

# Processing of Fine Ceramic Powders

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## Introduction

This article discusses the fundamentals required to produce narrow size distribution fine ceramic powders, make suspensions of fine ceramic powders, and make green bodies with a uniform packing of these particles. In all cases, the interface that fine ceramic powders present to their environment is a very important parameter in controlling the properties of the powders during processing.

There are two major classifications for ceramics: structural and functional. The former includes high and low temperature applications. High temperature ceramics are needed for kiln furniture, ladles, catalyst substrates, and insulations. Low temperature uses are represented by the traditional white ware, as well as hardness applications, such as coatings, armor, and cutting tools. Electrical functions include superconductivity, dielectrics, piezoelectrics, and varistors; magnetic functions are represented by ferrite magnets and SQUIDs (Superconducting Quantum Interference Devices); and optical functions include optical and infrared windows, as well as radar windows. Each class of ceramics has different processing problems and, therefore, different research and development directions. The major areas of research advances for structural and functional ceramics are described below.

## Structural Ceramics-Research Directions

In the early 1980s, Bowen at MIT<sup>1,2</sup> advanced the concept that sintered ceramic bodies could be improved by decreasing the defects in green bodies. In addition, his group promoted the idea that ideal green bodies should be composed of monodispersed particles packed into an ordered array. They used the hydrolysis of metal alkoxides to produce narrow-sized distribution

sol-gel amorphous powders. The latter were allowed to settle under the force of gravity into an ordered configuration and were then dried and sintered. Sintering took place at much lower temperatures and at a faster rate than traditional ceramic processing, e.g., when crystalline powders of broad size distributions were employed. Improvements in strength and toughness of the sintered body were never demonstrated by Bowen's group for these novel ceramics.

Ordered particles have packing faults which lead to domains similar to grains in polycrystalline materials. When sintered, the ordered domains shrink separately and pull away from each other. Consequently, defects in the sintered body occur in a size similar to that of the ordered domains, which can encompass as many as 10,000 particles. These ordered domains lead to weakness in the sintered body according to Griffith's fracture theory.

The long-range ordering of particles must be prevented in order to improve the microstructure; random close packing is therefore desired. By analogy with Lindemann's melting rule, such packing can be obtained by using particle size distributions where the standard deviation is greater than 10%.

The primary reason for the faster sintering at lower temperatures observed in Bowen's work is the use of narrow-size distribution sol-gel dispersions. These particles are produced by the aggregation of small, 0.01  $\mu\text{m}$ , particles which are in turn composed of aggregates of yet smaller units as shown in Figure 1. Onoda<sup>3</sup> has demonstrated that these particles have a classic fractal geometry where the fractal dimension,  $D$ , is defined as

$$D = 4.0 + 1n P/1n S$$

$P$  being the packing fraction of each aggregate and  $S$  the generation-to-

generation size ratio (i.e.,  $S > 1.0$ ). Since each particle is composed of much smaller subunits, the sintering of sol-gel solids occurs at much lower temperatures or shorter times than crystalline particles of the same size as the largest agglomerate. Figure 2 shows the faster sintering kinetics<sup>4</sup> of sol-gel aggregates as a function of the number of generations of aggregates. This is the same phenomenon as observed with other low density "reactive calcines" produced by aqueous sol-gel methods.

To take advantage of the fast sintering kinetics of sol-gel powders with their fractal geometry in the production of ceramic bodies, it is necessary to have agglomerate size distributions with standard deviations greater than 10%. This prevents ordered packing in the green body and its deleterious effects on strength. Broad size distributions, however, have the disadvantage of large particles being present, which produce large grains in the sintered ceramic and can also act as Griffith flaws. Suzuki et al.<sup>5</sup> have shown both theoretically and experimentally that a particle size distribution with a standard deviation between 10 and 30% can be packed to a relatively high green density of 60%. Saks<sup>6</sup> demonstrated that these higher green densities lead to less shrinkage during faster sintering. Also, broader size distributions lead to higher pore coordination numbers, which lessen the chance for stable pores to develop during sintering. Such stable pores give low sintered densities and low strength since pores can also be Griffith flaws.

## Functional Ceramics-Research Directions

The major research direction for electrical, magnetic, and optical ceramics is to decrease both the flaw size and the sintering temperature. In electrical ceramics, flaws lead to breakdowns at higher voltages. In optical ceramics, flaws cause light to scatter giving loss of transparency. Lower sintering temperatures are important for electrical and magnetic ceramics so that they can be co-fired with inexpensive metallization (i.e. not platinum, gold, or tungsten). In fact, a match of the sintering temperature of the ceramic to that of the metal is desired. The best metals are copper and nickel with melting points of 1083°C and 1453°C, respectively. In order to have sintering temperatures of approximately 1000°C, either isolated nanometer sized particles or sol-gel particles can be used where the smallest units in the fractal agglomerates are of nanometer size.



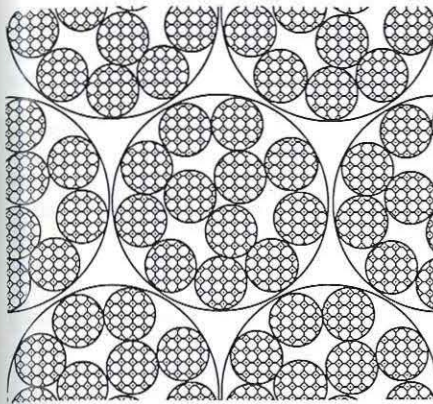


Figure 1. Aggregate structure of sol-gel particles.

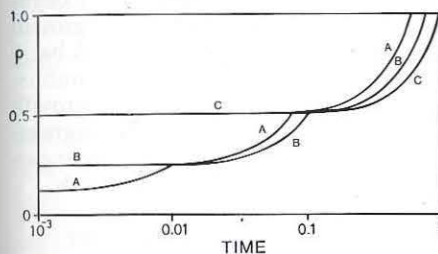


Figure 2. Sintering kinetics of sol-gel aggregates as a function of the number of aggregate generations.

Very small (nanometer) particles are very difficult to use to create a ceramic body, because the repulsive electrostatic forces are quite large and Brownian motion plays a dominant role in reversing any attempts to consolidate such powders. Most attempts to consolidate nanometer-sized particles have focused on some form of flocculation followed by pressing. Unfortunately, flocculation gives rise to aggregates with low fractal dimensions that do not pack to high density. To break up these agglomerates, exceedingly high pressures are necessary during the isostatic pressing to form a high density ceramic green body.

Recently, Aksay<sup>7</sup> has suggested that a lubricating layer be adsorbed on the surface of nano-sized particles so that lower pressures could be used for their consolidation. Traditional lubricants such as methyl cellulose, however, cannot be employed because these lubricant molecules are similar in size to the

particles themselves. By using low molecular weight ionic surfactants (e.g., soaps) instead, Aksay has been able to decrease the sintering temperature for silica to less than 1100°C.

### Ceramic Powder Processing

As we can see from the research directions presented above, ceramists are coming to grips with the processing of fine particles to improve the uniformity of ceramic microstructures and to decrease sintering temperatures. Processing fine ceramic powders involves their dispersion in aqueous and non-aqueous solutions. These slips and slurries are convenient for several shaping/forming technologies (e.g., slip casting, tape casting, filter pressing, and electrophoretic deposition) used to produce ceramic green bodies. As the demand for improving the properties of ceramic materials increases, more emphasis is being placed on controlling their microstructure, because microstructure influences the properties. The final sintered microstructures are highly dependent on (1) the initial powders, i.e., their degree of agglomeration and size distribution, (2) packing of the powder in the green body, and (3) the subsequent thermal processing: drying,

binder burn-out, and sintering. Uniformity of powder packing within a ceramic green body is needed to control differential shrinkage in single parts (e.g., cutting tools) and in complex parts (e.g., multilayer silicon-chip substrates). Well-defined ceramic powders and control of the process used to make the ceramic green body are the essential parameters to reliably and reproducibly assure the quality of the products (i.e., to keep rejection rates low, and to produce ceramic parts with consistent mechanical, electrical, and thermal properties).

This article reviews the pertinent fundamentals required to (1) produce narrow size distribution fine ceramic powders, (2) make suspensions of these ceramic powders, and (3) make green bodies with uniform packing of particles. For ceramic suspensions, agglomeration must be prevented for single component slips. For multicomponent suspensions, flocculation is often used to prevent segregation of the various components. The flocs are then broken during green-body pressing. For green body production, particle segregation due to size, density, and shape must be prevented when large quantities of liquids are removed.

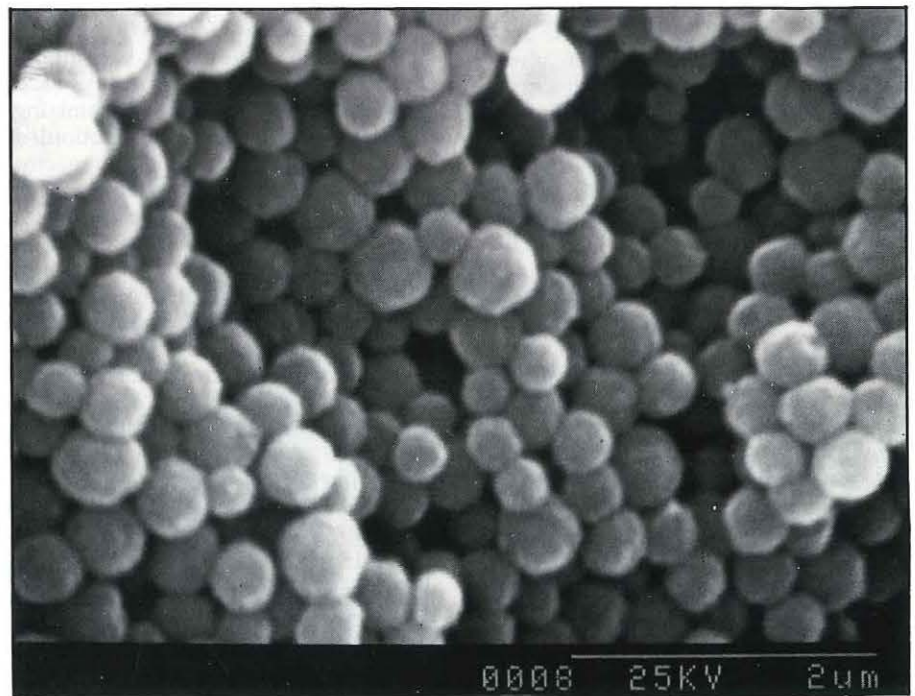


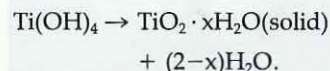
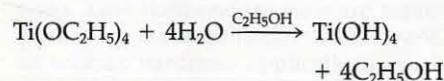
Figure 3. TiO<sub>2</sub> powder produced by the hydrolysis of titanium ethoxide.



### Producing Sol-Gel Powders of Narrow Size Distribution

To precipitate a powder of a narrow size distribution, a solution must be slowly supersaturated until nucleation takes place. Induction time refers to the period after the solution is mixed until nucleation takes place. During nucleation, a sufficient surface area of particles must be produced so that any subsequent supersaturation can be relieved by growth onto the existing particles and not by another nucleation event. The particles will continue to grow, until the supersaturation is relieved. Since nucleation is not instantaneous, the nuclei first produced will grow until the last nuclei are generated, giving a distribution of particle sizes at the end of the nucleation event. To narrow this size distribution, the growth must be limited by diffusion in the boundary layer surrounding the particle. The diffusing species or growth unit can be an ion, a complex, a polymer, or an aggregate. To maintain size uniformity, coagulation of the desired particles must be prevented by either electrostatic or steric means.

Jean and Ring<sup>8</sup> have produced TiO<sub>2</sub> powders of narrow size distribution by the following reactive sequence:



TiO<sub>2</sub> particles are precipitated when the ratio of the initial concentrations of H<sub>2</sub>O to Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> is greater than 2.5. The induction time is a function of the initial concentrations of Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> and H<sub>2</sub>O. Once nucleated, the particles grow by a diffusion limited mechanism. Figure 3 is a SEM photo of the powders produced by this reaction, consisting of aggregates ~0.01 μm in diameter. Separate electron diffraction experiments showed that these particles were composed of growth units 4 nm in size. Such aggregate structure is commonly found with fine sol-gel powders.

To achieve higher particle concentrations, coagulation must again be avoided. Mates and Ring<sup>9</sup> found that hydroxypropyl cellulose (HPC) could be used as a sterically stabilizing agent during the nucleation and growth of TiO<sub>2</sub> particles, permitting production of suspensions 8% in weight of TiO<sub>2</sub> with less than 1% multiplets of the largest particles. To continuously generate these

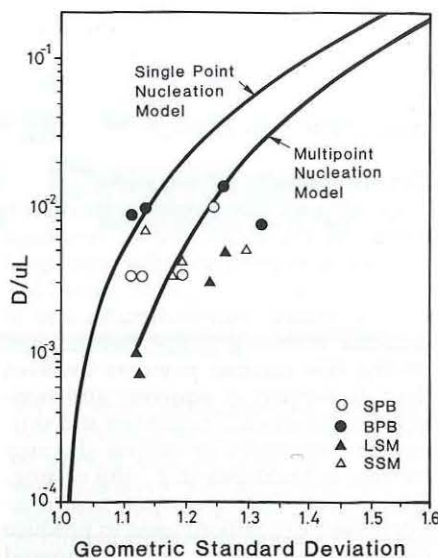


Figure 4. Dispersion number versus geometric standard deviation. SPB-short packed bed, LPB-long packed bed, LSM-long static mixer, SSM-short static mixer.

sol-gel agglomerates of narrow size distribution, a reactor design must prevent the backmixing of fluid elements as they flow through the reactor. This type of chemical reactor is referred to as a plug flow reactor. In real reactor designs, a small amount of backmixing cannot be prevented. Four types of chemical reactors minimize backmixing: (1) packed bed reactor, (2) motionless mixer reactor, (3) turbulent flow reactor, and (4) constant curvature laminar flow reactor. The degree of backmixing in each of these reactors is measured by the dispersion number,  $D/(uL)$ . Ring<sup>10</sup> has developed a model which predicts the geometric standard deviation,  $\sigma_g = \exp(\sigma_z)$ , of the particle size distribution precipitated in a reactor as a function of the dispersion number,  $D/(uL)$ , for both single and multipoint nucleation. As the degree of backmixing increases, the dispersion number and the geometric standard deviation of the particle size distribution increase (Figure 4). For the Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> with HPC reaction system described above, Jean et al.<sup>11</sup> have shown reasonable agreement with the multipoint nucleation model using both packed bed and motionless mixed reactors.

Another approach for continuous generation of narrow size distribution powders is to aggregate the particles in

a backmixed reactor (also called a constant stirred tank reactor, CSTR). An exact solution to this population balance equation is given by Dirksen<sup>12</sup> and is plotted in Figure 5. This theory predicts that quick agglomeration of nuclei will yield a narrow size distribution of solids, while in the absence of such agglomeration the size distribution will be broad for the Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> reaction system without HPC. Lamey<sup>13</sup> confirmed such expectations using a backmixed reactor.

Primarily, three methods are available for the precipitation of narrow size distribution powders, each based on a different technical approach as summarized in Table I. A plug flow reactor requires a single burst of nuclei. The subsequent supersaturation must be relieved by the high growth rate, which should be diffusion controlled. Coagulation must be prevented during growth by steric or electrostatic means. A backmixed reactor requires a continuous, high nucleation rate. Particle growth should be dominated by the aggregation of individual nuclei with larger particles and not by molecular growth.

### Generation of Ceramic Powder Suspensions

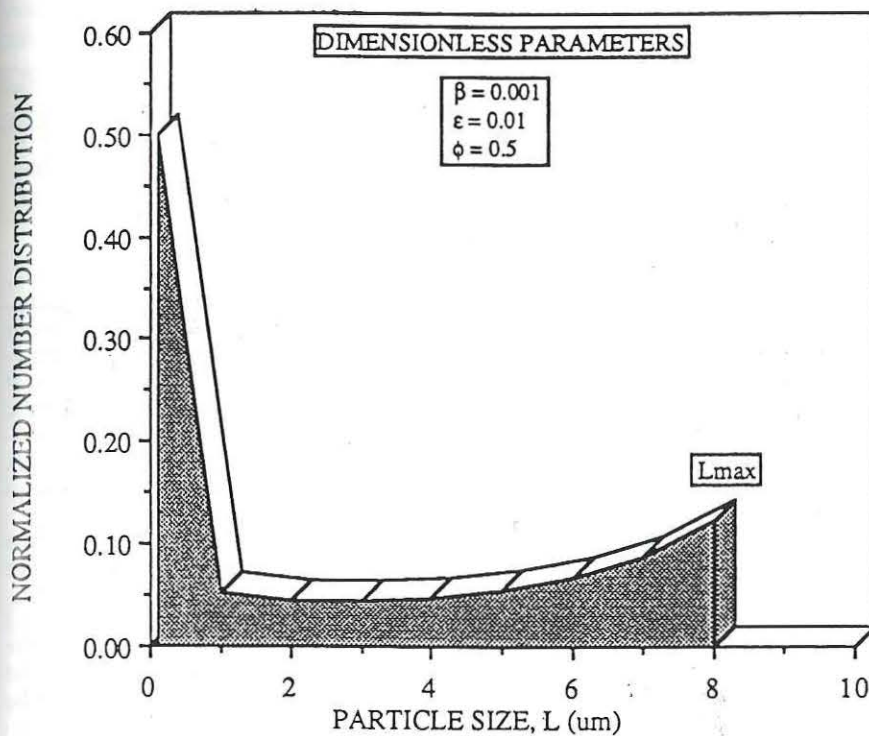
To generate a suspension of fine ceramic powders, the following sequence must be followed: (1) ceramic powder must be wetted by the solvent; (2) the powder must be deagglomerated; and (3) the particles once deagglomerated must be prevented from further agglomeration until a uniformly mixed suspension is obtained. With single component slips, the suspension must remain colloidal stable throughout the process of dewatering the slip to form a green body. With multicomponent slips, flocculation is usually performed on the well mixed suspension to prevent segregation due to density and size or shape differences between the various components of the slurry. The resulting green body after flocculation will have a low density and will require pressing to break up the flocs and to give a high-density well mixed green body.

**Wetting of a Ceramic Powder.** To obtain wetting, the contact angle between the ceramic powder and the solvent must be less than 90°. With a zero contact angle, the liquid spreads easily over the surface. Young's equation<sup>14</sup> governs the contact angle,  $\theta$ ,

$$\cos \theta = (\gamma_{sv} \cdot \gamma_{sl})/\gamma_{LV}$$



PREDICTION OF POPULATION DENSITY IN A CSTR



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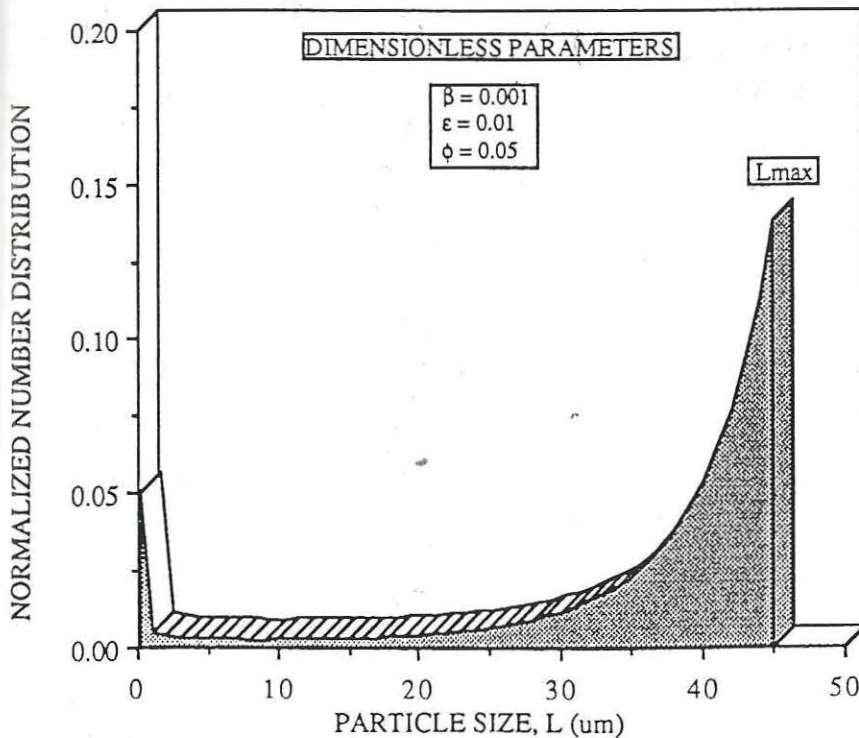


Figure 5. Population of particles produced in a stirred tank crystallizer with aggregation.  $\beta$  is the ratio of aggregation rate to growth rate,  $\epsilon$  is the ratio of half life for aggregation to mean residence time and  $\phi$  is the fraction of nuclei.

where  $\gamma$  is the specific surface energy and the subscripts refer to "Surface," "Vapor," and "Liquid," respectively. For wetting to occur,  $\gamma_{SL}$  and  $\gamma_{LV}$  should be made as small as possible. From the practical point of view, this is usually done by adding a surfactant to the liquid phase, which adsorbs and lowers the surface energy of the solid-liquid and liquid-vapor interfaces. The surfactants used for this purpose in ceramics processing are called dispersants and often have both ionic and hydrophilic parts to the molecule. These additives must be removed by thermal decomposition before sintering which can be a slow process with fine ceramic powders.

**Suspension Rheology.** Four basic types of rheological behavior of dispersions are illustrated in Figure 6. One type is a Newtonian fluid where the shear stress is proportional to the strain rate ( $du/dy$ ), the slope of which is the viscosity. The second type is a Bingham plastic, where there is a yield stress at zero strain rate, followed by a linear stress strain relationship. The third type is pseudoplastic which has a curving stress strain relationship that has a shape roughly similar to that of the Bingham plastic. The fourth type is shear thickening in which the shear stress increases with strain rate with an increasing slope.

Both Newtonian and Bingham plastic types of rheological behavior are commonly observed with suspensions of ceramic powders. Saks<sup>15</sup> has shown that Newtonian and Bingham plastic characteristics are observed for 30% by volume aqueous silica dispersions. At pH 9 and 10, Newtonian behavior was noted with a viscosity that was dependent on the pH, while at pH 4 Bingham plastic behavior exhibited a yield stress of 2 Pa. The latter is due to floc structures bridges that limit the flow.

**Coagulation in Fine Ceramic Powder Processing**

The coagulation time for a concentrated ceramic suspension undergoing shear due to differential settling is too involved to be calculated. For systems of particles less than 1  $\mu\text{m}$ , perikinetic (Brownian) coagulation dominates over the orthokinetic (shear induced) coagulation. Increasing the volume fraction decreases the settling velocities, which reduces the differential settling. The reduction in shear rate by an increase in volume fraction to 1% is sufficient to make perikinetic coagulation dominate



Table I: Generation of Narrow Size Distribution Powders.

Reactor Type	Nucleation Rate	Growth Rate	Coagulation Rate
Batch	Low	High	Low
Plug flow	Low	High	Low
Backmixed	High	Low	High

systems of particle sizes up to 3 μm. The following analysis of the coagulation time is for a concentrated polydisperse suspension undergoing perikinetic coagulation. This theory uses the colloid stability factor calculated for dilute, one-component suspensions (i.e., two-body interaction) and extrapolates to a concentrated suspension (i.e., multibody interaction).

**Coagulation Time.** The time,  $t_c$ , for a fraction,  $f$ , of particles to coagulate was calculated by Strauss et al.<sup>16</sup> The coagulation times shown in Figures 7 and 8 are for log-normal size distributions of titania (TiO<sub>2</sub>) powders (density 3.81 gm/cm<sup>3</sup>) suspended in aqueous salt solutions at 25°C. The Hamaker constant for this system was taken as a  $2.1 \times 10^{-20}$  J and the  $\zeta$ -potential as 25 mV. In all cases, the coagulation time should be larger than the time required for processing the ceramic suspension. Figure 7 shows that the volume fraction has a small effect on the coagulation time. Significant increases in this time occur at very low volume fractions where the particles are far apart and, therefore, the diffusion distances and times are very large.

Narrowing the width of the particle size distribution has a much larger effect on increasing the coagulation time, as seen more directly in Figure 8. Along each curve, the average particle size  $\langle a \rangle$  is kept constant and the logarithm of the coagulation time is plotted versus  $\sigma_z$ . For example, monodispersed particles of 0.6 μm take roughly a year to coagulate, while those with  $\sigma_z = 0.4$ , coagulate in about an hour. Larger particles are inherently more stable because of their high energy barriers; therefore, the rapid coagulation in polydispersed systems is caused by small particles in the distribution. The total stability factor for a polydisperse system is found by summing the reciprocals of the individual pairs of stability factors, much like resistances in parallel. In this way, pairs of particles which have large stability

factors contribute little toward the total, while pairs which have small stability factors contribute greatly. The energy barrier between particles is enlarged by increasing the surface potential or

decreasing the electrolyte concentration, which in turn increases the coagulation time. Even though the energy barrier for the average particle size may be high enough to hinder coagulation, polydispersity will cause some of the energy barriers to be small or nonexistent, thereby reducing the coagulation time.

**Flocculation of Ceramic Powder Mixtures**

With mixed ceramic suspensions, flocculation is used to prevent segregation of two or more ceramic powder components, for which purpose polymers are often used. The polymer must (1) adsorb on the surfaces of the ceramic powders, and (2) destabilize the suspension so that all particles stick together when they come into contact by Brownian diffusion.

Polymer adsorption takes place when the macromolecule has an affinity for the powder surface or when by increasing concentration it is pushed out of solution onto the powder surface by the approach of a solubility limit or a cloud point. The affinity of the polymer can be manipulated by its constituent conformation and functionality. The adsorption of polymers by ceramic powders often follows the Langmuir adsorption isotherm given by

$$\Gamma/\Gamma_m = bc_2/(1 + bc_2)$$

where  $b$  is the distribution coefficient and  $c_2$  is the concentration of the polymer. Once adsorbed, a polymer can either stabilize or destabilize a ceramic suspension. When the polymer likes itself better than the solvent, flocculation occurs. Conversely, when the polymer likes the solvent more than itself, steric stabilization occurs. In both cases, the same equation derived by Vincent<sup>17</sup> governs the interaction energy for two particles with radius,  $r$ , coated with a layer of polymer of thickness,  $\delta$ , at a separation  $H$ . The equation has two terms: The first term is the steric interaction energy derived by Fischer<sup>18</sup> and the second term is the van der Waals interaction energy derived by Vold.<sup>19</sup>

**Flocculation Kinetics.** According to Smoluchowski,<sup>20</sup> the flocculation kinetics is controlled by the collision rate between particles consisting of  $i$  and  $j$  units:

$$dN_{ij}/dt = 4 \pi R_{ij} D_{ij} N_i N_j$$

where  $N_i$  and  $N_j$  are the number densities of particles of size  $r_i$  and  $r_j$ , re-

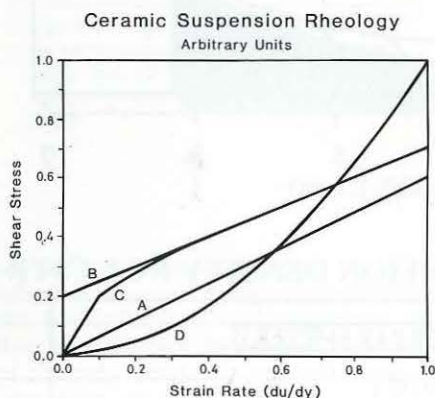


Figure 6. Rheological behavior of ceramic powder suspensions: (A) Newtonian, (B) Bingham plastic, (C) pseudoplastic, (D) shear thickening.

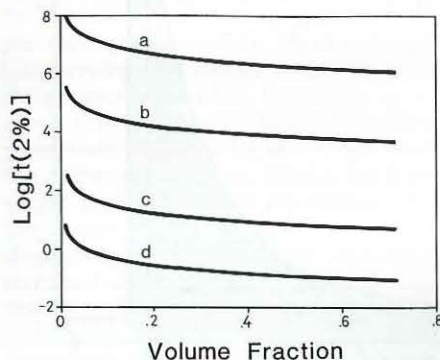


Figure 7. Coagulation time in seconds vs. volume fraction for a 2% dispersion at different distribution width parameters. Electrolyte concentration is 0.01 mol dm<sup>-3</sup>,  $\psi^0 = 25$  mV,  $A = 2.1 \times 10^{-20}$  J, (a)  $\sigma_z = 0.0$ , (b)  $\sigma_z = 0.25$ , (c)  $\sigma_z = 0.75$ .



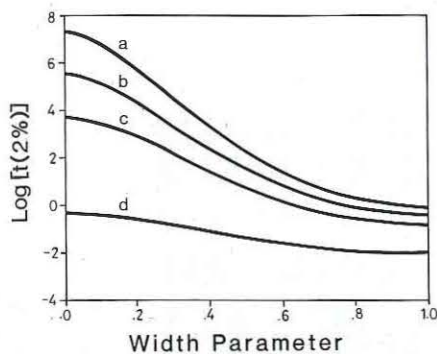


Figure 8. Coagulation time in seconds vs. distribution width parameters for a 2% dispersion of different average particle sizes. Electrolyte concentration is 0.01 M,  $\psi^0 = 25mV$ ,  $A = 2.1 \times 10^{-20} J$ , (a)  $\langle a \rangle = 0.3 \mu m$ , (b)  $\langle a \rangle = 0.25 \mu m$ , (c)  $\langle a \rangle = 0.2 \mu m$ , (d)  $\langle a \rangle = 0.1 \mu m$ .

spectively,  $D_{ij}$  is the mutual diffusion coefficient of the two particles, and  $R_{ij}$  is the sum of the radii of the  $i$ -th and  $j$ -th particle. The product  $R_{ij} * D_{ij}$  is given by

$$R_{ij} * D_{ij} = [r_i + r_j] * [1/r_i + 1/r_j] * kT / (6\pi\eta)$$

where  $K_B$  is the Boltzmann constant,  $T$  the absolute temperature, and  $\eta$  the viscosity of the medium.

If we let  $k = i + j$ , so  $N_k = N_{ij}$ , and further assume that initially all particles are identical ( $i = 1$ , monodisperse) and that the aggregates are spherical, then the number density of  $k$  particles from an initially monodispersed system is given by

$$N_k = N_0 (t/\tau)^{k-1} / [1 + (t/gt)]^{k-1}$$

where  $k$  is an integer and  $\tau$  is the flocculation half life ( $= 1/[8\pi N_0 k_B T / (6\pi\eta)]$ ), where  $N_0$  is the initial number density of particles.

These agglomerates are used to lock in the well-mixed structure of the suspension, preventing segregation of particles due to differences in size, shape, or density. Unfortunately, the agglomerates given an inhomogeneous, low density packing and, therefore, must be broken up by pressing.

### Green-Body Formation

The formation of a ceramic green body requires one or more forces to remove the excess liquid from a ceramic suspension. With slip casting, a combi-

Tape Cast Thickness for Bingham Fluid

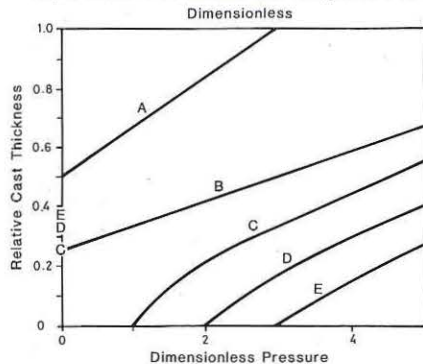


Figure 9. Cast thickness for a Bingham fluid as a function of dimensionless pressure gradient and dimensionless Bingham yield stress; (A)  $T_0^* = 0$ ; (B)  $T_0^* = 1$ , (C)  $T_0^* = 2$ , (D)  $T_0^* = 3$ , (E)  $T_0^* = 4$ .

nation of hydrostatic pressure and mold capillarity provides the necessary dewatering forces. With filter pressing and colloid pressing, only hydrostatic pressure is used. For tape casting, a polymeric binder is employed, which shrinks upon drying pulling the particles closer together. The fundamentals of each of these forming technologies will be discussed.

**Slip Casting.** With slip casting, a porous mold is used to give shape to the green body. The mold is filled with a ceramic suspension and a combination of hydrostatic pressure and capillary suction dewateres a thin section of the ceramic suspension adjacent to the mold. The thickness of the dewatered layer,  $D$ , is given by Darcy's Law:<sup>21</sup>

$$D^2 = 2 K \rho \kappa (\Delta P + 2\gamma/r) t$$

where  $K$  is the permeability of the cast layer,  $\rho$  the density of the cast layer,  $\kappa$  the factor converting the volume of water removed to the volume of ceramic powder deposited,  $\Delta P$  the hydrostatic pressure head,  $\gamma$  the surface tension of the solvent with all of its additives including dispersants, wetting agents, and binders,  $r$  the mean pore radius of the mold, and  $t$  is time.

The packing that is obtained during slip casting is essentially that of the collapsed slurry. When the dewatering rate is slow, the particles have ample time to diffuse laterally to find a packing

location which minimizes the defects in the structure before they are locked into location by the next layer of particles. Conversely, when the dewatering rate is high, the particles do not have enough time to rearrange themselves before they are fixed into a packing location by the arrival of the next layer. For this reason, the dewatering rate controls the packing of the particles in a slip cast.

**Pressure Filtration.** In pressure filtration, a piston is used with a frit bottom to allow the excess liquid to leave the chamber and catch the ceramic powder on the frit. The consolidated layer of ceramic powder grows according to a parabolic rate law, derived from Darcy's Law. The consolidated layer thickness,  $d$ , is given by

$$d = [2 K (\phi_1/\phi_2 - 1) P t/u]^{1/2}$$

where  $K$  is the permeability of the consolidated layer,  $P$  the applied pressure,  $\phi_1$  and  $\phi_2$  are the volume fraction of solids in the consolidated layer and in the suspension, respectively,  $u$  is the piston velocity, and  $t$  is the time. Using this equation, a plot of the piston displacement,  $d$ , versus  $t^{1/2}$  gives a straight line from which the permeability of the powder compact can be determined.

The permeability decreases as the applied pressure rises, resulting in higher packing density. Flocculation of the ceramic suspension before filtration enhances permeability, often by a factor of ten. Applying higher pressure decreases the permeability and increases the density to a much larger degree with floccled than with stable suspensions. To break flocs and aggregates, pressures in excess of 80 MPa are commonly needed.

With pressure filtration, the packing is essentially that of a collapsed slurry. When the dewatering rate is slow the particles have ample time to diffuse laterally to find a packing location which minimizes the defects in the structure before they are locked into location by the next layer of arriving particles. Conversely, when the dewatering rate is high, the particles do not have enough time to rearrange themselves before they are fixed into a packing location by the arrival of the next layer. For this reason, the rate of filtration controls particle packing in the cast layer. But unlike slip casting, the high pressures applied in filtration can cause further consolidation of the cast layer, increasing the packing density.



**Tape Casting.** Tape casting is a common way to produce thick film ceramic green bodies. A tape casting machine consists of a moving belt onto which a ceramic powder slurry is spread by a stationary rectangular doctor blade. Control of the thickness of the cast is of critical importance in this technique. In order to determine it, one needs to know the velocity profile in the gap between the doctor blade and the moving belt. Once this is established, the integrated average velocity can be calculated and the cast thickness determined. For a Bingham plastic fluid, the thickness,  $\delta$ , is given by<sup>22</sup>

$$\delta/h = (1/2 + P/6) [1 - (T_o^* - 1 + P)/2P]$$

where  $h$  is the thickness of the gap between the bottom of the doctor blade and the moving belt,  $P$  is the dimensionless pressure gradient across the doctor blade [ $P = h^2 - dp/dx / (2\eta u)$ ] and  $T_o^*$  is the dimensionless Bingham yield stress [ $T_o^* = \tau_o h / (\eta u)$ ]. The pressure gradient across the doctor blade is  $dp/dx$ ,  $u$  is the belt velocity,  $\tau_o$  is the Bingham yield stress of the suspension, and  $\eta$  is the viscosity of the suspension. When the pressure gradient is increased, the thickness of the cast increases for all Bingham yield stresses as seen in Figure 9. At a constant pressure, the thickness of the cast decreases as the yield stress increases.

Packing of the particles in tape casting is highly influenced by shear. High shear rates tend to orient nonspherical particles, leading to nonuniform packing. The forces which act to pull the particles together are essentially those of

polymer shrinkage upon drying. A polymeric binder is used to give the dried tape structural integrity; when dried, it shrinks pulling the particles closer together giving a higher green-body density.

## Conclusion

This article has reviewed the generation of ceramic powders by chemical precipitation methods, the generation of ceramic powder suspensions, and the processing of ceramic powders to make ceramic green bodies. These methods are used to produce chemically pure ceramic powders of narrow particle size distributions. Agglomeration must be prevented by electrostatic or steric means with single component suspensions. With multicomponent suspensions, flocculation is often performed to lock in the well mixed nature of the suspension, preventing segregation due to differences in particle size, shape, and density. During green-body formation, large amounts of liquid must be removed while packing the particles uniformly. The fundamentals of green-body formation are discussed with special attention to the details of particle packing in the green body since its microstructure has such a large influence on the final sintered microstructure and the mechanical and electrical properties of the piece.

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