. (2) Changes in the final sediment packing fraction can be correlated with change in the dispersant concentration not the apparent viscosity. (3) It seems that the polymer dispersant functions as a lubricant during sedimentation and compression.

Keywords: Slurry; Sedimentation; Apparent viscosity

1. Introduction

Fine solid particles are treated as suspensions or slurries in many industries such as ceramics, mining, foods, paints, pharmaceuticals and so on. There is a variety of treatment operations of slurries for example filtration, transportation, shaping, coating, granulation depending on purpose. Although the operations have been studied in each industrial field, there is no general theory or model that can cover whole suspensions or slurries due to the complexities of particulate dispersion systems. Almost all industries are treating particulate dispersion systems and have many problems in designing an operation process or optimizing process conditions. Advanced ceramic industry is a typical example. The improvement of reliability has been pointed out as a main technical issue of advanced structural ceramics. The reliability depends strongly on the defects in sintered bodies grown from those in green bodies during sintering process. The uniformity of green bodies, therefore, is very important to realize defect-free sintered bodies. As the uniformity is controlled by the characteristics of slurry, optimizing the characteristics is a key technique of ceramic fabrication processes. In general, slurries are characterized by apparent viscosity, but the apparent viscosity cannot characterize the slurries sufficiently, and finally the slurries are optimized by trial and error. The authors have considered that a ceramic forming process is a thickening and dehydration process and simulated the forming process by a sedimentation process in the gravity and centrifugal field. Using the centrifugal sedimentation test, the morphology of spray-dried granules can be successfully predicted, which has been hardly predicted by the apparent viscosity. Also, the density of tape cast green bodies is well estimated by the centrifugal sedimentation test. If the sedimentation behavior is correlated to the apparent viscosity being used popularly, it will be very convenient for the design and optimization of a forming process.

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The sedimentation has been studied mainly for designing of thickeners, and recently sedimentation mechanisms have been discussed (Buerger & Tory, 2000). The interactions between particles strongly affect the sedimentation behavior, and the mechanical properties of sediment have been discussed from the viewpoint of the particle interaction in ceramic forming field (Miller, Melant, & Zukoski, 1996; Velamakanni, Lange, Zok, & Pearson, 1994; Bergstroem, Schilling, & Aksay, 1992; Shih, Shih, Kim, & Aksay, 1994; Chang, Lange, & Pearson, 1994a; Chang, Lange, Pearson, & Pollinger, 1994b; Yanez, Shikata, Lange, & Pearson, 1996). The sedimentation processes, however, have been scarcely discussed from the viewpoint of the particle interaction. Font, Garcia, and Rodriguez (1999) discussed the influence of pH; however, there might be no report on the influence of the polymer dispersant.

In this paper, the alumina slurries of three different concentrations are prepared by changing the concentration of the dispersant, and the apparent viscosity, the sedimentation progress under gravity and the centrifugation sediment packing volume fraction are measured. The effects of dispersant concentration are discussed in relation to the apparent viscosity, the sedimentation progress and the sediment packing volume fraction.

2. Experiments

2.1. Samples and sample preparation

A low soda alumina powder (AES-11E, 0.48 μm) distributed by Sumitomo Chemical Co. Ltd. and polyacrylic ammonium distributed by Toagosei Co. Ltd. were used as sample and dispersant. As the sample preparation procedure is shown in Fig. 1, the sample powder, dispersant and distilled water were milled for 1 h. The milled slurries were stood for 2 h at 20°C under stirring after degassing. The dispersant amount added to the slurry was prepared based on the surface area of the sample powder in the slurry and expressed as dispersant concentration [g/100g-alumina] (Fig. 2). The amount of the dispersant adsorbed on the particles was measured by a total organic carbon analyzer (TOC) and the apparent viscosity was measured by a rotational viscometer for the 20, 35 vol% slurries by changing the amount of polyacrylic ammonium. The shear rates of the viscometer were 17.5 and 8.76 s⁻¹ for the 20, 35 vol% slurries, respectively. The additive amount of the dispersant was decided as 0.16, 0.24, 0.36, 0.60 g to 100 g-alumina powder according to the measurement results of the adsorbed amount and the apparent viscosity.

2.2. Sedimentation tests under gravity

Polyacryl tubes of 20 mm inner diameter were used for the sedimentation test. The initial slurry heights were 30, 45, 60, 75, 90 mm, and the depths of the clarification zones were measured with passage of time while keeping temperature constant at 20°C. The sediment packing volume fraction was calculated from the sediment height and the particle density.

2.3. Compression tests of the sediment in a centrifuge

The sediment for which initial slurry heights were 30 and 45 mm of 20 and 35 vol% slurries was compressed in a swing-type centrifuge after the sedimentation test under gravity. The rotation speed was increased from 500 to 3000 rpm by steps of 500 rpm after checking that the height of the sediment became constant. The distance between the rotation axis and the bottom of the tube is 250 mm. The sediment packing volume fraction was also calculated from the sediment height and the particle density.
density, and the compression stress was calculated from the rotation speed, the distance from the rotation axis to the center of the sediment and the sediment bulk density.

### 3. Results

#### 3.1. Absorbed amount of dispersant and apparent viscosity

The dispersant amount absorbed on the particles increases in proportion to the added amount keeping an absorbing equilibrium until 0.36 g/100 g-alumina regardless of the slurry concentration. At 0.36 g/100 g-alumina the surface of a particle is saturated with the dispersant, and no more dispersant can be absorbed on the surface even if one increases the dispersant concentration in the slurries. Fig. 3 shows the apparent viscosity. Although the denser slurry has higher viscosity, changes in the apparent viscosity are similar. The apparent viscosity becomes the minimum at 0.24 g/100 g-alumina and then increases gradually. The dispersant concentrations of 0.16, 0.24, 0.36 and 0.6 g/100g-alumina were selected for the sedimentation test, and the sample slurries were named as S-16, S-24, S-36 and S-60. S-16 represents coagulated slurry, S-24 is well dispersed but the surface of a particle is not saturated with the dispersant, S-36 is well dispersed and the surface is saturated and S-60 represents weakly coagulated slurry.

#### 3.2. Sedimentation under gravity

Fig. 4a shows the effect of the slurry concentration and the initial height on the sedimentation progress of S-24. As is obvious from the figure, in denser slurry the interface settles faster and deeper, and the depth increases with the initial height. Fig. 4b shows the effects of the dispersant concentration on the sedimentation progress of the 35 vol% slurry having 90 mm initial height. The initial settling rates are almost equal except S-16, and it is interesting that S-24 hardly settled in spite of well-dispersed slurry like coagulated slurry S-16.

Roberts (1949) proposed the experimental equation to express the decreasing settling rate that \( (h - h_0)/(h_0 - h) \) is in proportion to \( e^{-t} \). Based on the Roberts equation the data were plotted on semilogarithmic graph and section paper, and the following regression equations were obtained for each dispersant concentration.

**S-16, S-24:**
\[
\ln\frac{h - h_0}{h_0 - h_e} = - k_1 \frac{t}{h_0},
\]

**S-36:**
\[
\frac{h - h_e}{h_0 - h_e} = - k_2 \frac{t}{(h_0 - h_e) \phi_0^2},
\]

**S-60:**
\[
\frac{h - h_0}{h_0 - h_e} = - k_3 \frac{t}{h_0 \phi_0^2}.
\]

As shown in Fig. 5, regression equations (1)–(3) express fairly well the sedimentation progresses. Fig. 5a–c show the sedimentation progresses of S-16 and S-24, S-36 and S-60, respectively. In Fig. 5a the settling rates of the interface decrease with time and the effect of slurry concentration cannot be recognized. In Fig. 5b the settling rates are constant as if free settling; however, the settling rates decrease in inverse proportion to the square of the slurry concentration. In Fig. 5c, the settling rates decrease with time and the slurry concentration is the same as in Fig. 5b. According to the apparent viscosity S-24 and S-36 are well-dispersed slurries; however, their sedimentation progresses are quite different.

The final packing volume fractions of the sediment are shown in Fig. 6. In S-16 and S-24 the surface of a particle is not saturated with the dispersant as shown in Fig. 2, the final sediment packing fractions are almost equal to the initial slurry concentration, even though in S-24 the particles are well dispersed. On the contrary, S-36 and S-60 in which the surface of a particle is saturated with the dispersant have the dense sediment, and the sediment packing fractions of 30 and 35 vol% slurries are almost the same and smaller than that of 20 vol% slurry. In general, if the height of a packing bed is increased, the sediment packing fraction increases also due to own weight, and the final packing fractions of S-16 and S-60 slurries increase with the initial height reasonably as shown in Fig. 6a. The sediments of S-24 and S-36, however, decrease strangely with the initial height as shown in Fig. 6b. To clarify the reason for the strange decreasing, other systematical experiments are necessary.

#### 3.3. Compression tests of the sediment in a centrifuge

Fig. 7a shows the changes of the sediment packing fractions with time and the rotation speed. As mentioned before, the rotation speed increased by steps of 500 rpm after the sediment packing fractions became constant.
The results are in two groups, the same as the sedimentation under gravity, one is S-16 and S-24 group and the other one is S-36 and S-60 group. In S-16 and S-24 the sediment packing fractions are mainly affected by the initial concentrations, on the contrary in S-36 and S-60 the fractions are mainly affected by the adsorbed amount of the dispersant. Fig. 7b shows the final packing fraction at each rotation speed; it can be considered as the correlation curves of packing fraction and yield strength of the sediment. The sediments of S-16 and S-24 are compressed gradually if the rotation speed is increased. On the other hand, the yield values of S-36 and S-60 are low and compressed well even under gravity. The initial slurry height affects the sediment packing fractions in the manner of sedimentation under gravity.
4. Discussions

The effects of dispersant concentration on the apparent viscosity, the sedimentation progress and the sediment packing fraction are summarized in Table 1 and Fig. 8. The important thing is that changes in the apparent viscosity not always correlate with changes in the sediment packing fraction. This might be the reason why the centrifugal sedimentation test is available to estimate the green density or the morphologies of spray-dried granules. When slurry is condensed to sediment, the particles in slurry must slip at the particle contact points for rearrangement. From this condensation mechanism, if the static friction at the particle contact points is reduced, the denser sediment can be expected. Since the final sediment packing fractions increase with the dispersant concentration as shown in Fig. 4b, it is supposed that the dispersant reduces the static friction at the contact points like a lubricant.

The dispersant concentration of 0.24 g/100 g-alumina (S-24) is enough to reduce the shear resistance but insufficient for the condensation. Since the average particle contact points are constant during shearing process, the well-dispersed state can be kept. On the contrary, in condensation the particles in slurry are coagulating each other because the surface of a particle is not saturated with the dispersant and the particle contact points increase during condensation process.

The decrease of the final packing volume fraction with the initial slurry height is an experimental fact but it seems to be a strange phenomenon. Other systematic experiments changing the diameter of sedimentation tube, particle interaction, etc. are necessary for further discussion.

5. Conclusion

Using alumina slurry the effect of the concentration of a polymer dispersant on the apparent viscosity and the sediment packing volume fraction were measured under
Table 1
Conclusions of sedimentation experiments

| Polyacrylic ammonium [g/100g-Al2O3] | Apparent viscosity | Sedimentation Sediments under Compression Sedimentation/ viscosity |
|------------------------------------|-------------------|-------------------------------------------------|-----------------------------|
| 0.16                               | High (coagulated) | Eq. (1)                                         | φₙ ≈ φ₀                      |
| 0.24                               | Minimum (well dispersed) | Eq. (2)                                         | k₁ = 0.24                   |
| 0.36                               | Low (weakly coagulated) | Eq. (3)                                         | φₙ ≈ 0.45                   |
| 0.60                               |                   |                                                 | k₂ = 0.60                   |

Fig. 8. Effect of dispersant on apparent viscosity and sedimentation.

gravity and in a centrifuge. Comparing the results of the apparent viscosity and the packing volume fraction, the following are elucidated.

(1) The apparent viscosity and the sediment packing volume fraction change suddenly at different dispersant concentrations. It does not mean that a well-dispersed slurry changes always to a well-condensed sediment.

(2) Changes in the final sediment packing fractions can be correlated with change in the dispersant concentration not the apparent viscosity.

(3) It seems that the polymer dispersant acts as a lubricant during sedimentation and compression.

Greek letters

φ₀: initial volume concentration of slurry
φₙ: final packing fraction of sediment under gravity
φₙ: final packing fraction of sediment in centrifuge

Notation

hₚ height of slurry or sediment, mm
h₀ initial height of slurry, mm
hₙ final height of sediment, mm
k₁ rate constant, mm/h
k₂ rate constant, 1/h
k₃ rate constant, mm/h
φ₀ initial volume concentration of slurry
φₙ final packing fraction of sediment under gravity
φₙ final packing fraction of sediment in centrifuge

References


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