

Attaining High Solids in Ceramic Slurries

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ABSTRACT

Producing a free flowing, high solids slurry requires an understanding of the ceramic particles being processed, interactions among particles, the solvent in which the particles are processed, particle - solvent interactions such as wetting and dispersion, slurry rheology, and mixing equipment and techniques. The best results in attaining high solids loading with good slurry flow properties, excellent green part microstructure, and high green density is achieved when all of these factors are understood and well controlled.

WHAT IS THE NEED TO ATTAIN HIGH SOLIDS?

Ceramic engineers practice slurry processing for several of their forming techniques including spray drying, slip casting, pressure casting, tape casting, and gelcasting. Slurry processing, in general, requires attaining fairly high solids. Typical slurry volume fractions are between 40 and 80 vol %, depending on the process and the powder.

The definition of "high solids" depends critically on the powder being processed. For example, a refractory alumina mix may not act like a "high solids" slurry until it reaches 70 vol % solids. Conversely, a submicron silicon nitride slurry may act like a "high solids" slurry at 40 to 45 vol % solids. Also, the transition from acceptable slurry behavior to unacceptable slurry behavior may occur over a very narrow range of volume fraction solids. In general, a high solids slurry displays several characteristics, either in and of itself, during the mixing operation to achieve a good slurry, or upon attempting to achieve a slightly too high volume fraction solids. These characteristics include excessively high viscosity, difficulty in adding additional powder, dilatancy, and colloidal instability. In addition, producing a high solids slurry that processes well usually carries with it other advantages such as producing a superior green microstructure with good homogeneity and few defects such as agglomerates and pores.

Some forming methods require the ultimate in high solids; that is, in some forming operations, the slurry density defines the green density of the formed ceramic article. Injection molding, extrusion, calendaring, and gelcasting fall into this category. For these forming techniques, it is critical that the process engineer be able to increase the slurry solids loading to as high a level as possible. Higher solids reduces the shrinkage during drying and firing and increases the wet and dry green strength.

PRODUCING A HIGH SOLIDS SLURRY

Producing a free flowing, high solids slurry requires an understanding of the ceramic particles being processed, interactions among particles, the solvent in which the particles are processed, particle - solvent interactions such as wetting and dispersion, slurry rheology, and mixing equipment and techniques.

Powder selection

Powder selection is the over-riding factor in all slurry processing. If a “good” powder is selected, one might be able to achieve high solids. Conversely, if a “bad” powder is selected, then high solids might not be achievable under any circumstances. Unfortunately, the selection of a powder to process is often not the choice of the process engineer. Often such a selection has already been made by the composition developer or by the availability of raw materials. For example, Ube E10 silicon nitride (Ube Industries, Tokyo) is a difficult powder to process; however, for advanced silicon nitride compositions it is often the powder of choice.

Irrespective of whether the process engineer has input into the selection of the powder being processed, powder characterization is a crucial step in understanding and controlling the slurry making process. Particle size and particle size distribution are the two most important parameters that need to be measured. However, one must know what is being measured and often more than one type of measurement is required. Particle size measurements alone are often misleading. For many powders, additional information must be obtained through microscopy (SEM and TEM) and surface area measurements (BET method).

Powder conditioning

Powder conditioning may be needed before making a slurry if a high solids loading is to be obtained. Often the need for processing is determined by the history of the

powder: what precursors were used? was the powder calcined? what, if any, milling to achieve particle size reduction was conducted on the powder?

As an example of two powders having highly different histories, consider a commercial calcined alumina powder and a research-grade hydroxylapatite. Most commercial alumina powder is produced by the Bayer process, which involves calcining $\text{Al}(\text{OH})_3$ to form α -alumina. After calcining, the powder may be ground in a ball mill to break up hard agglomerates and to reduce the powder to its ultimate particle size. Because calcined aluminas are standard items of commerce, they are highly processed and repeatable. Furthermore, because the alumina suppliers sell mainly to the ceramic community, they understand the need for control of not only chemistry and phase, but also of physical properties such as particle size and distribution, compactability, and sintering response. In contrast, research-grade hydroxylapatite powder is typically made by a chemical house rather than a ceramic powder producer. The requirements for the material might be chemical purity and phase composition, with no concern for the physical properties of the powder. Often, powders of this type are listed only as -325 mesh (i.e., $<44 \mu\text{m}$ diameter). Concerns relative to particle size distribution, surface area, dispersibility, powder compaction, etc. are just not important to the producer. Such a powder may have been calcined at a temperature high enough to produce the proper crystallographic phase, but so low that the particles are far too fine to achieve high pressed density or reasonable slurry properties. This is typically indicated by a too high surface area (say, $>50 \text{ m}^2/\text{g}$). To make such a powder usable in a ceramic process requires a significant amount of processing. First, the powder needs to be recalcined to coarsen the powder, reduce its surface area, and increase the average primary particle size. What temperature is required and how long the powder needs to be held at that temperature must be determined by trial and error. Most often, surface area is used as the control variable. A target surface area of between 5 and $10 \text{ m}^2/\text{g}$ would be a reasonable choice. Second, the powder must be milled to break down hard agglomerates that were formed during calcining. This milling must be done in such a way that the desirable characteristics of the powder are not altered. This means using non-wearing media (e.g., partially stabilized zirconia - 3 mol% yttria balls) so that the powder is not contaminated. Again, this is a trial and error process and uses particle size and distribution as the control parameters. One requires that the hard agglomerates be fully broken apart, yet one does not want to over-mill the powder and produce excessive fines. Third, the appropriate firing conditions must be determined by conducting sintering trials at a variety of temperatures. Finally, if a

new lot of hydroxylapatite is obtained, the process must be conducted all over again. There is no guarantee that the manufacturer produces the same powder (from a ceramic viewpoint) each run.

The most common processing that needs to be done is milling the as-received powder to break up hard agglomerates or to reduce the primary particle size. Consider the model agglomerate shown in Figure 1. The agglomerate is comprised of primary particles with a diameter of about 1 μm , first generation agglomerates with diameters of about 5 to 10 μm , and second generation agglomerates with diameters of about 50 to 100 μm . A powder made up of agglomerates like those in Figure 1 will undergo a rapid decrease in particle size during milling. In most cases for an agglomerated powder, the initial distribution is bimodal and consists of a major peak in the 10 to 100 μm range and a small peak in the submicrometer to micrometer range. The major peak at large particle size reflects the agglomerate size and the smaller peak reflects the primary particle size. As milling proceeds, the peak for the large diameter agglomerates shifts to smaller sizes and diminishes in size. It may also transform into two peaks, which signals a transition from second generation to first generation agglomerates. At the same time, the peak representing the primary particles grows as more primary particles are released from their attachments to their neighbors. The mode of the primary particle peak may shift to slightly smaller values during milling, but that shift is usually small (<10%). Eventually one reaches "endpoint" milling at which point little more change occurs in the distribution. Figure 2 shows the milling behavior for indium-tin oxide, which is characteristic of a calcined, agglomerated powder. It should be noted that the rate of particle size reduction during milling an agglomerated powder follows more closely a logarithmic relationship than a linear one. That is, test samples should be taken at time intervals that are multiples of one another (e.g., 1, 2, 4, and 8 hrs) rather than at equal intervals (i.e., 1, 2, 3, and 4 hrs). One further caveat needs to be mentioned regarding particle size distributions and milling studies. That is that some ceramic powders can produce a "false agglomerate distribution" phenomenon. An example of this is shown in Figure 3 for potassium tantalum niobate. This powder started its existence as a single crystal. The single crystal boule was hammered into fine grit, then ball milled to make a sinterable, micrometer-sized powder. The initial distribution after hammering, Figure 3, looks very much like that for the agglomerated, calcined powder shown in Figure 2. The evolution of the distribution is similar to that for the agglomerated indium-tin oxide for much of the milling process. However, what appears to be a "first-generation" agglomerate peak at about 2 to 5 μm , is actually a primary particle

peak that does not mill away, even after prolonged milling. Also, notice that the peak for the fine primary particles does not shift at all, whereas its counterpart in the calcined powder did shift to smaller size, albeit a small amount (1.03 μm to 0.85 μm). This stable, bi-modal distribution on prolonged milling has been observed for other powders in this lab, typically for softer ceramic materials. One example is europium oxide, which actually oscillates in particle size distribution at extended milling times with the two peaks alternately increasing and decreasing with time.

Dispersing the powder

Selection of a dispersing technique and chemical dispersant system ranks immediately below powder selection as a factor critical to achieving a high solids slurry. Dispersion depends on several processes, any one of which can cause difficulties. For a powder to become well dispersed it must be wet by the solvent, the particles must become separated from one another and mixed with the solvent system, and they must remain separated and not reaggregate.

Wetting, is primarily a condition described by surface thermodynamics. For aqueous systems, this is typically reported as the powder being hydrophilic or hydrophobic. A hydrophilic powder will be easily wet by the water in the slurry while a hydrophobic powder will sit on the surface of the water and not be wet at all. There is a continuum of states between these extremes, which can be affected by the surface chemistry and history of the powder (aging, calcining conditions, milling aids, etc.). From a practical point of view, a powder that wets poorly can be assisted by the addition of a wetting agent to the solvent used to make the slurry. Very often, that is all that is required. Other approaches are to treat the surface of the powder with surface modification agents or to heat treat the powder to remove organic contaminants that might be causing the problem. A powder that is somewhat hydrophilic may wet out quite well, but may take time to do so. In such a case, the rate of adding powder to the slurry may be critical. Typically in such cases, the powder should be added in small aliquots, with a fairly long mixing period allowed before additional powder is added.

Mixing techniques range from ball mills to high shear mixers to ultrasonic mixers. Which technique is selected is dictated by the type of suspension needed, the final and intermediate slurry viscosities, the level of contamination tolerated, and the size of the batch being processed. The bottom line is that the mixing technique selected should provide complete mixing in a useful amount of time. These issues will be

covered in detail in the next section.

Perhaps the most widely used technique is the ball mill. Ball mills are used for lab-scale 20 ml batches and industrial level 1000 gal batches. They can be run at high speeds for very fluid systems and at low speeds for highly viscous ones. They are used for making batches that are insensitive to contamination from mill lining or media to those that require linings and media that are completely non-contaminating.

To keep the particles dispersed once they are mixed with the solvent typically requires the addition of a chemical deflocculant or dispersant. Screening for dispersants is usually an Edisonian exercise. It depends on experience and luck. Experience tells one where to begin the search. For example, many oxide ceramics can be dispersed readily using poly (acrylic acid) and poly (methacrylic acid) derivatives. However, finding which of the hundreds of polyacid derivatives is the best for a given powder made by a given manufacturer is a matter of trial and error. The dispersant screening process usually starts at low solids loading using either sedimentation or light scattering to determine the degree of dispersion of the particles in the solvent. Then rheometry or other tests are conducted on higher solids systems.

First, a list of potential dispersants for the powder is developed. For a new powder for which the process engineer has little or no experience, the types of dispersants should cover a wide range of anionic, cationic, and non-ionic dispersants. The initial screening might be conducted using sedimentation tests in small (10 to 50 ml) test tubes. A 1 to 2 vol% suspension of ceramic powder is made in water (or other solvent) using ~1 to 2 wt% of each dispersant. The choice of 1 to 2 wt % dispersant is based on powders having surface areas in the range 0.5 to 10 m²/g; higher surface area powders will require greater levels of dispersant. Also, for aqueous suspensions, the effects of pH probably need to be addressed by running tests over a reasonable range of pH. The suspensions are usually mixed with a sonic probe for 30 sec before being set aside for sedimentation. The suspensions are allowed to settle under quiescent conditions. The following information should be noted for each sample: the sediment height after 24 hours, the sediment height after a longer period of time, say 1-2 weeks; and, the height of the interface between clear liquid and cloudy liquid after 1-2 weeks. For a good dispersant, the following conditions should be obtained. The 24-hour sedimentation height should be high; i.e., the powder should not have settled out of suspension in a short time. The long-term

sedimentation height should be low; i.e., the powder should pack very well when it does finally settle out of suspension. The 3-week cloudy/clear interface height should be high; i.e., the finest of the particles should stay in suspension for a very long time and should not reaggregate and settle.

Results for a typical study made using silicon nitride (Ube E10) are shown in Figure 4. (The details of this study may be found in Reference 1). Many of the dispersants looked promising after 24 hr sedimentation and showed little tendency for the powder to settle. The most promising dispersants included numbers 13, 16, 17, 20, and 21. At three weeks, all these except 20 and 21 still looked promising in terms of their sediment level. All had packed into fairly tight sediments. However, there were some significant differences in the behavior of the supernatant cloudy layer, which is an indication of the settling behavior of the finest particles in the system. For example, 13 settled into a tight sediment at three weeks. However, there was no cloudy layer above the sediment at all, which indicated that none of the finest particles were still in suspension. In contrast, 16 and 17 exhibited cloudy layers that were a large fraction of the total liquid height, which indicated that they held the finest particles in suspension quite well, even after a long settling time. These dispersants were selected for additional study.

Further study of the most promising dispersants can be done rheometrically using slurries at relatively high solids loading. Slurries should be formulated at a solids loading that is high enough to give a good approximation of particle - particle and particle - solvent behavior at a working solids loading. For example, if the target working solids loading is 50 vol %, then rheometry should be run on slurries in the 30 to 40 vol% range. It is critical that the slurries be well mixed, as well. Ball milling, attritor milling, or other high shear technique should be used.

The results of a typical set of rheometric tests are shown in Figure 5. All of these suspensions were made using dispersants that showed extremely good results in sedimentation tests.¹ The suspensions made using Daxad 19 and PEI 70K were too thick to be tested rheometrically, which eliminated them from further consideration. These results demonstrate that a dispersant that provides good dispersion at low solids concentration will not necessarily provide good dispersion at high solids concentration. The remaining suspensions were tested at shear rates up to 400s^{-1} . Of these, Dolapix PC33 was the most fluid, followed closely by Disperse-Ayd W22, and then Darvan 821A/PVP K15 (control). Quantitatively, the PC33 suspension had

a yield stress that was only 1/3 that of the control (28 vs 82 dyne/cm²) and a plastic viscosity that was only about 1/2 that of the control (0.38 vs 0.63 poise).

ROLE OF MIXING IN ATTAINING HIGH SOLIDS

Imparting a high amount of shear into a slurry is the key to good mixing. The practical question is how to do that. Ball milling is standard ceramic practice; however, other particle size reduction mills such as the turbomill, attritor, or sand mill can be successfully used for mixing, if certain adjustments are made to the practice. In general, impeller mixers are not especially useful for making high solids slurries for difficult to disperse powders. Kneading mixers, such as sigma blade, Banbury, and twin screw mixers are useful for mixing extrusion pastes. Finally, it should be noted that some systems do not respond well to direct mixing of powders with solvents to achieve high solids. In those cases, low solids processing may be required followed by solvent elimination. The approach here is to mix at a lower solids loading where the viscosities are low enough to allow good homogenization to occur. This is followed by a step that removes solvent to increase solids, such as vacuum drying in a sigma blade, double planetary or other mixer. Such an approach is sometimes used to formulate wax- or polymer-based injection molding molding mixes that would be too viscous to mix any other way.

Ball mills used for mixing need to be run under different conditions than those used for particle size reduction. First, it should be remembered that size reduction is not the goal during mixing; the goal is simply to make as homogeneous a slurry as possible. In fact, particle size reduction would in many cases be detrimental to the mixing process. In using a ball mill for particle size reduction, a typical media to powder ratio is 10:1. Such a high ratio is not required for mixing operations. Typical ratios of media to powder use for mixing operations are between 1:2 and 2:1. This turns out to be primarily a geometric consideration. For a high solids slurry, e.g. 50 vol %, if the media to powder ratio gets too high, say above 4:1, there will be too little slurry to fill the voids between the media and the media will not move effectively within the mill.

What follows is a short discourse on the factors that are important for mixing in a ball mill. While the details of the analysis will be different for other intensive slurry mixers, the general trends will be similar.

Factors influencing media motion in a ball mill

The classic analysis of media motion in a ball mill considers a single ball rotating in a dry mill. (REF) It requires knowledge only of the radius and mass of the ball and the diameter of the mill. The result for this analysis is typically given in terms of the critical speed of the mill, i.e., the rotational speed at which the ball is held to the wall of the mill by centrifugal force. Thus, for a ball located at the top of the mill (where the gravitational force is just balanced by the centrifugal force) at the critical speed, n_c -

$$\text{Force due to gravity (down)} = F_{\text{gravity}} = mg = \frac{4}{3} \pi r^3 \rho_s g \quad (1)$$

$$\begin{aligned} \text{Force due to rotation (up)} = F_{\text{rot}} &= m (2 \pi n_c)^2 (R-r) \\ &= \frac{4}{3} \pi r^3 \rho_s \frac{4}{3} \pi n_c^2 (R-r) \quad (2) \end{aligned}$$

$$n_c = \left(\frac{1}{2} \right) \left(\frac{g}{(R-r)} \right)^{1/2} \quad (3)$$

where

- n_c = critical rotational speed in RPM
- g = acceleration due to gravity
- R = radius of the mill
- m = ball mass
- ρ_s = ball density, and
- r = ball radius.

This analysis is effective for predicting a range of rotational speeds that is a reasonable starting point for mill operation. Typical optimized mill speeds are 65 to 80% n_c for grinding operations. The caveat is that the speeds predicted for the mill are only appropriate if the mill is operating in a dry or dilute slurry condition.

For the real case of a mill operating with a viscous slurry having a significant slurry density, one also has to consider viscous drag and surface tension. Viscous drag (including viscosity and slurry density) will tend to retard the rate of descent of a ball through the slurry per Stoke's Law. Surface tension will provide a force that tends to stick the ball to the wall, once it finds its way there and assuming that a meniscus is formed (i.e., that the mill is not completely filled by fluid).

A total force balance will consider the sum (upward) of the centrifugal, surface tension, and viscous forces balanced against the sum (downward) of the gravitational force. For a single ball at the top of its rotation in the mill -

$$F_{\text{viscous}} + F_{\text{rot}} + F_{\text{surface tension}} = F_{\text{gravity}} \quad (4)$$

or

$$6 \mu r v_b + \frac{4}{3} r^3 \rho_b \omega^2 (R-r) + 2 r \gamma_{\text{slurry}} = \frac{4}{3} r^3 \rho_{\text{slurry}} g \quad (5)$$

where

- μ = slurry viscosity
- v_b = ball velocity
- ρ_b = density of ball
- ρ_{slurry} = density of slurry
- γ_{slurry} = slurry surface tension

Combining, grouping terms, and solving for v_b yields -

$$v_b = \left\{ \frac{2}{9} r^2 (\rho_b - \rho_{\text{slurry}}) [g - \omega^2 (R - r)] \right\}^{1/2} \quad (6)$$

the relationship between the velocity of a ball in the mill and the mill operational parameters. While this analysis does not reflect the entire situation in the mill (e.g., it ignores interactions among balls), it does provide a useful point of departure for describing how the balls in a rotational mill move and what controls that motion. Table 1 summarizes the effects of these mixing parameters.

If we conduct a parameter by parameter analysis of the equation, with all others being held constant, we find the following trends -

1. Increasing the density of the media, ρ_b , increases the velocity of the media proportionally. It also increases the critical speed of the mill.

Implications - With denser media the mill can be run at a higher rotational speed before centrifuging occurs. Faster mill speeds should correspond with faster mixing. For a given mill speed, higher media density corresponds to faster movement of the media through the slurry (a la Stokes law, velocity increases linearly with density difference). The ability to increase media density is a function of the availability of higher density media, contamination concerns, and the availability of coating technology. For example, several mill media suppliers sell polymer coated (nylon, polyethylene, polyurethane) steel

media . Such media are non-contaminating to most ceramic systems and represent a reasonable choice in mixing media. However, the effective density of these media (composite density of steel balls with polymer coating) is only about 4.0 g/cm^3 because the polymer coating is relatively thick. This density is similar to the density of alumina media, and is far short of the base density for the steel balls themselves at 7.8 g/cm^3 . These media also tend to be rather expensive. One could achieve an extremely high media density if tungsten instead of steel were chosen for the core material and if a thinner polymer coating were applied. A composite media density approaching 16 g/cm^3 could be obtained in this manner.

2. Increasing the diameter of the media greatly increases the critical speed (inverse relative to gravity). Increasing the media diameter increases the media velocity.

Implications - Smaller media must be run at slower speeds to prevent centrifugation. Both viscous and surface tension forces dominate as the media become smaller. For a given mill speed, Stokes law dictates that the velocity of movement goes down as the square of the media diameter is decreased. Therefore, reducing the media diameter by one half, reduces the speed of media movement by a factor of 4. The slower the media move, the less mixing will occur in a given time period.

Another effect of reducing media diameter is to increase the amount of slurry effectively removed from the mixing operation. If we assume that the slurry wets the media used for mixing, then there will be a small amount of slurry that forms a coating on the surface of the media. Over long periods of time the slurry coating will be incorporated back into the slurry and a new coating composition will appear. But, at any given instant in time, that coating of slurry on the mixing media is effectively not available to help move the balls through the slurry. As the ball diameter is decreased, the amount of slurry not available to help move the media around increases inversely with the media diameter, Figure 6. The situation considered in the figure is for a 50 vol% solids alumina slurry being mixed using 1 kg of alumina balls. At 50 vol% solids, a 2 kg alumina batch (2 kg alumina and 500 ml water) occupies a volume of about 1000 ml. For a 20 mm ball diameter, only about 7 cm^3 of slurry are removed from the mill. In contrast, for a 1 mm ball diameter, 150

cm³ of slurry are removed from that available for motion. That is, for 1 mm mixing media, about 15% of the volume of the slurry is occluded. (The volume of slurry occluded was calculated by assuming that a 0.1 mm coating of slurry formed on the surface of the spherical media.) Thus smaller media hinder, rather than help the mixing operation. Since most ceramic milling media are available in a variety of diameters, larger media should be used when mixing is the primary concern, especially in dedicated plant situations;. The cost of having two sizes of media on hand in the plant (one dedicated to size reduction operations and one dedicated to mixing operations) will be more than offset by the improvements in mixing efficiency achieved by using the larger media for mixing, while using smaller media for particle size reduction tasks.

3. Increasing the slurry viscosity decreases the critical speed and decreases the media velocity.

Implications - Again, per Stokes Law, velocity is inversely proportional to viscosity. A more viscous slurry will require a slower mill rotational speed to produce effective mixing. If a high rotational speed is used for a high viscosity slurry, the slurry and media will simply centrifuge to the walls of the mill and no mixing will occur. This is especially true if the slurry is dilatant, in which case, the viscosity is only low at low shear rates (low rotational speed) and hence low rotational speeds MUST be used to achieve any mixing at all, Figure 7. As mixing proceeds, both the viscosity of the slurry and its dilatancy are reduced. Thus, slow rolling at the beginning of mixing a dilatant slurry leads to a less viscous and less dilatant slurry as mixing proceeds. The speed of the mill can be slowly increased to take advantage of the reduction in slurry viscosity achieved through mixing. The effect of slow rolling followed by faster rolling on slurry viscosity and dilatancy is shown in Figure 8 for a 40 vol % solids slurry of Ube E05 with 1 wt % addition of Dolapix PC35 dispersant in water.

4. Increasing the surface tension decreases the critical speed (negative square root, term 3).

Implications - The ability to change the surface tension of the slurry is subject to other considerations such as the effect that current processing aids like

dispersants, wetting agents, and defoamers already have on the slurry, and the possibility of interfering with those additives by the introduction of a surface tension reducer. Given that there are no adverse consequences, trying to lower the slurry surface tension is a reasonable way to increase mixing efficiency.

Eliminating the meniscus between the media and the mill wall by filling the mill completely with fluid will eliminate the surface tension force altogether. This should increase the critical speed for the mill.

Changing the shape of the media will also change the relative importance of the surface tension term. Spherical media will have the smallest surface tension force because contact is at a point (or small circle). Short rods will have a higher surface tension force because contact is either along a line (side contact) or along a circle of the same diameter as the cylinder (end contact). Long rods should fall somewhere between spheres and short rods.

SUMMARY

Attaining high solids in a ceramic slurry requires consideration of the entire system which includes the powder characteristics, powder dispersion and wetting, slurry rheology, introduction of shear into the slurry, and equipment performance. Powder characterization is the most important tool to determine if a particular powder can even be considered for making a high solids slurry. Dispersant selection, which is second in importance to powder selection, is often an Edisonian exercise. Success in this area depends on the experience of the process engineer and knowledge of other's experience. Mixing and how to get the best performance out of mixing equipment such as a ball mill depends on understanding the mixing process and which parameters are most important. For ball milling, media density and media size are the two parameters most likely to be controllable by the process engineer. Increasing either of these should result in improved mixing at high solids. The best results in attaining high solids loading with good slurry flow properties, excellent green part microstructure, and high green density is achieved when all of these factors are well controlled.

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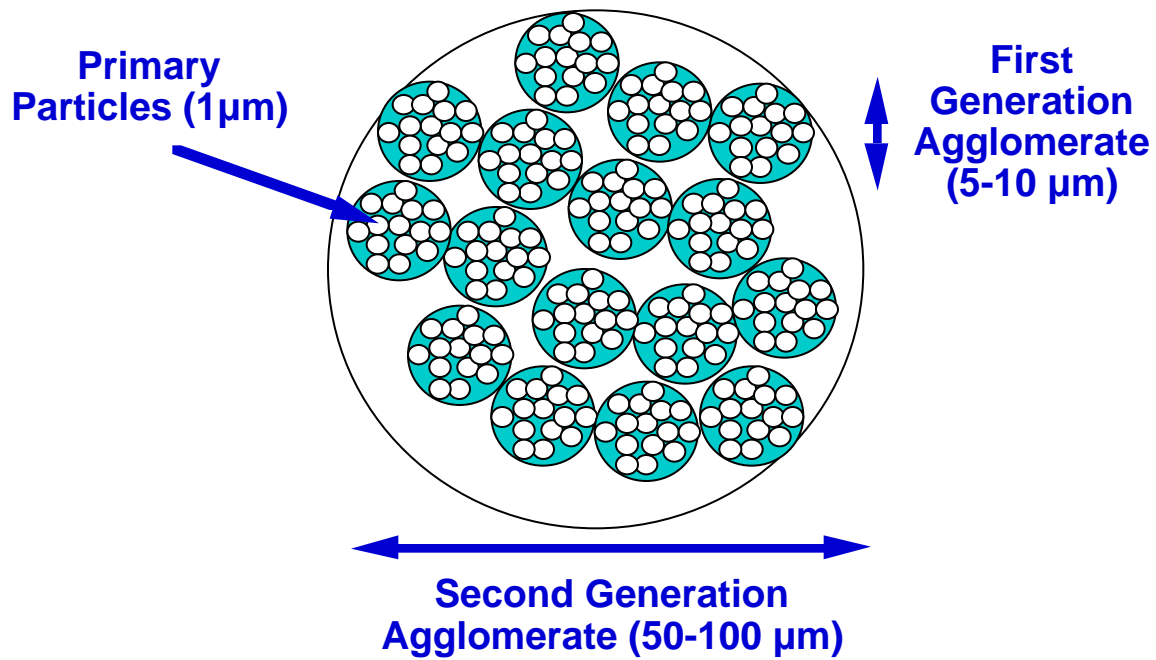


Figure 1 A model agglomerate. Agglomerates tend to occlude liquid in a suspension, which effectively increases the solids loading.

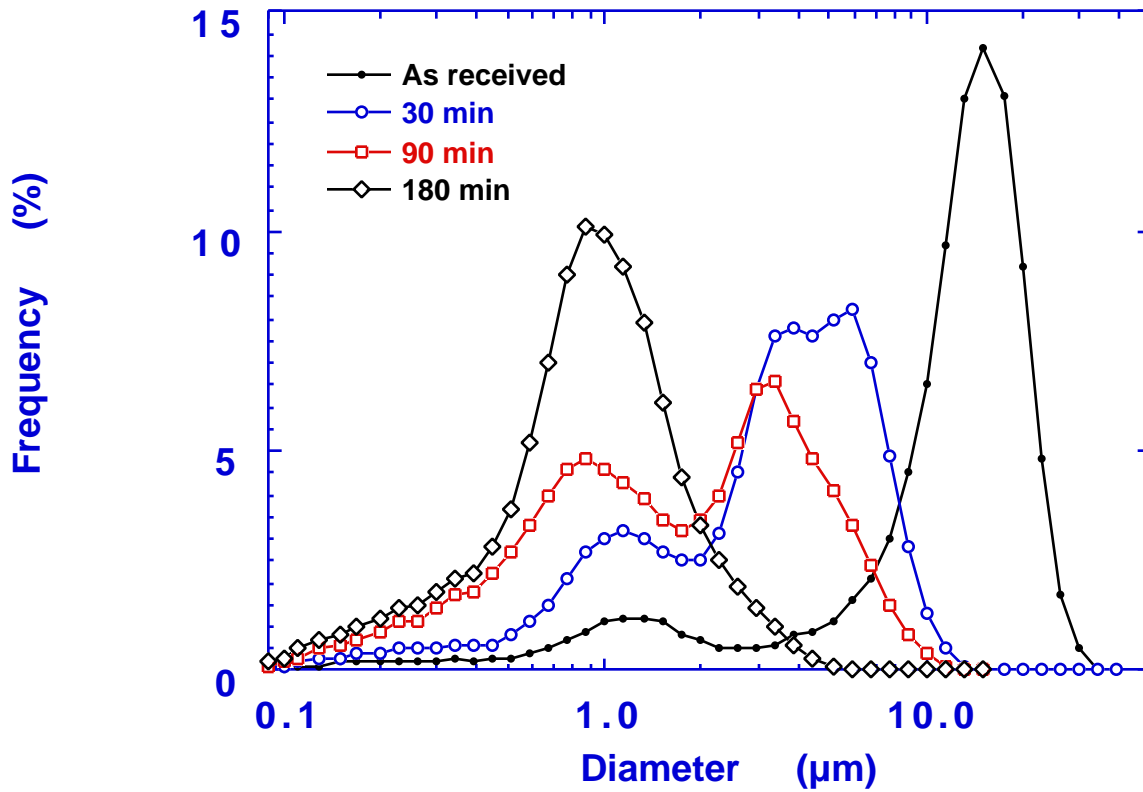


Figure 2. Milling an agglomerated powder follows a standard pattern, generating smaller agglomerates and primary particles. (200g indium-tin oxide, Indium Corp., milled in water using 1600g 3mm diam yttria partially stabilized zirconia balls in a 1 liter polypropylene jar.

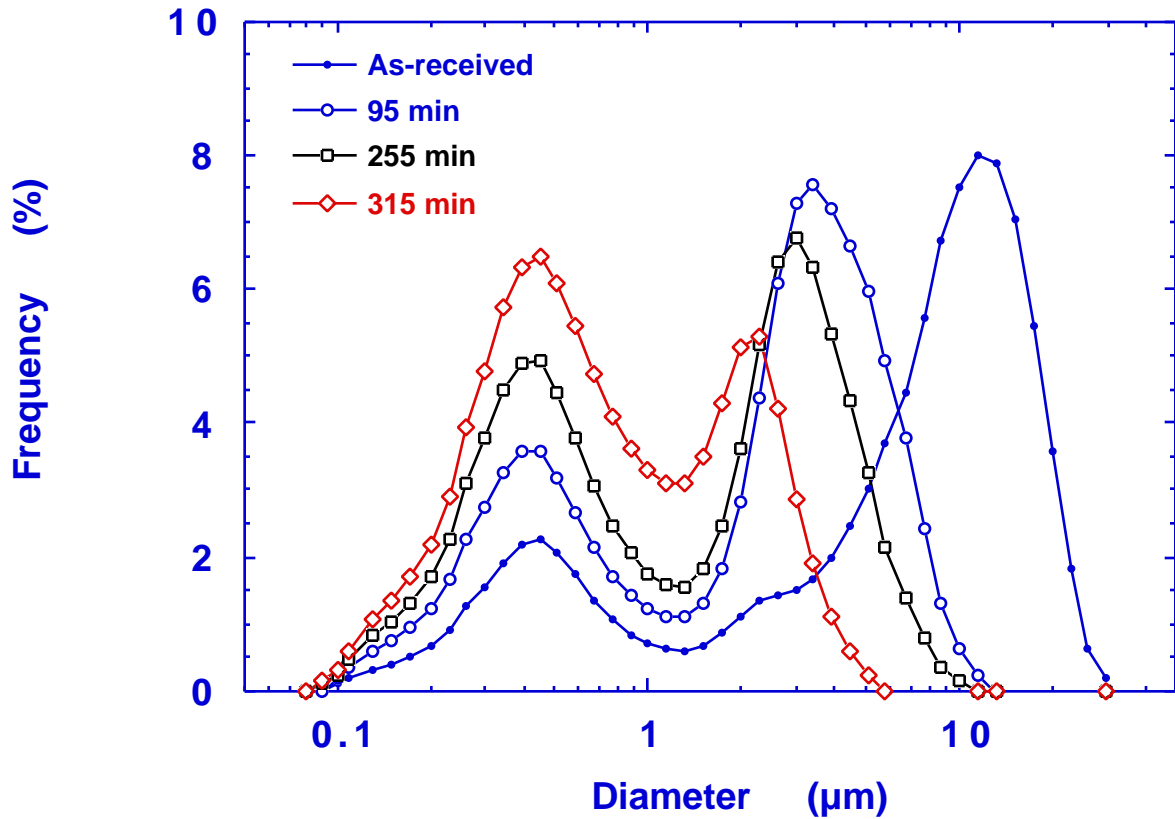


Figure 3. Potassium tantalum niobate (KTN) powder derived from a single crystal milled to a stable bimodal distribution. Milling conditions: 3 kg partially stabilized zirconia 3mm media, 100g KTN powder, 4 liter mill, isopropanol.

Sedimentation Volume (ml)

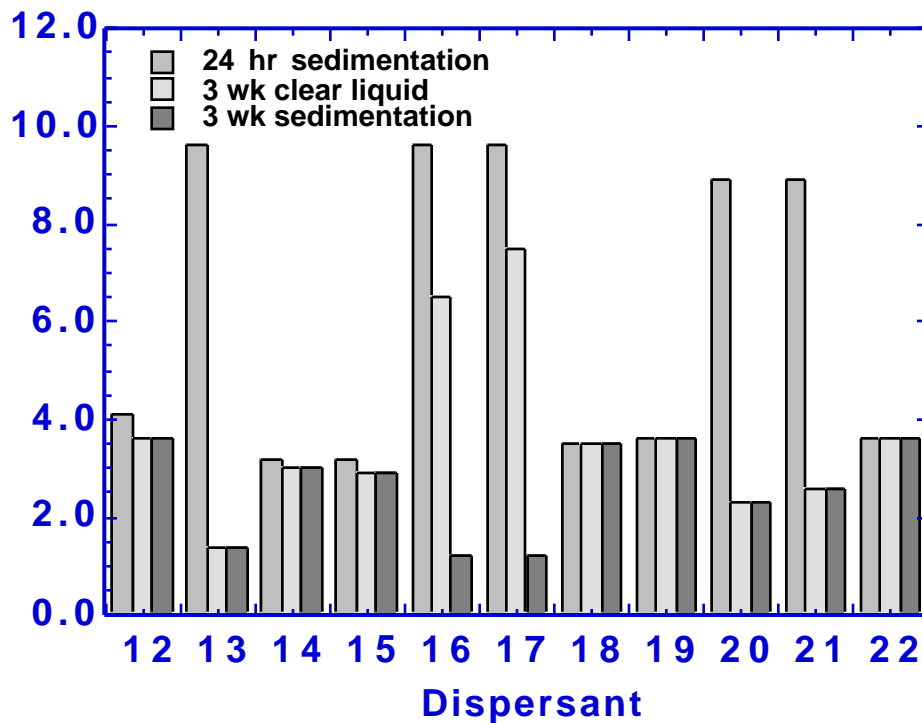


Figure 4. Sedimentation behavior of Ube E10 silicon nitride powder in aqueous suspension at pH 8. Height of the sediment at 24 h and 3 weeks is reported, as well as height of the interface between clear liquid (supernatant) and cloudy liquid above the sediment at 3 weeks.

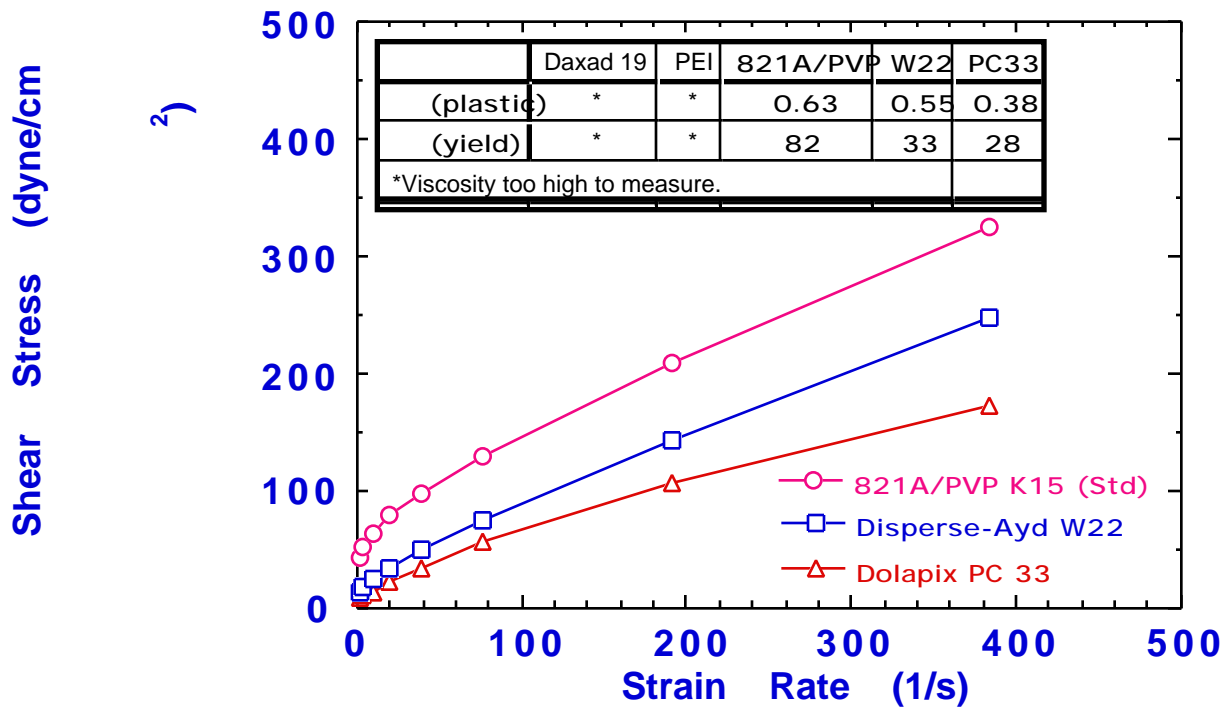


Figure 5. Rheometric tests are useful in determining which of several dispersants that are effective at low solids will be useful at high solids. Ube E10 silicon nitride, 35 vol % solids in water, 1 wt % dispersant added based on silicon nitride weight.

in 1 kilogram of alumina media (cm³)

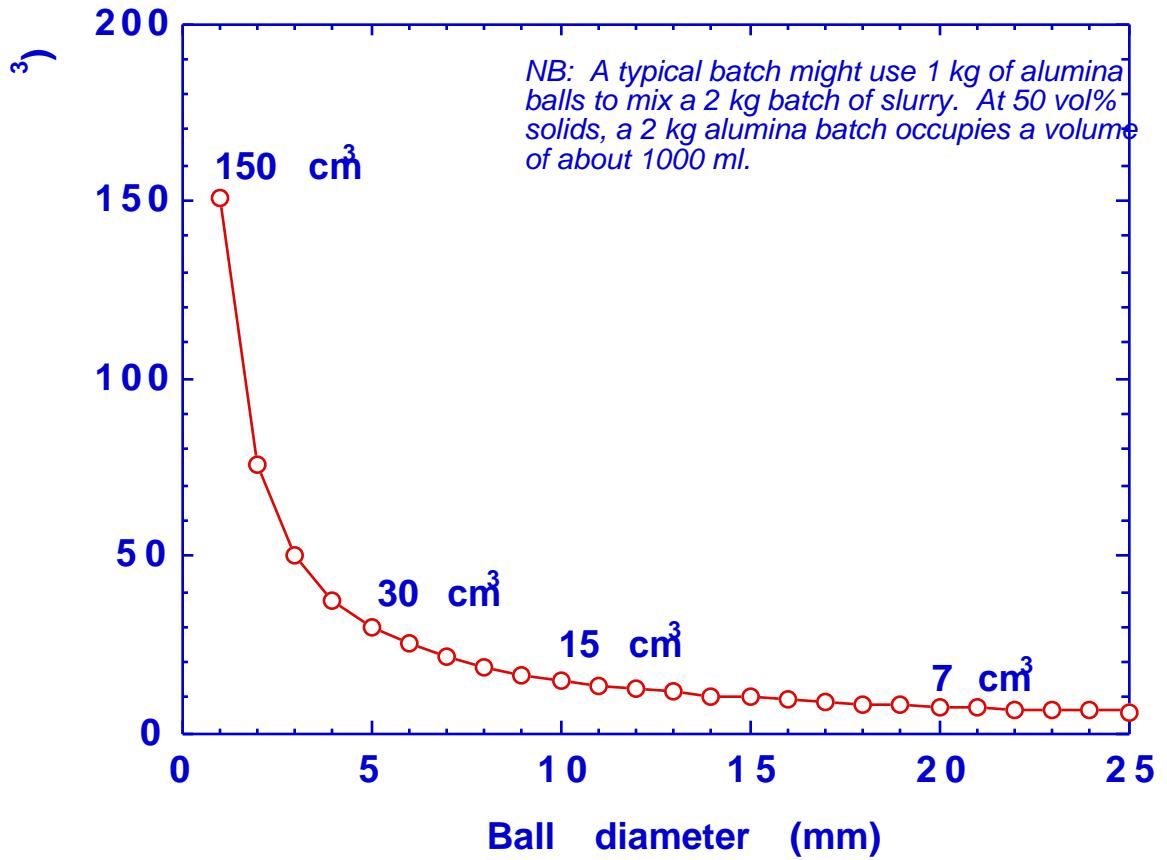
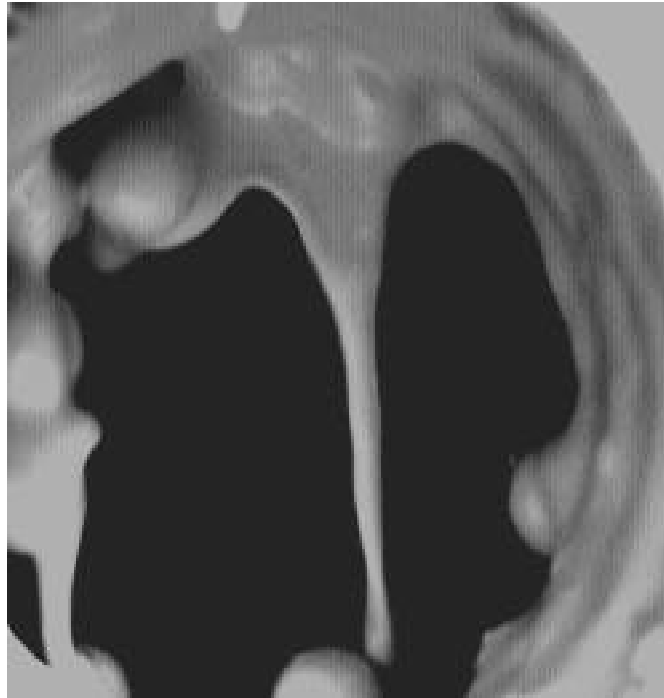
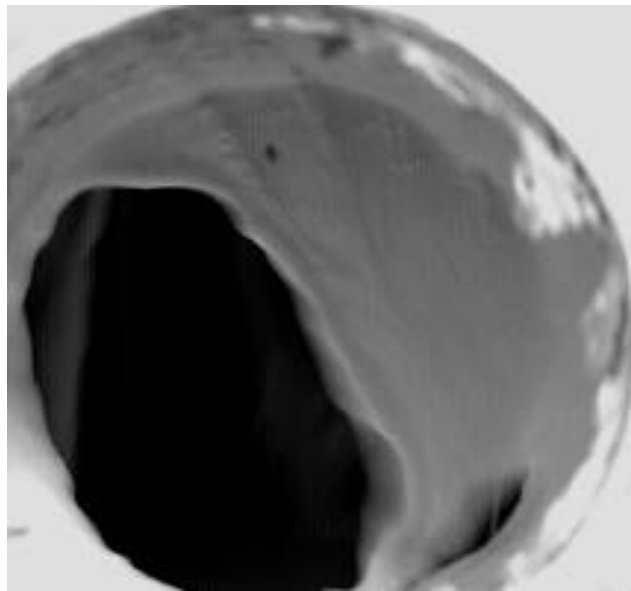


Figure 6. The volume of slurry occluded by the surface layer on the mixing media increases rapidly with decreasing media diameter. The coating thickness was assumed to be 0.100 mm on spherical media.



(a)



(b)

Figure 7. Slow rolling effectively mixes dilatant slurries; Ube E05 silicon nitride, 45 vol %, 4 rpm. (a) Drips and (b) sheets help to shear and move the slurry.

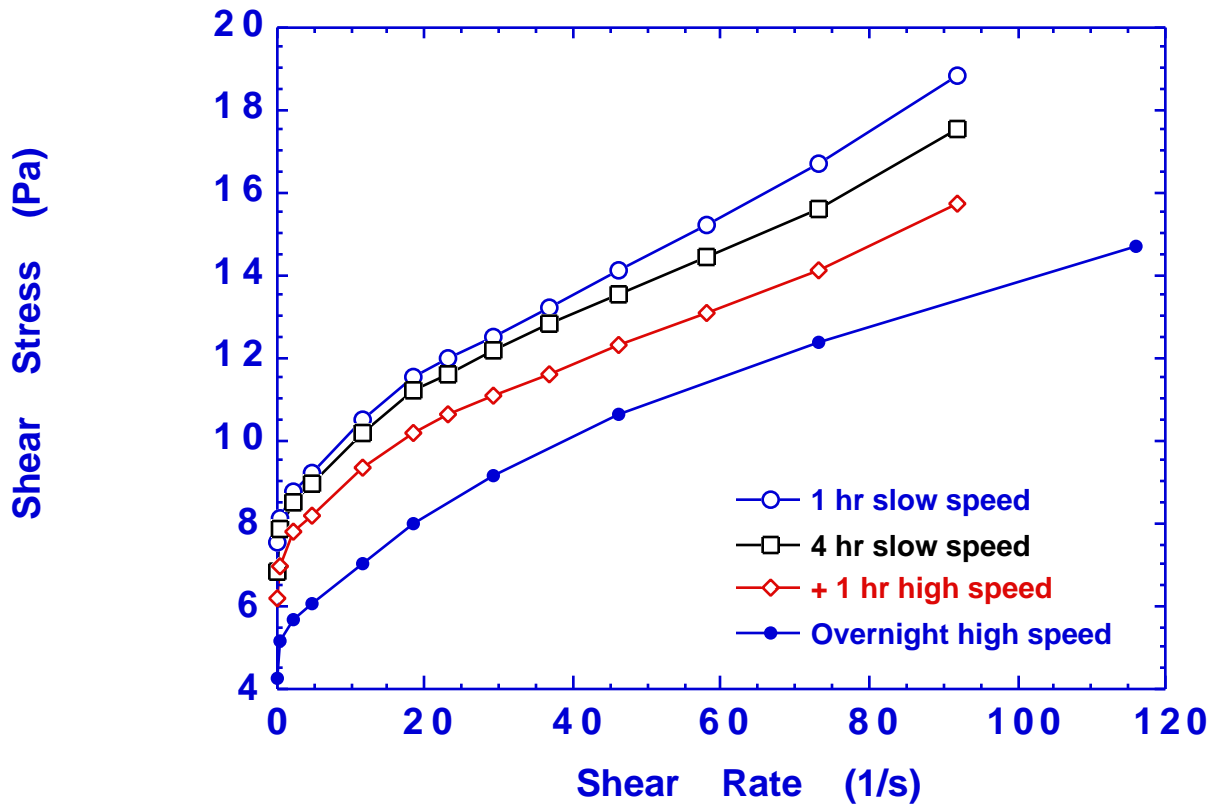


Figure 8. Mixing progression can be followed rheometrically. (40 vol % UBE E05 in water, 1 wt % Dolapix PC33 dispersant)