

# Understanding Ceramic Slips

by J.E. Funk Jr.

**D**uring my years of experience in production facilities and research laboratories in several ceramic industries, I have found a number of concepts useful when dealing with ceramic slips, their chemistry and their properties. This is the first in a series of four articles that, while not intended to be comprehensive, provides a review of the basics of ceramic slips along with information that is less well known, especially by those newly employed in the ceramic industry. In addition to my observations, the articles are a compilation of general experience and some of the information available in industry literature.

This first article deals with definitions of slips, concepts of mixing efficiency, the general effects of chemistry and slip density on rheology, and the rheology of slips used for plastic forming and slip casting.

## Terminology

We use the term *slip* to denote a mixture of largely insoluble ceramic raw materials, suspended or dispersed in a fluid phase that is normally water, with perhaps an addition of a soluble modifying chemistry to provide desirable fluid properties. *Slurry* differs from slip in that it normally comprises only one raw material in addition to the fluid phase, although it usually includes some or all of the dissolved chemical additives. Slurries can be made of many materials, of which ceramic raw materials are just a subset.

Most slip properties and behavior characteristics also apply to slurries, but the inclusion of plastic clays in ceramic slips often gives improvements in fluid and forming properties over those of non-plastic slurries. The specific desirable fluid properties depend on the process in which the slip is used, but low viscosity and stability are usually near the top of the wish list. Other desirable properties may be high slip density or specific gravity (SG), thixotropy, or pseudoplasticity.

## Efficient Mixing

Slips are blended from the component materials, which may be added dry or in pre-blended slurry form. In the interest of good slip dispersion, the fluid phase is added to (or the initial slurry is made in) the mixing vessel first, followed by any other slurry components. Dry components are added last. Mixing should begin as early as possible, and always before the addition of dry components, while applying the maximum shear available.

Finer, higher-surface-area materials should be added first so that they receive the benefits of longer mixing time, because the mechanical energy input necessary to separate particles from each other is proportional to their surface area of contact. Dry components also increase the slip's SG and decrease the inter-particle spacing (IPS), which, if the particle velocity does not change, increases the shear rate between adjacent particles. At a constant mixing speed, this effect drives the necessary power input upward.

With increasing SG, the increasing interactions between particles constrain flow from turbulent to laminar (higher to lower



Deflocculants are added to slip to create chemically coated and charged particle surfaces. Photo courtesy of R.T. Vanderbilt, Co. Inc., Norwalk, Conn.

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energy), resulting in a lower shear rate locally. Increasing the mixing speed can move the flow behavior toward turbulent again. This increases the scrubbing action between particles and works to physically disperse agglomerates into their component individual particles. At a high energy input, this can lead to the rounding of rough particles and more fines by autogenous grinding, creating a change in particle size distribution. Additional shear is more efficient than additional time for good dispersion.

### The Role of Additives

Dispersants or deflocculants are commonly added during dispersion (blunging) to create chemically coated and charged particle surfaces, which mutually repel. Charge and repulsion decrease with increasing IPS, so the maximum distance between particles is maintained. Van der Waals attraction forces between particles are the sum of the attractive interaction between constituent polar molecules. These forces are not affected by additive chemistry but vary with distance and are maximized at a short IPS. In the absence of repulsive forces, particles in suspension can approach each other and form loose bonds, increasing viscosity. The repulsive forces generated by dispersing chemistry serve to maximize particle spacing so the attractive forces are weak, which decreases the slip viscosity and also allows an increase in slip density, leading to increased local shear rates and improved mixing.

Thus the IPS (as a function of slip density and particle size distribution) and the chemistry of the system determine viscosity. Decreased IPS results from higher slip density or through finer particle size or roughened or platy particles, which have a higher ratio of specific surface area (SSA) to volume than larger particle sizes or spheres. Decreasing IPS increases the strength of attractive forces acting on adjacent particles, which increases bonding, slows their motion relative to each other, and therefore increases viscosity. For a given average IPS, viscosity can be modified by adding chemical dispersants



**Blungers are commonly used to disperse additives in slips. Photo courtesy of Eirich Machines Inc., Gurnee, Ill.**

(deflocculants) or flocculants, depending on the relative surface chemistry as-mixed.

### Chemistry and Rheology

Slips containing substantial amounts of soluble multi-valent cations such as  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  or  $\text{Al}^{+3}$ , either inherently (dissolved from the slip components or water) or from additions, will typically be flocculated to high viscosity, while those having low levels of multi-valent cations along with higher levels of mono-valent cations such as  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{NH}_4^+$  will be more deflocculated. The effect of each cation will be modified by the accompanying anion, which may be inorganic or organic. For mono-valent cations to cause deflocculation, their anions must create a change in the particle surface, either by adsorption to the surface (as with organic based anionic deflocculants that add repulsion via electrostatic and steric effects) or by desorption of ions from the surface (e.g., at high pH, hydroxides will remove hydronium cations from a clean surface, leaving a net negative charge with only electrostatic repulsion). There will generally be a viscosity range with a minimum and a maximum for each set of flocculants and deflocculants used, but this range also depends on the shear rate of measurement and shear history, as well as any other chemistry present as additions or solubilized from the components with time.

The language of rheology includes terms such as Newtonian, in which fluid viscosity is constant with time and shear; shear thinning, or pseudoplasticity, in which viscosity decreases with shear; the opposite case of shear thickening, or dilatancy; thixotropy,

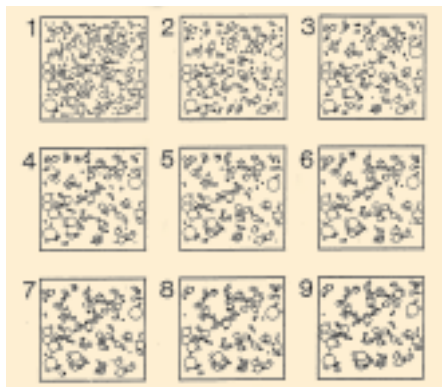
wherein viscosity decreases with time at constant shear; and its opposite, rheopexy. A related term is syneresis, which refers to a compression of agglomerates (flocs) over time at low or zero shear and under highly flocculated conditions due to minimum repulsive charge conditions. Accompanied by the release of suspending fluid as supernatant, syneresis gives a “thixotropic” but detrimental rheology. Pseudoplasticity or dilatancy are usually shown on graphs of shear stress or viscosity vs. shear rate, while thixotropy or rheopexy are shown on graphs of shear stress or viscosity vs. time (gel curves).

Ceramic slips are complex systems and usually have variable flow behavior as a function of shear rate or time or both, as well as a function of slip density and chemistry. Therefore, all of the above terms may apply in such systems.

### Rheology for Plastic Forming

Ceramic plastic forming is carried out with flocculated bodies; in the case of modern wet processing, bodies are made from a filter-pressed, low-SG, flocculated slip. These slips usually exhibit pseudoplasticity and thixotropy because of the dominance of weak van der Waals attractive forces when flocculated. The attractive forces increase the amount of weak bonding between particles and cause the formation of flocs in the slip at rest or at low shear, increasing viscosity (buildup). But because the attractive forces are weak, the flocs are easily broken and viscosity decreases with increasing mechanical shear. For partially flocculated systems, pseudoplasticity will be shown as a linear plot with a negative slope on a graph of log viscosity vs. log shear rate.

As particle size decreases or SG or chemical flocculation increases, attractive forces become more dominant and bonding increases between particles, resulting in higher viscosity. The flocs form a three-dimensional network comprising loose bundles of particles bi-continuously interspersed with a liquid phase. Figure 1 shows a two-dimensional computer modeled sequence of the coagulation of

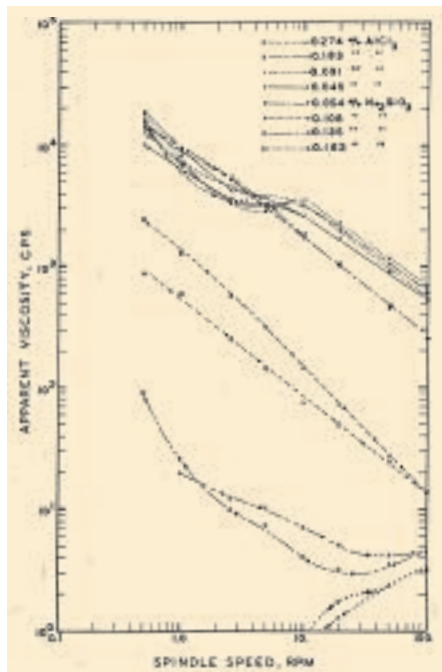


**Figure 1.** Behavior with time of a highly flocculated suspension of polydisperse particles.

spheres over time in a liquid phase in the absence of repulsive forces.<sup>1</sup> On the log-log viscosity vs. shear rate graph, the negatively sloped plot moves upward but in parallel and is linear until the point where, at low shear, the rheology becomes time dependent due to syneretic compression caused by attractive forces. The three-dimensional floc network breaks into individual flocs surrounded by fluid.

Syneretic behavior has been described and the underlying phenomena postulated for kaolin and ball clays.<sup>2</sup> Figures 2 and 3 show flow behavior for two clays with shear increasing, then decreasing.<sup>2</sup> Low flocculation levels show only slight time dependence. More flocculation produces more time dependence, eventually causing syneresis. The floc compression releases liquid phase, which then surrounds the densified flocs (just as if the particle size had become more coarse), and decreases the apparent viscosity with time at lower shear rates. This is thixotropy, but not the right kind, and the results can be disastrous in the factory.

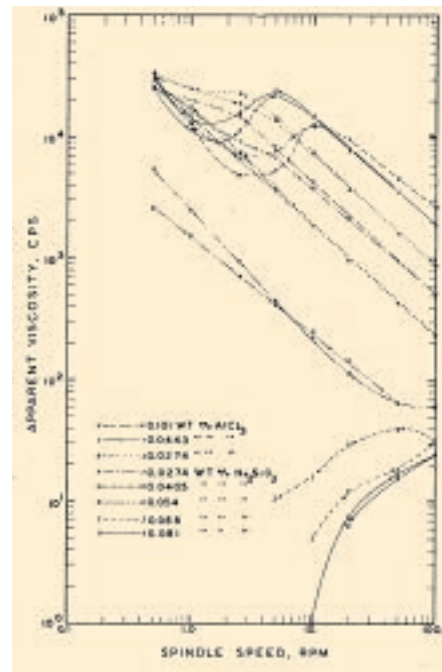
At rest, the extra liquid phase migrates to the surface of the slip as supernatant. This regime is over-flocculated and is poor for ceramic plastic forming purposes, because while the bonding between individual particles within flocs is strong, the bonding between flocs is weakened, and green strength will be low. Proper flocculation gives a high-viscosity but time-stable slip (no long-term increase or decrease in viscosity) without the breakdown of the floc network or syneresis. The water should be removed through filter pressing a properly flocculated slip, not by the formation of supernatant from an over-flocculated slip.



**Figure 2.** Flow curves relating apparent viscosity to spindle speed for suspensions of Old Mine #4 at 19.4 vol. % solids (1.30 g/cc) at various amounts of electrolyte additions and measured directly following a period of high shearing.

Use of this concept will allow an increase in SG for flocculated slips (if sufficient mixing power is available). The rule of thumb is that if supernatant forms above a flocculated slip at rest, then that volume of liquid did not belong in the slip as originally produced. Often in such situations, the settled slip below the supernatant appears cracked, even though it is “under water.” The cracks are the major channels by which the supernatant comes to the surface, but they are also an indication of decreased bonding between flocs, and thus lower plastic strength. If the supernatant is decanted and the slip remixed, the viscosity will be very high because the SG is too high and IPS too small. A too-small IPS means that the repulsive forces in the slip are dominated by attractive forces. A further addition of deflocculant is necessary to increase surface charge and repulsion forces, and thereby decrease viscosity into a useful range for mixing, pumping or pouring. Both slip stability and pseudoplasticity will actually increase if the addition is made correctly.

The goal here in terms of attractive and repulsive forces and colloidal theory is to set the IPS (using SG) and the degree of deflocculation or flocculation so that



**Figure 3.** Flow curves relating apparent viscosity to spindle speed for suspensions of Edgar Plastic Kaolin at 19.4 vol. % solids (1.30 g/cc) at various amounts of electrolyte additions and measured directly following a period of high shearing.

adjacent particles reside in the “secondary energy minimum” with respect to each other. When this is the case, an energy input is necessary to move particles either closer together or farther apart. Without that energy input, the slip is stable, and a gel curve will show neither thixotropy nor rheopexy after the initial recovery from mixing and/or shear rate change.

With finer particle sizes, the log-log viscosity vs. shear rate plot becomes steeper (more pseudoplastic). That is, for a comparable viscosity at a mid-range shear rate (the slip will probably need a lower SG or slightly more deflocculation to achieve this because the IPS decreases), low shear viscosity will be higher, but high shear viscosity will be lower.

Figure 4 illustrates this effect for non-deflocculated coal-water slurries ground at three solids contents.<sup>3</sup> Here the effect was not achieved by a longer grinding time, but by a lower solids content, which produces a less coarse fraction during milling. The equivalent effect in clays would be the removal of the coarse end of the size distribution, which is usually the non-plastic fraction. More pseudoplasticity in slip means higher plasticity in the formed body, as long as the material is the same and there is no difference in the intrinsic plasticity of the material.

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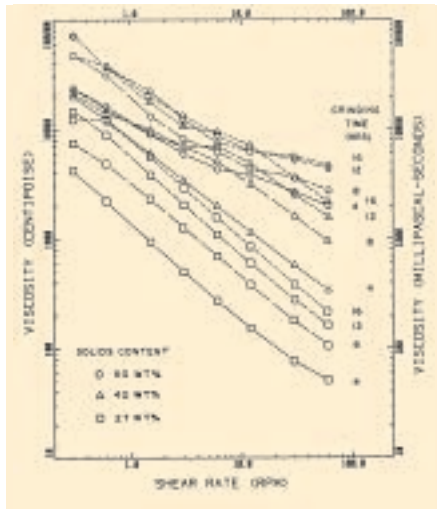


Figure 4. Undeflocculated apparent viscosity as a function of shear rate (RPM) with increasing grinding time and solids content for the ball milled slurries.

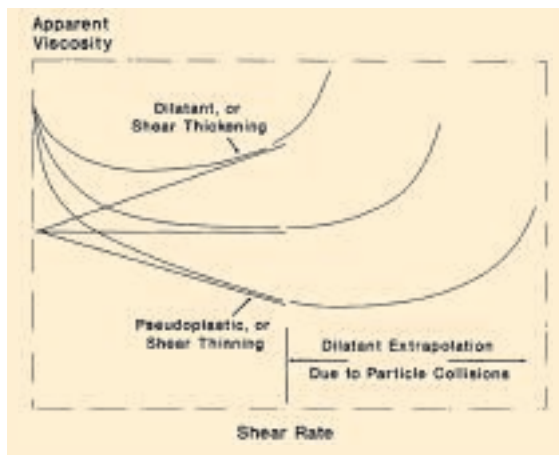


Figure 5. Similarities of the six classical time independent rheograms when extrapolated into the dilatant regime.

### Rheology and Casting Slips

Slip casting is carried out with more deflocculated systems, typically at a higher SG than slip that is filter pressed for plastic forming. The repulsive forces generated by deflocculation hold the particles apart so that the van der Waals attractive forces are not as dominant and bonds between particles are less numerous. Viscosity decreases with deflocculant to well below the range where syneresis occurs. Such slips have decreased pseudoplasticity and often show dilatancy, depending on the shear rate of measurement and degree of deflocculation, as well as SG and fineness of particle size distribution.

Figures 2 and 3 showed the transition from pseudoplasticity to dilatancy with deflocculation and increasing shear on a Brookfield viscometer for kaolin and ball clay. Dilatancy is caused by the interaction of fast moving particles that are repelling each other but cannot avoid each other due to a small IPS. For a given local surface charge, finer particle size and more rounded particles tend to decrease dilatancy or at least move it to higher deflocculation levels or higher shear rates. Increasing SG decreases IPS and increases the tendency for dilatancy. All fluids become dilatant if the shear rate is high enough. Figure 5 shows a set of theoretical rheological curves extended to high shear.<sup>4</sup>

If possible, dilatancy should be avoided in all slips by keeping the viscosity high enough to maintain a linear plot on the log-log viscosity vs. shear rate graph. A slip showing dilatancy during pumping or pouring will not only require more energy to move, but must relax after the shear is removed. The slip is unstable, and in slip casting that can cause problems. Dilatancy problems are particularly difficult in situations where very coarse, non-plastic materials such as silicon carbide (SiC) are being formed. Such problems can be partially addressed with particle size

distribution and/or slip chemistry changes. In some instances, the deflocculant can be tailored or chosen to provide a high minimum viscosity, above the region where dilatancy will occur. In extreme cases, a plastic forming body can be totally deflocculated but still act flocculated due to the properties of the deflocculant.

The time functions of thixotropy and rheopexy are dependent on the shear rate being used for the measurement and also on the previous shear history. For example, an over-flocculated system in syneresis will decrease in viscosity over time at very low shear, will increase in viscosity over time at low to intermediate shear, will break down to

lower viscosity at higher shear (pseudoplastic), and will build up viscosity over time at very high shear (in turbulence). A qualitative check on slip stability can be made by choosing one or more shear rates and measuring the viscosity over time for each, in gel curves.

Future articles in this series will focus on rheology and slip stability as measured by gel curves, the effect of plasticity imparted by clays and associated chemistry, and the relationship to casting properties; simple and more complex deflocculation systems, with a focus on sodium silicate; and other types of deflocculants, as well as the effects of aging on slips. 🌐

**Editor's note:** Neither the author nor *Ceramic Industry* endorses any of the products mentioned. Supplier information can be found with this article online at [www.ceramicindustry.com](http://www.ceramicindustry.com).

### About the Author

J.E. Funk Jr. holds degrees in ceramic engineering and biology, as well as a Ph.D. in chemistry. He has worked in industry with clay-based ceramics and silicon carbide, and in university research on emulsion polymerization and coal-water slurries designed for electrical power generation. He specializes in developing the combination of processing, particle physics and slip chemistry necessary to predictably maximize yields.

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