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Evaluation of Dispersant Efficiency for Aqueous Alumina Slurries by Concurrent Techniques

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This article reports on results from a comparative study assessing a suitable method for dispersant efficiency evaluation in the case of water-based suspensions of ultrafine alumina stabilized by a commonly used dispersant, Dolapix CE64. The following measurements were evaluated: zeta potential, specific surface charge, sedimentation behavior, and capillary suction time. The suitability of each of the tested techniques is discussed. A good agreement between the zeta potential and the specific surface charge as a way to determine the optimal dose of dispersant is documented.

Keywords Alumina powder, suspension, dispersant, electrokinetic phenomena

INTRODUCTION

Direct consolidation techniques, gel casting being one of them, based on colloidal processing and claiming to yield complex near-net shape bodies with consistent properties and minimal defects have been recently taking a place as viable alternatives to conventional routes of ceramics manufacturing. The common element among all of them is that they make use of well-dispersed suspensions with high solids loading. However, regardless of their acknowledged advantages, many of them have not succeeded in leaving the laboratory level or pilot plants of ceramic companies, with only few small-scale installations running for some complicated parts. One main challenge is the low production rate, which still cannot compete with dry pressing. The gel-casting process is based on the development of an aqueous or nonaqueous slurry of colloidal-size ceramic particles, together with predetermined amounts of dispersant, gelling reagents, initiators, and catalysts. Since the optimal dispersion of the particles and the stability of powder suspension is a key factor for the development of desirable end products, the appropriate choice of dispersant type and its dose level is of paramount importance for realizing a successful gel-casting process. Often it is imperative to reach as high a solids loading as possible in the slurry. This is because high solids loading reduces the drying and firing shrinkage with a parallel increase in the green strength.

Usually dispersants are selected on an empirical basis, which involves a time-consuming screening procedure to evaluate their performance. The conventional technique employed most often is to assess the macroscopic properties of the suspension, such as sedimentation behavior and viscosity, which, however, does not provide information about the interfacial phenomena taking place during particle-dispersant interaction. Therefore, it is desirable to choose a method capable of evaluating the dispersant-powder compatibility, that is uncomplicated, fast, and reliable as well able provide information about the surface behavior of the dispersant. With entering the colloidal size range in particulate systems, the control over particle dispersibility becomes increasingly difficult, since surface properties of particles and associated interfacial phenomena determine to large extent their behaviour. Hence, to control particle aggregation one should possess sound knowledge about surface and interfacial properties. Dispersibility could be viewed as the ease with which particles are distributed in a continuous phase, so that each one of them is completely surrounded by the liquid phase and there is no permanent contact with any particles so that they do not subsequently agglomerate (Klimpel, 1999). As a rule, the process of dispersant screening begins at low solids loading by using straightforward methods like sedimentation or light scattering for evaluation of the degree of particle dispersibility. Nevertheless, it has been documented that not every dispersant that demonstrates efficient dispersibility at lower solids loadings will maintain good dispersion at high solids loading (Singh et al., 2002). The present article reports on results from a systematic evaluation of the dispersive behavior of ultrafine alumina suspension stabilized by means of a commonly used dispersant, Dolapix CE64. The suspension stability has been assessed through the following parameters: zeta potential, surface charge density, capillary suction time, and sedimentation behavior.

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EXPERIMENTAL SECTION

Materials

An α-type calcined alumina powder, CR6, obtained from Baikowski-Chemie (France) was used. According to the producer's data, it is characterized by a mean particle size of 0.53 μm and specific surface area (BET) of 5.8 m^2/g. For verification purposes, the powder suspended in water was subjected to particle size distribution measurement by the means of a DT1200 spectrometer in acoustic attenuation mode, the results of which are shown in Figure 1. One can see very good agreement between the measurement and the data coming from producer. The dispersant used was Dolapix CE64, a cationic ammonium polyacrylate, supplied by Zschimmer & Schwarz (Germany). Its deflocculating effect is attributed to the interaction between the bivalent functional groups of the additive and the surface-charged ceramic particles. It was used as a 10% solution and was applied in a concentration range between 0.25 and 6 mg/g for the sedimentation tests and between 1 and 24 mg/g for the rest of the studies. Unless stated otherwise, bidistilled and deionized water from a Modulab purification system with conductivity under 0.2 μS/cm and a pH of 6.7 was used.

Measurement of Zeta Potential and Specific Surface Charge

The electrokinetic properties of the alumina powder in suspension have been expressed two ways: as a zeta potential coming from measurement of colloid vibration current (CVI) by an acoustic and electroacoustic spectrometer DT1200 and as a specific surface charge coming from streaming current measured by a particle charge detector PCD-O3-pH from Mütek (Germany). The operational and measurement principles of both systems are reported elsewhere (Dukhin and Goetz, 2002; Wäsche et al., 2002). For the CVI tests, 5.5 g of powder were added to 110 mL water, giving solids loading of 4.36% W. The suspensions were agitated for 2 min by magnetic stirrer, followed by 20 s with an ultrasonic disintegrator model UP 400 S, Dr Hilscher (Germany). Immediately after, they were transferred inside the measuring chamber, where they were kept in circulation by the built-in magnetic stirrer.

For estimation of the optimal dose of dispersant, two separate volumetric titrations were performed. First, the titration was done using the CVI instrument, where a predetermined amount of dispersant calculated on solid mass was added inside the chamber by means of an integrated burette and thoroughly mixed before zeta potential values were taken. In the second approach, using the PCD, the powder-liquid mixing was realized by the piston movement directly inside the 10 mL sample cell for 2 min, a duration considered sufficient as indicated by establishment of stable steaming current. A small pH electrode was fitted to the cell, enabling on-line pH monitoring. The exact magnitude of the charge, expressed as specific surface charge or charge density, was estimated by titration with oppositely charged standard polyelectrolyte until neutralization of the streaming potential to zero value.

Thus, the optimum dispersant dose level leading to maximum powder dispersion was considered to be the one coinciding with the inflection point of the plots between dispersant dose level and zeta potential and between dispersant dose level and surface charge density, derived respectively from CVI and streaming current measurement.

Sedimentation Studies

Sedimentation tests were performed using 25 mL calibrated glass cylinders. For each test, 1.25 g of alumina powder was mixed with 25 mL water containing a predetermined amount of dispersant: 0.25, 0.5, 0.75, 1, 3, and 6 mg/g. The suspension was vigorously shaken and allowed to stand undisturbed for 21 days. The sediment heights were read directly from the graduated cylinders. The higher the sediment height, the more stable the suspension.

Capillary Suction Time

Additionally, the optimal dose level of dispersant was evaluated by subjecting the powder suspensions to a capillary suction time (CST) measurement. This was realized with a CST 100/A device from HeGo Biotech (Germany), equipped with a hollow cylinder standing on a filter paper similar to Whatman 17 type. The operation of the CST instrument is based on the principle of capillary suction pressure of porous medium and could be viewed as a means for evaluation of the water-holding capacity of sludge or suspension and to some extent of its viscosity. The suspensions for the CST tests were prepared at a solids loading of 4.36% W under the same mixing procedure used for the samples measured in the CVI instrument. Two successive measurements, each one involving 5 mL suspension, were carried out and the mean from both values taken. The optimal dispersant dose level was chosen as the one yielding maximum capillary suction time or longer drainage rate, similar to the proposed method by Singh et al. (2003).

RESULTS AND DISCUSSION

The results from the volumetric titration of the suspensions are summarized in Figure 2. For the CVI case, the dispersant was progressively dosed in a step-by-step mode inside the same sample and accordingly each zeta potential value relates to measurement of the same sample. Each single point taken for the surface charge density however, was derived from measurement of an individual sample.

As can be seen from Figure 2, without addition of dispersant the alumina-water suspension is positively charged, as a result of the surface hydroxyl groups, which dissociate in water or act as proton acceptors. Without dispersant addition, the suspension was characterized by a pH of around 7 and appeared to

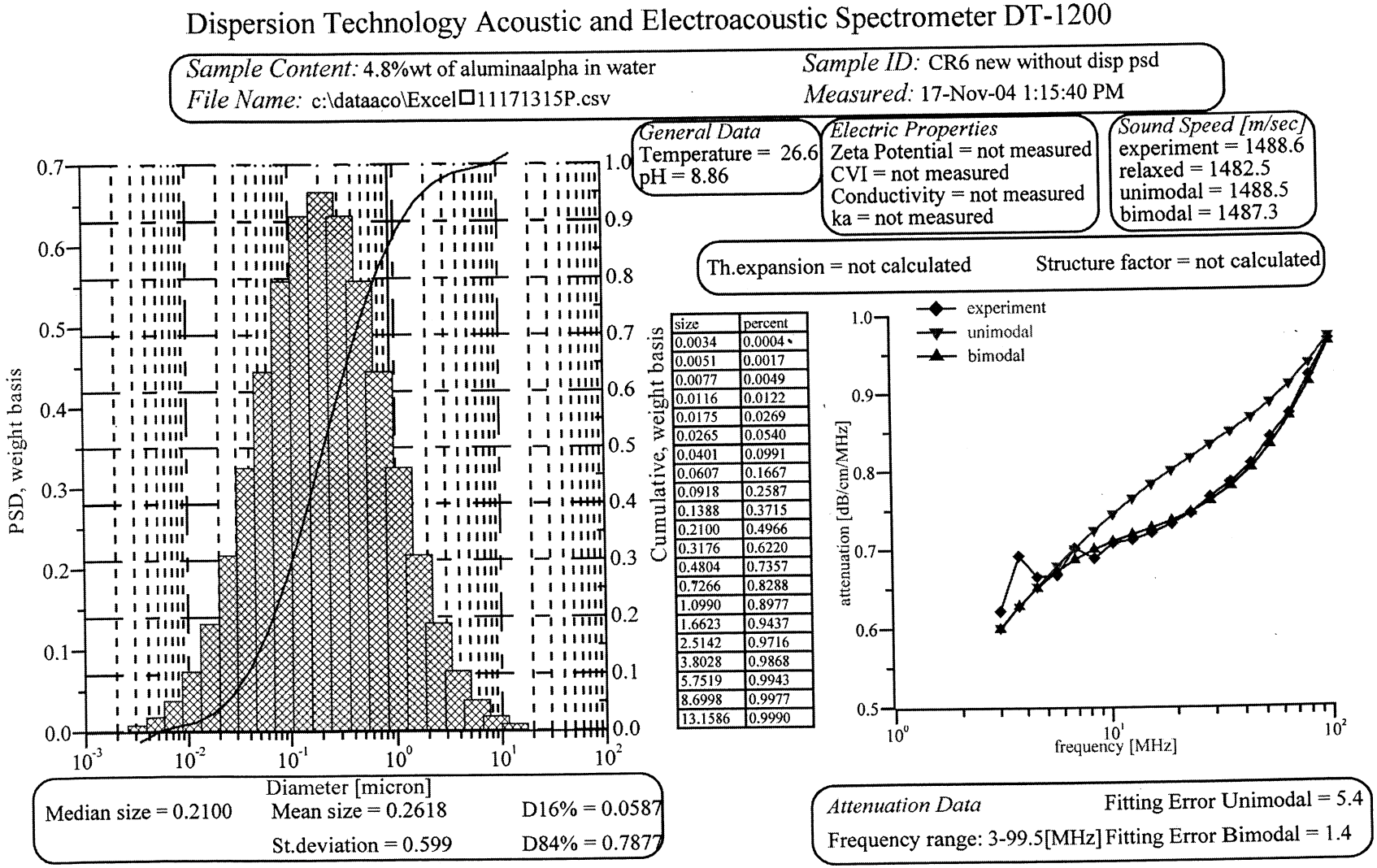

FIG. 1. Particle size distribution of powder suspension in water at 4.8% W solids loading.

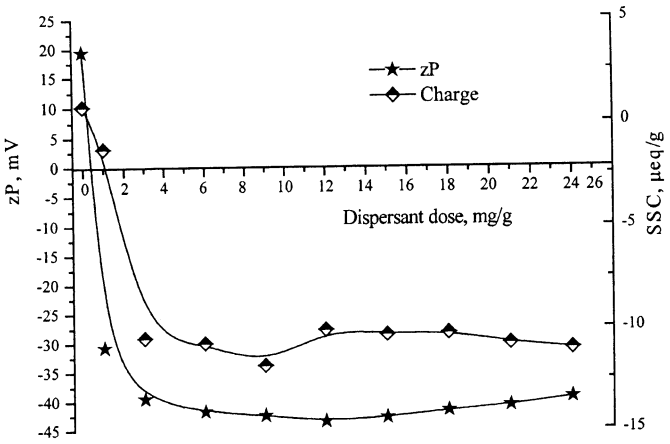

FIG. 2. Zeta potential and specific surface charge of powder suspension as function of dispersant dose level.

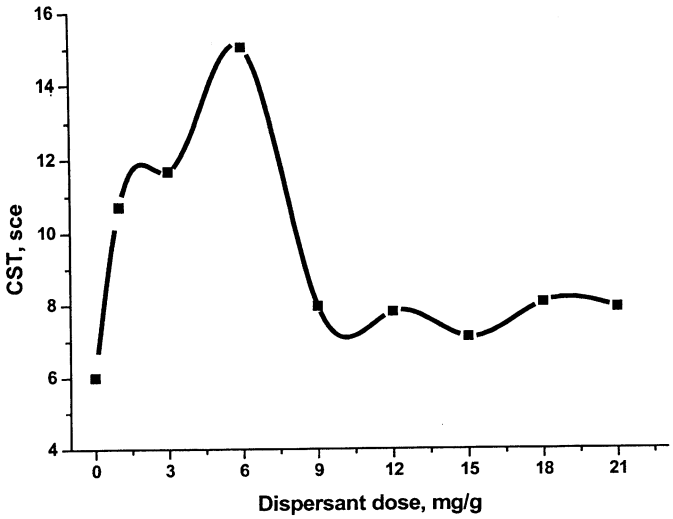

FIG. 4. CST of suspension as function of dispersant dose level.

be naturally stabilized by electrostatic repulsion forces, which are known to be weak and short ranged. With increase in the amount of supplied dispersant, the positive zeta potential dropped, and after passing through the zero charge, the powder acquired negative charge. After 3 mg/g dispersant dose level, an inflection point could be noticed, and above that point, both the zeta potential and the surface charge density curves flattened. As a rule, any amount of dispersant supplied above the optimum will remain unbounded in suspension, leading to unwanted high viscosity. Hence the optimum dispersant dose level lies between 3 and 6 mg/g. Within this range, the zeta potential approached −40 mV, which implies stronger stabilization involving electrosteric mechanism. It has to be noted that the progressive addition of dispersant within the envisaged range did not shift the suspension pH dramatically. The pH was found to slightly decrease from 8.9 at 1 mg/g, to about 8.2 at 24 mg/g dose level.

Further, it was interesting to investigate if the optimal dispersant dose suggested by the zeta potential and the specific surface charge would be reconfirmed by sedimentation and CST tests. Figure 3 summarizes the results from the plain sedimentation of powder suspensions with and without addition of dispersant. A perusal of these results indicates that without addition of dispersant the sediment height was maintained high within the first 24 hours, implying, as already noted, a naturally stabilized suspension. After that period, the suspension stability collapsed. Similarly, the addition of dispersant in dosages up to 1 mg/g has not led to notable stabilization, since after 24 hours the powder settled out of suspension. The supply of dispersant at concentration levels of 3 and 6 mg/g contributed to a relatively stable suspension in the long term. After 18 days, the sediments of the suspensions treated with 3 and 6 mg/g dispersant were characterized by a nearly double decrease in height, i.e. from 9 to 4.5 cm. However, after three weeks of settling under quiescent conditions, the powder from these two suspensions almost settled out in a packed bed, leaving a relatively high cloudy/clear interface height. According to Janney et al., behavior like this suggests, that Dolapix CE64 supplied between 3 and 6 mg/g is a quite appropriate choice for stabilization of the powder under study. Obviously, the suggestions regarding the optimal dose level of dispersant from the sedimentation study are in good agreement with those obtained from the CVI and PCD tests.

In Figure 4, the results derived from the CST experiments are shown. It should be noted that parallel to the increase in dispersant concentration up to 6 mg/g, capillary suction time rose as well. After that point, the CST dropped sharply. Since the CST reached its maximum value at 6 mg/g, this dose level

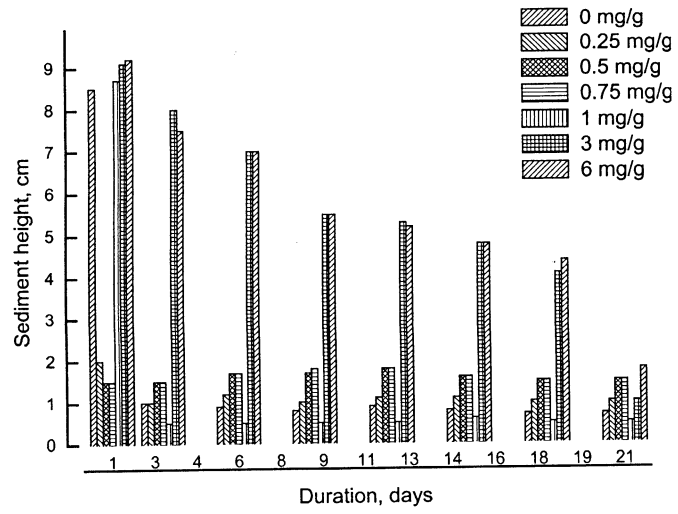

FIG. 3. Time variation of sedimentation heights at various dispersant concentrations.

can be again viewed as an optimal one. Under this condition, a full stabilization leading to the highest water holding capacity of the suspension could be expected. On the other hand, the short suction times imply particle agglomeration and accordingly faster water drainage rate.

When comparing the results from the electrokinetic studies, the sedimentation and CST tests, it is clear that for the studied suspensions a dispersant dose level of 6 mg/g could be finally chosen as the optimal one. Regardless of the different modes used for dispersant introduction inside the slurry during the CVI and streaming current determination, the trend of the zeta potential and specific surface charge curves was similar.

CONCLUSIONS

The following conclusions could be drawn based on the presented results:

- Each of the investigated techniques possesses advantages and drawbacks.
- Good agreement between the optimum dose level of dispersant required to stabilize the suspension was noted, as indicated by the zeta potential from the CVI and the specific surface charge derived from the streaming current measurements. This is in line with results reported by Wäsche et al. (2002), where during determination of pH_{iep} for suspensions of alumina, silicon carbide, and silicon nitride at different solids loadings, a linear correlation between the zeta and streaming potentials was established.
- For the powder under consideration, the CST technique has proven a fast and simple way for evaluation of the dispersion stability and for checking the optimal dispersant dose level. However, how CST relates to suspension rheology should be further studied.
- The use of plain sedimentation, although time consuming, has appeared as a relatively accurate approach for optimization of dispersant dosage, provided secondary effects like temperature and physical disturbances are eliminated. Additionally, the sediment volume could provide information about the nature of dispersed particles.
- It remains to be proven whether the current optimal dose level of dispersant will maintain similarly stable dispersions at the much higher solids loading of powder usually employed in gel casting.

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