CONSOLIDATION OF COLLOIDAL SUSPENSIONS

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INTRODUCTION

A key step in the processing of ceramics is the consolidation of powders into engineered shapes. Colloidal processing uses solvents (usually water) and dispersants to break up powder agglomerates in suspension and thereby reduce the pore size in a consolidated compact. However, agglomeration and particle rearrangement leading to pore enlargement can still occur during drying. Therefore, it is beneficial to consolidate the compact as densely as possible during the suspension stage. The consolidation techniques of pressure filtration and centrifugation were studied and the results are reported in this paper. In particular, the steady-state pressure-density relationship was studied, and information was obtained regarding the consolidation process, the microstructure, and the average density profile of consolidated cakes. We found that the compaction processes in these two consolidation methods are quite different. In general, a consolidated cake is a particulate network made up of many structural units which are fractal objects formed during aggregation in the suspension. In pressure filtration, compaction is a process of breaking up the fractal structural units in the particulate network by applied pressure; the resulting particle rearrangement is produced by overcoming energetic barriers which are related to the packing density of the compact. Recently, we performed Monte Carlo simulations on a cluster-cluster aggregation model with restructuring,[1] and found the exponential relationship between pressure and density is indeed the result of the breaking up of the fractal structural units.[2] On the other hand, in centrifugation, compaction involves the rearrangement of the fractal structural units without breaking them so that the self-similar nature of the aggregates is preserved. Furthermore, we calculated density profiles from the bottom to the top of the consolidated cakes by solving the local static force balance equation in the continuum particulate network. In pressure filtration of alumina and boehmite, the cakes are predicted to have uniform density. The results of γ-ray densitometry[3] on a pressure-flitrated alumina cake confirmed this prediction. In contrast, in centrifugation, the density profiles are predicted to show significant variation for cakes on the order of one centimeter high. Moreover, the pressure-filtered boehmite cakes showed no cracking during drying. This indicated that pressure filtration is a good consolidation technique for nanometer-sized particles such as boehmite. The improved drying property is probably a result of a minimal shrinkage due to the formation of higher packing densities during filtration.

PRESSURE FILTRATION

Pressure filtration of a colloidal suspension involves filtration of a fluid and compaction of a particulate network. The filtration part is described by the well-known Darcy's Law,[4] whereas the compaction of the solid part is less understood. During the early stages of filtration, pressure is applied to the suspension by means of a piston. At the final stage of filtration, the piston contacts the cake, and the cake is compressed (expression[4]). When the piston no longer moves and fluid no longer comes out of the filtrator, the system reaches

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a steady state. We measured the cake density at the steady state by comparing the cake height to that of the initial suspension. The steady-state density as a function of applied pressure is shown in Figure 1 for both alumina and boehmite suspensions at various pH values. The Sumitomo AKP-30 alumina powders have a median diameter of 0.4 µm. The Vista Catapal-D boehmite powders are plate-like and have an approximate diameter of 50-100 Å and a thickness of 10-20 Å. The density was found to be a logarithmic function of the applied pressure:[5,6]

$$\varphi = A\ln(P/P_0) + \varphi_0 \qquad (1)$$

where φ is the packing density (volume fraction) of solid particles, P is the applied pressure, φ_0 is a reference density, P_0 is the pressure at the reference density, and A is the slope. The reference density is chosen to be the packing density of the dispersed state, which is 0.65 for alumina.

The exponential relationship between pressure and density is the result of the compaction process and implies the breaking up of the fractal structural units in the particulate network due to the applied pressure. Resulting densification involves particles overcoming energetic barriers that are related to packing density. Here, we present an argument explaining how the exponential relationship may come about. The change in density $\Delta\varphi$ due to an increment in pressure ΔP, $\Delta\varphi/\Delta P$, is proportional to the probability of overcoming an energetic barrier for rearrangement, $\exp(-\alpha\varphi)$, where α is a constant. Here, it is implicitly assumed that the barrier height is proportional to the density. Therefore, we have $\Delta\varphi/\Delta P = \exp(-\alpha\varphi)$ which gives the exponential relationship between the pressure and the density after integration.

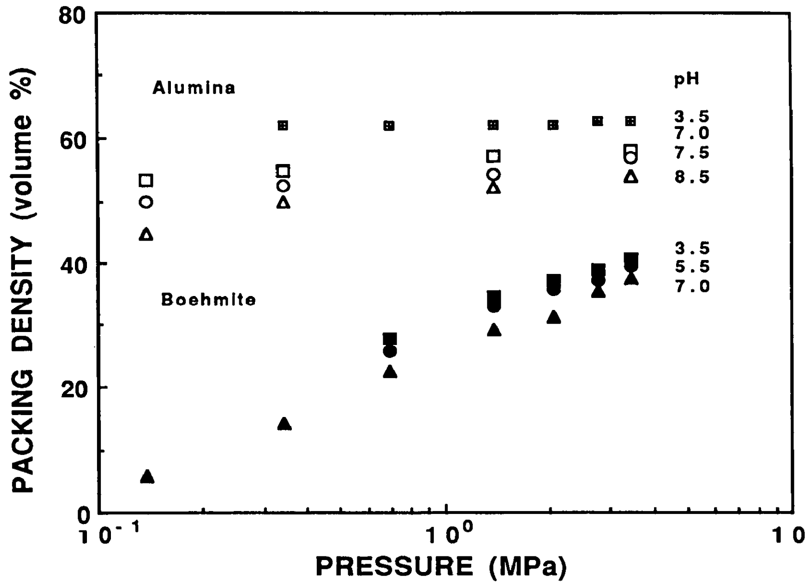

Figure 1 Packing density at steady state by pressure filtration as a function of applied pressure for micrometer-sized alumina and nanometer sized boehmite suspensions at various pH values.

The pressure-filtered boehmite cakes studied showed no cracking after drying for several days. However, a mullite-precursor gel made up of boehmite and silica particles needed to be dried very slowly over a few months' time in order to avoid cracking. The improved drying behavior is due to less shrinkage in pressure-filtered cakes. For the boehmite cakes we studied, typical shrinkage is around 10% compared with the typical 50% shrinkage of boehmite gels.[7] Less shrinkage produces less stress in the cakes and reduces the possibility of cracking.

CENTRIFUGATION

Centrifugation speeds up the sedimentation process of a suspension. However, the accelerating force is not uniform throughout the suspension and depends on the distance from the center of rotation. Buscall[8] showed that one can use an approximate mean force to describe the forces exerted on the sediment, provided the cake height is much smaller than the distance from the rotor center. We adopted Buscall's approach and estimated the mean pressure $\bar{P}$ as $\bar{P} = \omega^2(R - H_e)\varphi_0 H_0 \Delta\rho/2$ where ω is the angular velocity, R is the distance from the rotor center to the bottom of the cake, H_e is the cake height, φ_0 and H_0 are the initial concentration and suspension height respectively, and $\Delta\rho$ is the mass density difference between the particle and the solvent. The density as a function of the mean pressure is shown in Figure 2 for both alumina and boehmite suspensions. The pressure-density relationship can be described by a power law:

$$P = \beta\varphi^n \quad (2)$$

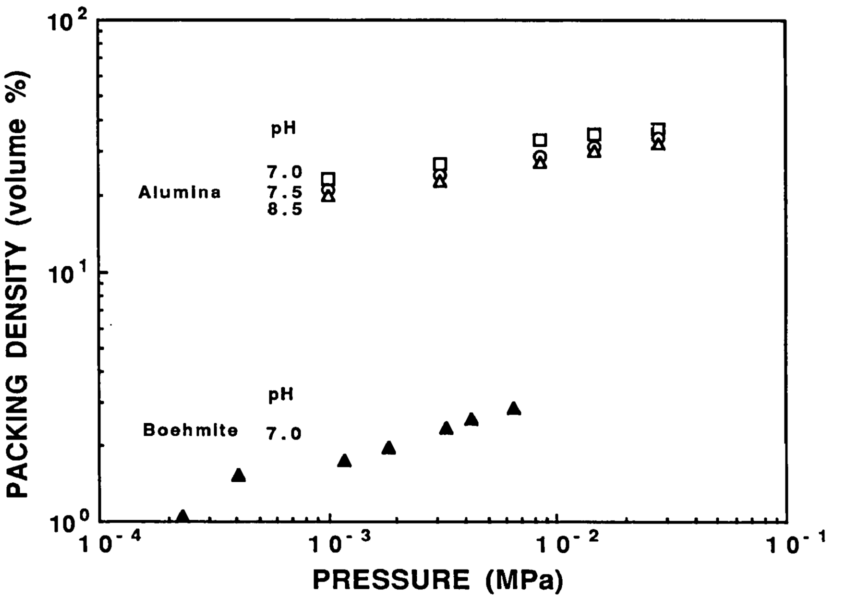

Figure 2 Packing density at steady state by centrifugation as a function of the mean pressure for micrometer-sized and nanometer-sized boehmite suspensions.

We can define an irreversible bulk modulus, K, as $K = -dP/d\ln V \sim dP/d\ln\varphi$ where V is the volume of a given cake.[9] Thereby, the irreversible bulk modulus behaves as $K = B\varphi^n$, where B is a constant. For boehmite cakes at pH=7.0, results of Figure 2 can be used to calculate $K = 3.024\times10^{10}\varphi^{3.68}$ (dyne/cm^2). Previously we measured the storage moduli of boehmite gels at pH=5.5 using a rheometer in the dynamic mode,[10] and the results are $G' = 4\times10^9\varphi^{4.1}$(dyne/cm^2). Similar power-law behavior for yield stress as a function of φ was also found in polystyrene latex suspensions by Buscall[11] with an exponent of 4.31.

We have developed a scaling theory[10] to relate K and φ, and results indicate that power-law behavior is attributed to the elastic deformation of fractal structures within the particulate network. Power-law behavior shown in Figure 2 indicates that the fractal structures formed during aggregation in the suspension may be preserved in the centrifuged cake. There appears to be very little restructuring, which is in direct contrast to the behavior observed in pressure filtration. The results for centrifuged alumina cakes can also be fitted to the form of equation (2) with $n \sim 8$ (Figure 2).

DENSITY PROFILE

With the results of the pressure-density relationship available (Figure 1), we can calculate the density profile from the bottom to the top of a consolidated cake. Based on local static force balance, Tiller et al.[4] have derived an equation for the pressure gradient within the solid network as

$$\frac{dP}{dZ} = -g\Delta\rho\varphi - \frac{\eta\varphi_l}{k}\left(\frac{q_l}{\varphi_l} - \frac{q_s}{\varphi}\right) \tag{3}$$

where Z denotes the distance from the bottom of the cake, g is the acceleration of gravity, $\Delta\rho$ is the mass density difference between the solid and the fluid, η is the viscosity of the fluid, k is the permeability of the cake, φ_l is the volume fraction of liquid, and q_l and q_s are the flux of the fluid and solid, respectively. In the final steady state, q_l and q_s are zero and we can ignore the second term on the right-hand side. Now we can substitute the empirical relationship between density and pressure, equation (1), in equation (3) to obtain a differential equation for the density profile. After integration, we obtain

$$Ei(\varphi/A) = Ei(\varphi_{max}/A) - \frac{\Delta\rho g A}{P_0}\exp(\varphi_0/A)Z \tag{4}$$

where $Ei(x)$ is the exponential integral

$$Ei(x) = \int_{-\infty}^{x} \frac{e^t}{t}dt\ . \tag{5}$$

In equation (4), the argument of the exponential integral is $x = \varphi/A$. The values of $Ei(x)$ are tabulated in mathematical tables. It should be noted that equation (4) describes the behavior of density profile when the packing density at the bottom of a cake φ_{max} is given. The present approach does not predict the value of φ_{max}. With the experimental data of A, P_0, φ_0, and φ_{max} for a particular material, the density profile can be calculated. For alumina at pH=8.5, with $\varphi_{max}=0.5$, we get $Ei(\varphi/A) = 352.5 - 8.2\times10^{-3}Z$, provided Z is measured in cm. This indicates that the density profile is constant since the first term on the right-hand side is much larger than the second term. Similarly, for boehmite cakes at pH=3.5, with $\varphi_{max}=0.3$, we get $Ei(\varphi/A) = 3.8 - 0.4\times10^{-4}Z$. Therefore for pressure filtration, the consolidated cake is predicted to have a uniform density profile from the bottom to the top of the cake. Recently, we measured the density profile of pressure-filtered cake using γ-ray densitometry.[3] For alumina at pH=8.5, the density profiles are shown in Figure 3. As is clear, in the final steady state, the density profile is uniform. Therefore, our prediction based on the empirical pressure-density relationship is in good agreement with the direct density profile measurement.

The density profile of centrifuged cakes can be calculated similarly. There are two differences, however, from the pressure filtration calculations. First, the acceleration of gravity, g, should be changed to the corresponding effective acceleration of gravity, $g_e = \omega^2 R$, assuming $H_e << R$. Second, the pressure-density relationship is changed to a power-law behavior, equation (2). Incorporating these two changes, we obtain the equation of the density profile for centrifugation:

$$\varphi^{n-1} = \varphi_{max}{}^{n-1} - \frac{(n-1)}{\beta n}\Delta\rho g_e Z \ . \tag{6}$$

For alumina with pH = 8.5, $\varphi_{max} = 0.4$, and $g_e = 824g$, we have $\varphi^{7.27} = 1.3\times10^{-3} - 2.57\times10^{-4}Z$. Whereas for boehmite at pH = 7.0, $\varphi_{max} = 0.03$, and $g_e = 824g$, we have $\varphi^{2.68} = 8.29\times10^{-5} - 2\times10^{-6}Z$. Based on these equations, it can be seen that for a typical cake height of 1 cm, there will be significant density variations with elevation. The density profile of flocculated alumina at pH = 8.5 in gravitational sedimentation has been studied by γ-ray densitometry.[3] The density profile showed sharp decreases from the maximum density at the bottom, in qualitative agreement with our prediction.

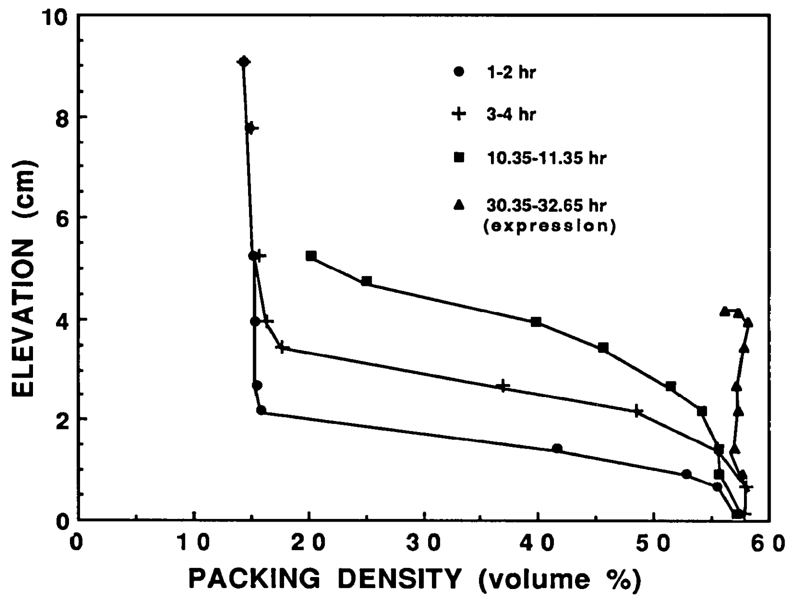

Figure 3 Density profiles of a pressure-filtered alumina cake (pH = 8.5) at various time steps, based on γ-ray densitometry. The density profile at steady state (expression) is uniform with elevation.

SUMMARY AND DISCUSSION

Two consolidation techniques, pressure filtration and centrifugation, were studied and the steady-state pressure-density relationships obtained. It was found that for pressure filtration the pressure-density relationship has an exponential form. The exponential form implies that compaction is a restructuring process where the movement of particles requires overcoming energetic barriers which are proportional to packing density. For centrifugation, the pressure-density relationship exhibits a power-law behavior. Power-law scaling suggests that the centrifuged cakes contain fractal aggregates which were formed during aggregation. The two consolidation techniques involve different compaction processes, resulting in different structures within each cake. Furthermore, we calculated the density profile within the cake, using the empirical pressure-density relationship. The pressure-filtered cakes are predicted to have uniform density profiles. The constant density profile was confirmed by the results of γ-ray densitometry on a pressure-filtered alumina cake. On the other hand, centrifuged cakes are predicted to show density variations for cakes a few centimeters in thickness. Previous γ-ray densitometry results on sedimented alumina cakes showed significant density variations, in qualitative agreement with the prediction.

Finally, we comment on the validity of equation (2). The data in Figure 2 can also be fitted to the form of equation (1) due to the finite number of data points. However, when the data is fitted to equation (1), the irreversible modulus is too large to be physically reasonable. For instance, for boehmite cakes with pH$=7.0$ at $\varphi=0.1$, the power-law fit gives $K=6.3\text{x}10^6$(dyne/cm^2), whereas when fitted to the logarithmic form of equation (1), it gives $1.3\text{x}10^{11}$(dyne/cm^2). Therefore, the power-law behavior of equation (2) is indeed more appropriate for description of the centrifuged cakes.

ACKNOWLEDGMENTS

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