Slurries and rheology

Introduction to the rheology of suspensions

Antonio Licciulli
The slip casting process

- Slip casting is the process of filling a porous mold, usually a gypsum mold, with a ceramic slurry.

- The water is removed from the slurry via capillary action through the small pores in the mold. As the water is removed the ceramic particles are collected against the surface of the mold.

- This process is allowed to continue until the correct thickness is achieved, after which the remainder of the slip is drained out of the mold.

- The green body is dried further and removed from the mold. After the green body is removed it is dried and fired so that it can go through the final machining process.
The slurry (or slip)

A slurry is any fluid mixture of a pulverized solid with a liquid, often used as a convenient way of handling solids in bulk. Slurries behave in some ways like thick fluids, flowing under gravity and being capable of being pumped, cast, coated if not too thick.
Examples of slurries

• Soil/cement slurry, also called Controlled Low-Strength Material (CLSM), flowable fill, controlled density fill, flowable mortar, plastic soil-cement, K-Krete, and other names
• A mixture of pyroclastic material, rocky debris, and water produced in a volcanic eruption and known as a lahar
• A mixture of bentonite and water used to make slurry walls
• A mixture of wood pulp and water used to make paper
• A mixture of animal waste, organic matter, and sometimes water known simply as "slurry" in agricultural use, used as fertilizer after ageing in a slurry pit
• An abrasive substance used in chemical-mechanical polishing
• A mixture of raw materials and water involved in the rawmill manufacture of Portland cement
• A mixture of minerals, water, and additives used in the manufacture of ceramics
The suspension rheology

- Suspensions of particles have a complex rheology.
- Most suspensions have nonviscous forces which drive the suspension to a well-defined rest state when the flow is turned off.
- Colloidal suspensions of hard particles have Brownian, electrical double-layer and van der Waal’s forces.
- Soft particles can have capillary forces, elasticity or bending stiffness.
Rheology

- Study of deformation and flow of matter

- A fluid is a substance that deforms continuously under the action of a shearing force.
  - Intuitively, a fluid flows!

- Inquiry into the flow behavior of complex fluids

- Complex fluids do not follow Newton’s Law or Hooke’s Law (of elasticity)
Rheology and slip castig

Optimization of the Rheological Properties is important for slurry with:

- High stability
- Agglomerate – free
- High solids content

Ceramic suspensions to produce high quality slip – cast ceramics, as well as to correlate the slurry properties to the final objects properties.
Newton and Simple Fluids

• Reflected upon the resistance of liquids to a cylinder rotating in a vessel.

• **Newton (-Stokes) Law**
  • Deformation rate is expected to be proportional to stress and the constant coefficient of proportionality is called viscosity.

\[ \tau = \eta \dot{\gamma} \]

• The study of simpler fluids have their own well-defined field, called *fluid mechanics*.

• Purely viscous fluid.
Examples of Complex Fluids

- **Foods**
  - Emulsions (mayonnaise, ice cream)
  - Foams (ice cream, whipped cream)
  - Suspensions (mustard, chocolate)
  - Gels (cheese)
- **Biofluids**
  - Suspension (blood)
  - Gel (mucin)
  - Solutions (spittle)
- **Personal Care Products**
  - Suspensions (nail polish, face scrubs)
  - Solutions/Gels (shampoos, conditioners)
  - Foams (shaving cream)
- **Electronic and Optical Materials**
  - Liquid Crystals (Monitor displays)
  - Melts (soldering paste)
- **Pharmaceuticals**
  - Gels (creams, particle precursors)
  - Emulsions (creams)
  - Aerosols (nasal sprays)
- **Polymers**
Rheology’s Goals

1. Establishing the relationship between rheological properties of material and its molecular structure (composition).

- Related to:
  - Estimating quality of materials
  - Understanding laws of molecular movements
  - Intermolecular interactions

- Interested in what happens inside a point during deformation of the medium.

What happens inside a point?
Rheological Properties

- Stress
  - Shear stress
  - Normal stress
  - Normal Stress differences
- Viscosity
  - Steady-state (i.e. shear)
  - Extensional
  - Complex
- Viscoelastic Modulus
  - \( G' \) – storage modulus
  - \( G'' \) – loss modulus
- Creep, Compliance, Decay
- Relaxation times
- and many more …
Common Non-Newtonian Behavior

- shear thinning
- shear thickening
- yield stress
- viscoelastic effects
  - Weissenberg effect
  - Fluid memory
  - Die Swell
Shear Thinning and Shear Thickening

- shear thinning – tendency of some materials to decrease in viscosity when driven to flow at high shear rates, such as by higher pressure drops
Shear Thickening

- shear thickening – tendency of some materials to increase in viscosity when driven to flow at high shear rates
Generalized Newtonian Equation

- Generalized Newtonian Equation: \[ \tau = \eta(\dot{\gamma})\dot{\gamma} \]

- Power Law Model:
  \[ \eta = m\dot{\gamma}^{n-1} \]
  - \( m = \mu \) \( n = 1 \) Newtonian
  - \( m \) \( n > 1 \) Shear Thickening, Dilatant
  - \( m \) \( n < 1 \) Shear Thinning

- Slope of log \( \eta \) vs log \( \dot{\gamma} \) is constant
- Advantages: simple, success at predicting Q vs \( \Delta P \)
- Disadvantages: does not describe Newtonian Plateau at small shear rates
Modeling of Shear Thinning and Thickening

- Carreau-Yasuda Model

\[ \frac{\eta(\dot{\gamma}) - \eta_\infty}{\eta_0 - \eta_\infty} = \left[ 1 + (\dot{\gamma} \lambda)^a \right]^{\frac{n-1}{a}} \]

- \( a \) – affects the shape of the transition region
- \( \lambda \) – time constant determines where it changes from constant to power law
- \( n \) – describes the slope of the power law
- \( \eta_0, \eta_\infty \) – describe plateau viscosities

- Advantages: fits most data
- Disadvantages: contains 5 parameters, do not give molecular insight into polymer behavior
Yield Stress

- Tendency of a material to flow only when stresses are above a threshold stress

- Bingham Model:

\[
\tau \leq \tau_y \\
\tau \geq \tau_y \\
\eta(\dot{\gamma}) = \begin{cases} 
\infty \\
\mu_0 + \frac{\tau_y}{\dot{\gamma}} 
\end{cases}
\]

\(\tau_y = \text{yield stress, always positive}\)
\(\mu_0 = \text{viscosity at higher shear rates}\)
Elastic and Viscoelastic Effects

- **Fluid Memory**
  - Conserve their shape over time periods of seconds or minutes
  - Elastic like rubber
  - Can bounce or partially retract
  - Example: clay (plasticina)
Elastic and Viscoelastic Effects

- Viscoelastic fluids subjected to a stress deform
  - when the stress is removed, it does not instantly vanish
  - internal structure of material can sustain stress for some time
  - this time is known as the relaxation time, varies with materials
  - due to the internal stress, the fluid will deform on its own, even when external stresses are removed
  - important for processing of polymer melts, casting, etc.
Elastic and Viscoelastic Effects – Die Swell

- as a polymer exits a die, the diameter of liquid stream increases by up to an order of magnitude

- caused by relaxation of extended polymer coils, as stress is reduced from high flow producing stresses present within the die to low stresses, associated with the extruded stream moving through ambient air
Flocculation and deflocculation

The particles in suspension tend to coagulate spontaneously unless they are deflocculate. There are two ways of deflocculation:

- By adsorbing molecules with a strong connotation steric able to prevent the particles are in close contact
- Through the creation of the particles on the surface of a layer of charges

To obtain a repulsive effect on the complex colloidal particles of the repulsive forces must be greater than the kinetic energy:

\[ 10K_bT \]

this means at 20 °C that the zeta potential \( \xi \) must be higher in module to 25mV

stabilized suspensions are observed even at \( \xi = 15\text{mV} \), in which case the mechanism electrostatic was added a contribution of steric repulsion
Flocculation and deflocculation
Types of stabilization

- **Electrostatic stabilization**
  - working in a water solvent. Two particles having the same charges approaching each other will result in a repelling effect.

- **Sterical stabilization**
  - for water and solvent based systems, the surface of the solid particles are completely covered by polymers making particle-to-particle contact impossible. Strong interactions between polymers and solvents prevent the particles from coming too close and flocculate.

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Steric stabilisation

Electrostatic Stabilisation

Electrosteric Stabilisation

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Ion distribution on a particle in ionic liquid

On the surface of a charged particle in solution a quantity of ions which vary with the pH are attracted
Double layer theory

- Developed by Guy Chapman and allows to explain the mechanisms of coagulation and deflocculation due to Coulomb forces.

- Around the charged particle are formed two layers of charges: a layer of counterions related properties and integral with the particle and a concentration gradient there fillers.

- When an electric field $E$ is applied to the solution will tend to move with a speed $v_e$ together with the first layer and part of the charges of the second.

- Forms a sliding surface (slip) located beyond the first layer.

The electrical potential measured on the sliding plane is called zeta potential $\xi$, the following relation holds:

$$\xi = \frac{f_H \eta v_e}{E \varepsilon_r \varepsilon_0}$$

$\eta$ = viscosity, $f_H$ = costante di Henry
Double layer in daily life

- Interfacial DL is most apparent in systems with a large ratio of surface area to volume.
- The DL plays a fundamental role in many everyday substances. For instance, milk exists only because fat droplets are covered with a DL that prevent their coagulation into butter. DLs exist in practically all heterogeneous fluid-based systems, such as blood, paints, inks, ceramic slurries and cement slurries.
- The DL is closely related to electrokinetic phenomena and electroacoustic phenomena.
The isoelectric point

- The isoelectric point (IEP) is the pH value for which $\xi = 0$
- The isoelectric point is the situation of greater instability and risk of flocculation for a ceramic suspension
- The ceramic technologist must first move away from the isoelectric point by maximizing the absolute value of zeta potential

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Deflocculant quantity effect on good casting

Taken from JS Reed, 1995; case A, range of “good” cast is wider and favorable; S = soft; H = hard;

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Quantity Effects

Too much lubricant, lower tensile strength; increase strain-to-failure

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Viscosity of Slurry

- Viscosity too high or low: not ideal
- Slurry may have yield strength
- Good stability for storage life
Dip Coating

- Pull at an angle and speed to get coating;
- Film thickness depend on slurry rheology; for Newtonian fluid

\[
\frac{\partial \tau_{xy}}{\partial y} = \rho g \sin \alpha
\]

\[
h_{\text{max}} = \sqrt{\frac{U\eta}{\rho g \sin \alpha}}
\]

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Particle Orientation

Dip coating: shear force may cause special arrangement of particles to minimize resistance

FIGURE 13.19 SEM micrograph showing a horizontal view of the dip coated layer of mica particles. Photo courtesy of M. Albers and T. A. Ring, LTP-DMX-EPFL, Lausanne, Switzerland.

Taken from TA Ring, 1996;
Additives: binders and plasticizers

<table>
<thead>
<tr>
<th>Binder</th>
<th>Plasticizer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonaqueous</td>
<td></td>
</tr>
<tr>
<td>Polyvinyl butyral</td>
<td>Dioctyl phthalate</td>
</tr>
<tr>
<td>Polymethyldiacrylate</td>
<td>Dibutyl phthalate</td>
</tr>
<tr>
<td>Polyvinyl alcohol</td>
<td>Benzyl butyl phthalate</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>Aqueous</td>
<td></td>
</tr>
<tr>
<td>Acrylics</td>
<td>Glycerine</td>
</tr>
<tr>
<td>Methyl cellulose</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>Polyvinyl alcohol</td>
<td>Dibutyl phthalate</td>
</tr>
</tbody>
</table>
Cast thickness as a function of casting time

\[ L = \left[ \frac{2J\Delta P}{\eta R_c} + \left( \frac{R_m}{R_c} \right)^2 \right]^{1/2} - \left( \frac{R_m}{R_c} \right), \]

- \( L = \) cast thickness
- \( J = \) vol.of cast/vol.of liq. Removed
- \( R_c = \) resistivity to liq. transport in the cast,
- \( \Delta P = \) apparent mold suction
- \( \eta = \) viscosity of liq. transported
- \( R_m = \) liquid transport resistance of the mold
Capillary suction on the slip

\[ \Delta P = 2\gamma_i v \cos \theta / R_c \]

- \( \Delta P \) = suction,
- \( \gamma \) = surface tension
- \( \theta \) = angle
- \( R_c \) = radius of curvature

The flow of liquid through a porous medium is:

\[ \frac{dV}{dt} = \frac{K}{\eta} \times \frac{dP}{dx} \]

- \( \frac{dP}{dx} \) = the pressure gradient across the filter
- \( \eta \) = filtrate viscosity,
- \( \frac{dV}{dt} \) = volumetric flow rate of the filtrate and \( K \) is the filter permeability

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Particle Size and Loading Effects

The goal for slip casting is to produce a body that will sinter at a low temperature to save energy and time. In order for this to happen the slip must be produced with the optimum variables determined by laboratory testing.

To achieve the maximum packing density of about 75% for a green body, a bimodal particle alumina powder with a volume fraction ratio of coarse to fine particles equal to 7:3.

The ratio of diameter sizes between the coarse and fine particles is 7:1. This ratio yields the maximum packing density after casting. A bimodal system packs better because the fine particles will fill into the interstices created by the large particles.

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Solid loading with trimodal particle distribution

- If a larger range is used like a tri-modal or greater, the packing factor will increase according to the following equation:

\[ \text{Pf}_{\text{max}} = \text{Pf}_G + (1 - \text{Pf}_G)\text{Pf}_M + (1 - \text{Pf}_G)(1 - \text{Pf}_M)\text{Pf}_F \]

- This takes up the void space and decreases the size and amount of pores. The slips containing between 40% and 50% alumina produce the best green bodies with the easiest water removal.
Winkler diagram

- The diagram of Winkler alloy particle size distribution to the type of brick
Slurry viscosity vs solid loading

- The viscosity of a suspension $\eta_s$ is greater than that of a liquid $\eta_l$ and their ratio is defined relative viscosity:

$$\eta_r = \frac{\eta_s}{\eta_l}$$

- Interactions during the flow of slip are complex and are described by empirical equations:

$$\eta_r = (1-f_p)^{-K_f}$$

- $f_p$ = volume fraction of dispersed particles
- $K_f$ ranges from 3 to 21 when switching between fine particulates and with continuous distribution to a large particle size and uniform
Slurry homogenization

Milling balls
\( \text{Al}_2\text{O}_3 \)
The preparation of the slip

The mixtures of powders binders and additives for the preparation of suspensions and granules are mixed and homogenized in horizontal rotary mills with ceramic beads to act as a grinding media.
Milling receipt for horizontal rotary mill

Out of the total rotary mill volume:

✓ 50% empty
✓ 25% grinding spherical balls
✓ 25% slurry

Fig. 21. Disegno schematico di un mulino continuo con tamburo cilindrico e rivestimento classificante elliodale.
Volume loading and dispersant concentration

<table>
<thead>
<tr>
<th>Volume loading</th>
<th>Dispersant concentration (mmol)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>7.5</td>
<td>Unimodal size distribution; varied volume loading; optimized dispersant concentration</td>
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<tr>
<td>37</td>
<td>9.25</td>
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<tr>
<td>42</td>
<td>7.7</td>
<td>Bimodal size distribution; varied volume loading; optimized dispersant concentration</td>
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<tr>
<td>50</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>8.0</td>
<td>Bimodal size distribution; varied volume loading; optimized dispersant concentration</td>
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<tr>
<td>42</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>32</td>
<td>Unimodal size distribution; constant volume loading; varied dispersant concentration; cakes analyzed as a function of position</td>
</tr>
<tr>
<td>37</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

*The alumina suspensions were dispersed with tetrasodium pyrophosphate, and the SiC suspensions were dispersed with sodium silicate.*
Time dependent and independent viscosity

Shear stress (Pa)

Shear rate (1/s)

1.4% DISPERSANT

0.9% dispersant
Ceramic powders in resin dispersion

Acrylic modified silicon alkoxides are used to modify the surface properties of alumina powder.

This modification allows the dispersion of the powder in the resin.
The influence of dispersant content
High temperature (1800°C) rheometer

- StressTech UHT: instrument for measuring the **rheological and mechanical** properties of Molten Metals and Glasses. Performs steady, transient and dynamic shear measurements using couette/concentric cylinder systems and other fixtures. First prototype installed in Modena and Reggio Emilia University,