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Rheology Control of Highly Concentrated Mullite Suspensions with Polyelectrolyte for Robocasting

John N. Stuecker[*] and Joseph Cesarano III[*], Sandia National Laboratories,
Albuquerque, NM 87106
Deidre A. Hirschfeld[*], New Mexico Tech,
Socorro, NM 87801

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ABSTRACT

Highly concentrated, aqueous mullite slurries were characterized and stabilized at solids concentrations as high as 60 vol% using less than 2 vol% of an organic polyelectrolyte dispersant. The maximum slurry concentration (60 vol%) is within 3 vol% of the maximum consolidated density of the slurry. The slurries were subsequently cast into parts by a solid freeform fabrication technique termed robocasting and characterized. Sedimentation analysis and viscometry provided the means of slurry characterization, while knowledge of polyelectrolyte and interparticle forces was used to interpret the sedimentation and viscometry data. Through proper control of slurry conditions, pseudoplastic mullite slurries were fabricated for use in the robocasting process. The slurries were robocast at 52 vol% solids and subsequently yielded a green density of 55 vol%. Fired densities of the robocasted slurries were high, with mullite >96% dense at 1650°C.

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[*] Member, American Ceramic Society

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I. Introduction

In colloidal science, there is a necessity to understand interparticle and surface forces experienced among neighboring ceramic particles in order to control the rheology of concentrated suspensions. Attractive (i.e., Van der Waals) forces between particles are always present and induce agglomeration Electrostatic and/or steric forces are the primary means of inducing interparticle repulsion. Electrostatic forces arise from Coulombic interaction, where the force is repulsive if both particles are of similar charge and decreases with the square of the distance between particles.[1] The reasoning behind this repulsion is that these charged particles attract free ions from solution creating an electrical double layer which repels the electrical double layer of other charged particles. Steric forces are related to the dimensionality of the interacting objects where two hard spheres cannot come closer than twice their radius. Adsorbed polymers have been used to enhance the steric effect between ceramic particles in suspension.[2,3,4] Further, polyelectrolytes, which combine the physical steric dispersion mechanism with electrostatic repulsion, may adsorb onto particle surfaces, increasing dispersive forces.

Flocculation of particles in a suspension occurs when the particles become attracted to each other, touch, and remain touching. Stable slurries require deflocculated particles where the net repulsive force is high. It is possible to overdeflocculate the particles, however, in which the electrical double layer becomes compressed and particles may effectively touch, the coagulated state. A more detailed description of deflocculation, flocculation , and coagulation can be found in several references.[5,6] High solids loading slurries require good dispersion of particles for long shelf life and predictable rheological characteristics. Sedimentation behavior, as well as rheological behavior, can give qualitative insight into whether a suspension is flocculated, deflocculated, or coagulated. Although sedimentation is not applicable to high concentrations, low concentrated slurries can be studied and the findings extrapolated to higher concentrations.

Polyelectrolytes are a favorable choice for dispersion because suspension shelf-life is extended, the state of particle flocculation is more readily controlled, and multiphase systems may be dispersed.[4] Probably the most important aspect for implementing polyelectrolytes is understanding the adsorption characteristics of the polymer onto the particle. While the goal for 100% polyelectrolyte adsorption is sought for maximum dispersion forces, excess polymer in solution can induce flocculation through a 'depletion effect'.[3,7] Therefore, truly optimized suspensions have neither an excess nor deficiency of polyelectrolyte.

Mullite ceramics exhibit low density (~3.16 g/cc), low thermal conductivity (2~kW/mK), a low thermal expansion coefficient (α~$40\text{x}10^{-7}$ 1/K), and high strengths at high temperatures (>400MPa at 1200°C).[8] These properties make mullite attractive for electronic ceramic applications as well as structural applications. Therefore, obtaining a working knowledge of mullite slurry response to processing conditions leads toward a more reliable and repeatable method of fabricating such ceramics. Colloidal ceramic processing has advantages of high green density parts with low occurrence of defects resulting in high sintered densities and high strengths. Colloidal processing also lends itself to near net shape processing and solid freeform fabrication techniques. One such solid freeform fabrication (SFF) technique has been developed at Sandia National Laboratories (Albuquerque, NM) and is termed robocasting.[9,10] The process by which mullite colloidal slurries were characterized and then optimized specifically for the robocasting process, is described in the following paper.

II. Experimental Procedure

Materials and Chemicals

Mullite powder (MULSM) was supplied by Baikowski Corp. (Charlotte, NC). The average mullite particle size was 1.6 μm with a purity of >99.9%. The accepted value for the isoelectric point of the powder is 7.4.[4] Dispersion of particles was accomplished with Darvan 811 (R.T. Vanderbilt, Norwalk, CT), a commercially available sodium salt of poly(acrylic acid) (Na-PAA) which has a molecular weight of ~6000. Deionized water was used for all experiments and pH adjustments were accomplished with 1.0 M NaOH and HCl.

Experimental Methods

It is basic knowledge that it takes a finite amount of time to homogenize separate species as they are combined together. The same is true for the formation of ceramic slurries. A 43 vol% mullite slurry was chosen to perform pH equilibration studies using two methods of slurry mixing, ball milling and shaking. Shaking was performed on a modified Red Devil paint shaker (model 5400, Union, NJ). Slurries of mullite were created and pH measurements were immediately taken with a pH meter accurate to 2 decimal places (Orion Model 420A, Beverly, MA) and then periodically taken throughout the experiment to determine the time for pH equilibration. The pH was then adjusted and the time for equilibration was noted using both methods.

Sedimentation analysis was performed over a pH range of 4.5 to 9.5 and polyelectrolyte dispersant concentrations of 0.0 to 5.0 wt% based on powder. Sedimentation slurries were composed of 7 vol% powder, adjusted for pH, and ball milled for 24 hours to equilibrate the slurries. Once the desired pH values were stabilized, the slurries were poured into 50 mL centrifuge tubes and the final sedimentation height recorded as surface plots. Stability maps outlining the combined stabilization effects of pH and polyelectrolyte concentration were created from these same sedimentation results.[2] Viscosity measurements were taken with a concentric cylinder viscometer (Brookfield model LVT, Stoughton, MA) over a pH range of 4.5-10.

Freeform fabrication of pseudoplastic mullite slurries was performed on a rapid prototyping machine at Sandia National Laboratories. Syringes filled with slurry are loaded into the robocasting machine and the slurry is dispensed through a cylindrical nozzle of 0.25 - 1.5 mm in diameter at a rate of 0.01 - 0.05 ml/s onto a plate. The slurry was extruded in layers of 0.8 mm until complete samples were fabricated. Within a few hours of part completion, robocast parts are dry and can be placed in a burnout furnace. The robocast mullite parts were burned out at 3°C/min to 600°C, 5°C/min to 1050 °C (2 hours) and then sintered at 10°C/min to 1650 °C for 2 hours. All heat treatments were completed in air.

III. Results and Discussion

pH Equilibration

From Figure 1, it was determined that mechanical shaking decreased slurry equilibration time from over 24 hours to less than 10 minutes for a 43 vol% mullite slurry. It is assumed that higher concentrated slurries will have a slightly longer time to equilibration based upon the increased viscosity of the slurry, however, the benefits of the paint shaker system can clearly be seen. Due to the fact that only two milling media were used in the mixing process, it is assumed that no significant amount of grinding occurred. This is a significant decrease in the slurry production time (typically 24 hours to 10 days) as reported in previous studies for similar slurries.[11, 12]

(2) Sedimentation Analysis

The charge of a particle in suspension is dependent on the surrounding environment and the isoelectric point (IEP) of the particle. At every pH there are positive, negative, and neutral sites on the particle surface. However, if the environment is at a pH greater than the particle IEP then the particle will have more negative sites and the particle surface will be relatively negatively charged. Further increasing the surrounding pH creates even more negative sites and less positive sites and a relatively more negative surface. Conversely, decreasing the pH below the IEP will create a relatively positive particle surface. The polyelectrolyte chosen (Darvan 811) possesses carboxylic acid functional groups (COOH) along the backbone of the polymer chain. At pH values ≤ 2, all of the functional groups remain as COOH and the polyelectrolyte behaves like a neutral polymer.[3] Increasing the pH of the slurry allows the H^+ ion to dissociate from the functional group leaving negatively charged sites along the polymer chain (COO^-) which repel other negative, neighboring polymer chains. The sodium ion dissociates from the head group leaving a negatively charged head group which may attach to positive sites on the ceramic particles. The polyelectrolyte is fully dissociated into its most negative state at pH values ≥ 7.[3]

In order to strongly adsorb dissociated polyelectrolyte onto the ceramic particles, there must be an appreciable concentration of positive sites on the particle surface. Therefore, in order to strongly adsorb Darvan 811 onto mullite, the pH must be slightly higher than the IEP, or lower (i.e., pH ≤ 7.8). At the IEP (pH 7.4), the overall surface charge is neutral but there is still a large concentration of positive surface sites that are available for adsorption. However, if the pH is decreased appreciably below pH 7, the number of dissociated functional groups on the Darvan dispersant will correspondingly decrease and the Darvan will cease being an efficient dispersant. For pH values appreciably above pH 7, the driving force for adsorption of Darvan onto the mullite decreases, and in order to saturate the surface, free polyelectrolyte must exist in the solution. Free polyelectrolyte can effect dispersion in highly concentrated suspensions. Therefore, the optimal pH for processing highly concentrated aqueous Darvan/mullite suspensions is presumed to be just below 7.4, where there are enough positive sites on the particle surface to induce strong adsorption, and, the solution is at a high enough pH to dissociate the functional groups for high dispersive forces. This relationship will be verified with an analysis of data presented below.

A contour plot of settling height vs. pH and polyelectrolyte concentration is provided in Figure 2. For a stable slurry, the sedimentation height must be either very low or nonexistent, corresponding to a fully deflocculated state. Figure 3 is a two dimensional projection of the contour plot in Figure 2 where regions of unstable and stable suspensions are outlined. For the given solids content (7 vol%), stability cannot be achieved below pH 6.2. At pH 6.3 approximately 2 wt% dispersant is required for dispersion, with the required amount decreasing to 0.75 wt% at pH 7.5. Points A, B, and C (at pH levels 6.08, 6.99, and 7.91 respectively) along the 2.5 wt% dispersant line are noted on Figures 2 and 3. Rheologies at these selected points will be examined subsequently and will demonstrate the utility of Figure 3.

(3) Rheological Properties

Before slurries can be created with the goal of high solids content, it is important to know what the highest possible solids content is. This limit is the final green density of the slurry and is dependent on the average particle size and size distribution. A green density of 63 vol% was obtained with slip cast slurries of highly dispersed 30 vol% mullite. The goal, is to create slurries as close to this value as possible while still maintaining the desired rheological properties.

The magnitude of the dispersive forces and thus the stability of the ceramic slurries can be determined qualitatively by viscometry. Large dispersive forces yield high particle mobility and low viscosity. Similarly, as solids loading is decreased, the frequency of particle collisions decreases, therefore reducing the viscosity. Figures 4 and 5 demonstrate these two principles. From Figure 4, viscosity values versus log shear rate for pH 6.99 and 7.91 at 2.5 wt% dispersant (points B and C respectively on Figures 2 and 3) are nearly identical, however, much less than viscosities for pH 6.08 (point A on Figures 2 and 3). This viscosity change corresponds to decreasing polyelectrolyte efficiency, lower dispersive forces, and subsequently, particle coagulation. The change may be seen qualitatively on Figures 2 and 3 where points B and C are well within the stable region, but point A has crossed over into the unstable region. Additionally, the inset graph in Figure 4 shows that slurry A exhibits a noticeable yield stress which is indicative of partial coagulation. The 12 N/m^2 yield stress is not seen in slurries B or C which are fully stabilized. The coagulated structure begins to break down with modest shear rates (<1 1/s), allowing the slurry to flow. This type of shear thinning rheology with a yield stress is optimal for the robocasting process in which a yield stress is required to maintain extruded bead shape, yet the material will shear thin and flow through the extruding orifice.

Important to note is that each data point in Figure 5 is a slurry optimized for polymer content based upon the stability map in Figure 3. These data points must be unique due to the pH dependent nature of the adsorption behavior and dissociation behavior of the polyelectrolyte.[3] Therefore, each slurry measured in Figure 5 was made at the pH and dispersant concentration that puts the slurry comfortably in the stable region. As the pH is decreased from 7.4, the viscosity for all solids content slurries increases as the Darvan becomes less dissociated and less efficient. As the pH is raised from 7.4, viscosity again increases as the driving force for adsorption of Darvan decreases. Adsorption decreases because the concentration of positive adsorption sites decreases and reduces the affinity of Darvan for the mullite. Therefore, in order to obtain saturation adsorption there must be an appreciable amount of non-adsorbed, free Darvan in solution. The free Darvan will enhance polymer chain entanglement, reduce particle mobility and increase viscosity. This effect is more dramatic at high solids and has been seen in other polyelectrolyte stabilized suspensions.[2,3] Increasing solids content from 23 to 52 vol% shows not only an increase in viscosity, which is expected, but also a narrowing of the low viscosity region. With this knowledge, stable slurries of mullite were created at a pH of 7.4 and solids content of 60 vol%. Remarkably, this value is within 3% of the ultimate green density. Unfortunately, while the 60 vol% suspension was fluid, it was too difficult to handle for viscosity measurements. The minimum in the viscosity vs pH curve for the 52 vol% solids slurries in shows that the pH should be between 7.0 - 7.5 in order to achieve dispersed slurries with very high solids loadings. However, larger deviations from the optimal pH will significantly increase viscosity as shown in Figure 6.

(4) Altered Rheology

The unique SFF process, robocasting, requires a pseudoplastic (shear thinning) slurry with a small yield stress for the fabrication of freeformed parts. All high solids content mullite suspensions (>55 vol%) created previously are dilatant (shear thickening) in nature, as is to be expected from well deflocculated particles in high solids content slurries. The objective then is to form coagulated or, more specifically, partially coagulated slurries which are pseudoplastic with an associated yield stress. Aluminum ions in the form of $Al(NO_3)_3$ are added to complex with the dissociated functional groups, effectively reducing the efficiency of the polymer just enough to cause partial coagulation. Polymer bridging is also thought to occur in which two particles are attached to the same polymer chain.[7] The pH of the slurry drops a small amount as well, changing the position of the slurry on the stability map from the low sedimentation height (electrosteric repulsion) area to part way into the flocculated (high sedimentation height) region.[13] Figure 7 shows the change in rheology for a 52 vol% slurry from a low viscosity pseudoplastic slurry with minimal yield stress to a slurry with Bingham plastic behavior and a yield stress of 30 Pa. The Bingham fluid requires a 30 Pa stress to induce slurry flow, then behaves as a Newtonian fluid as the shear stress increases. This rheology is also suitable for robocasting and may be optimal. Slurries with solids loadings over 54 vol% were not able to be partially coagulated into slurries suitable for robocasting because of the extremely high resulting viscosities.

Syringes were loaded with 52 vol% Bingham plastic mullite slurry and then robocast into solid blocks, thin walled structures, and three dimensional meshes (Figure 9). Smallest pore size of the three dimensional mesh was 100 μm. Build rates were on the order of 0.05-0.1 ml/s at table speeds of 10-20 mm/s using orifice sizes of 0.26-0.84 mm ID. Consolidated densities of robocast mullite parts were 55 vol%. This consolidated density is not as high as densities of slip cast samples (63 vol%) due to the pseudoplastic nature of the slurry. The induced partial flocculation creates an open, coagulated particle structure instead of the more compact structure created from fully suspended and deflocculated particles, resulting in the lower consolidated density. Robocast mullite parts were burned out in air and sintered to over 96% theoretical density at 1650 °C for 2 hours within 24 hours of fabrication. Low organics content and quick consolidation time allow for high furnace ramp rates (3 to 5 °C for burnout and 10 °C for firing) and short burnout times (2 hours).

IV. Conclusions

Mullite suspensions of 60 vol% solids (within 3% of the maximum packing density) were created by maximizing the interparticle forces from small additions of polyelectrolyte. Settling studies provided the most insight into the optimal dispersion with rheological data focusing even more on the exact conditions for high solids slurry formation. Slurries were created from raw materials within one hour by using alternative mixing techniques, previous times for similar slurries using standard mixing methods were 24 hours.

The use of stability maps and manipulation of slurry conditions such as pH and polyelectrolyte efficiency allow for the control of slurry rheology to suite the specific application in which the slurry is to be used. Specifically, for freeform fabrication by robocasting, a slurry must exhibit a yield pseudoplastic or Bingham rheology with a yield stress on the order of 30 Pa. A very good performing mullite slurry with a Bingham plastic rheology and a 30 Pa yield stress achieved by proper control of dispersive forces and solids loading. The final slurry had a mullite solids loading of 52 vol% and was achieved at pH 7.4 with 3.0 wt% Darvan. Partial coagulation for rheological modification was induced by small additions of $(AlNO_3)_3$. Samples were robocast to green densities of 55% and sintered to 96% theoretical density at 1650°C.

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Figure Captions:

Figure 1: Comparison of 43 vol% slurry equilibration using two different methods.

Figure 2: Surface plot of settling height as a function of polyelectrolyte and slurry pH for a 7 vol% mullite slurry. Points of interest are noted at 2.5 wt% for pH 6.08 (A), 6.99 (B), and 7.91 (C).

Figure 3: 2D projection of Figure 2. Stable and unstable regions are outlined for 7 vol% mullite suspensions. Points of interest are noted again at 2.5 wt% for pH 6.08 (A), 6.99 (B), and 7.91 (C).

Figure 4: Viscosities for pH values of 6.08, 6.99, and 7.91 (noted points on Figures 2 and 3) for a 45 vol% slurry with 2.5 wt% dispersant. The inset graph shows shear stress versus shear rate for the same pH values.

Figure 5: Viscosity dependence on pH and solids loading (shear rate =120 1/s) for slurries comfortably in the stable region, defined in Figure 3.

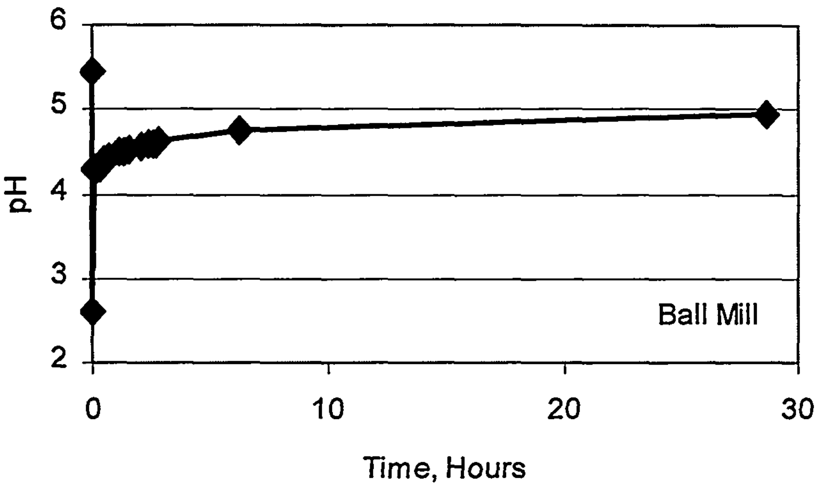
Figure 6: Rheology change associated with significant deviation from the IEP (7.4) for a 52 vol% slurry.

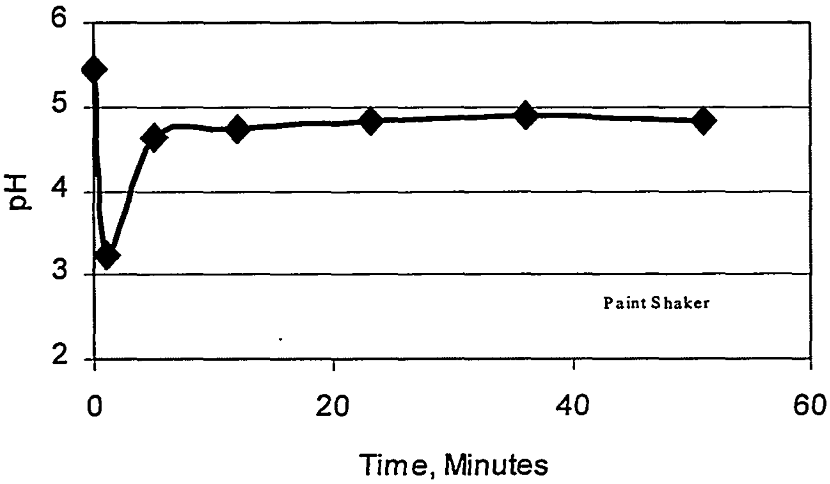
Figure 7: Change in rheology of a 52 vol% slurry from pseudoplastic to Bingham plastic with small additions of $Al(NO_3)_3$.

Figure 8: Effect of $Al(NO_3)_3$ additions on the viscosity of a 52 vol% slurry containing 3 wt% dispersant.

Figure 9: Examples of robocast mullite (52 vol% with a Bingham plastic rheology).

Figures:





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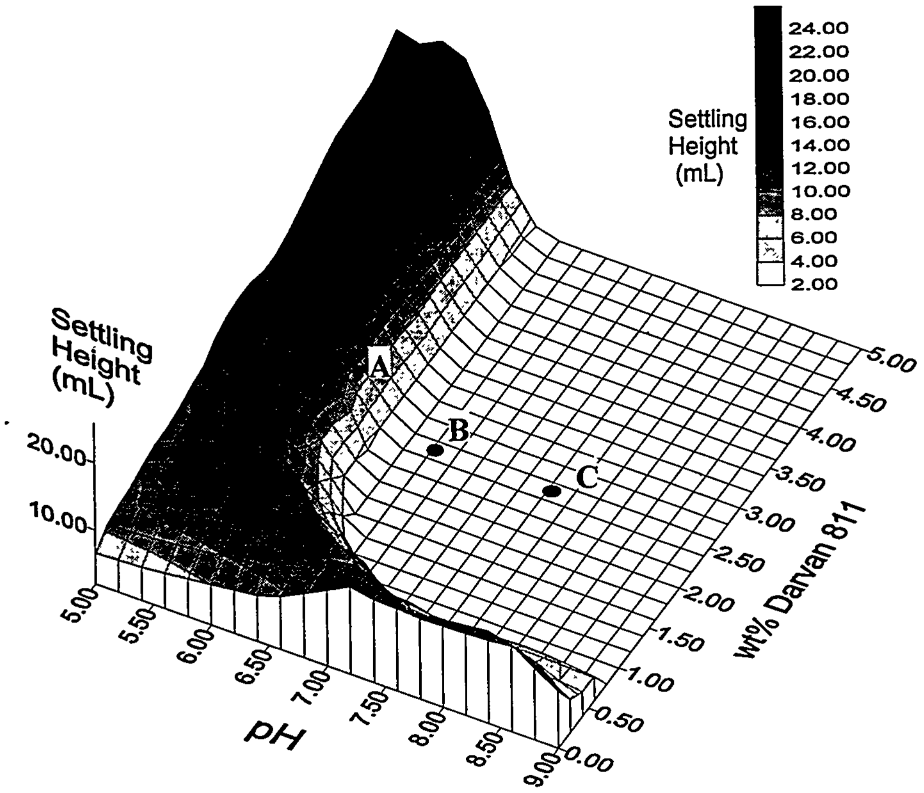

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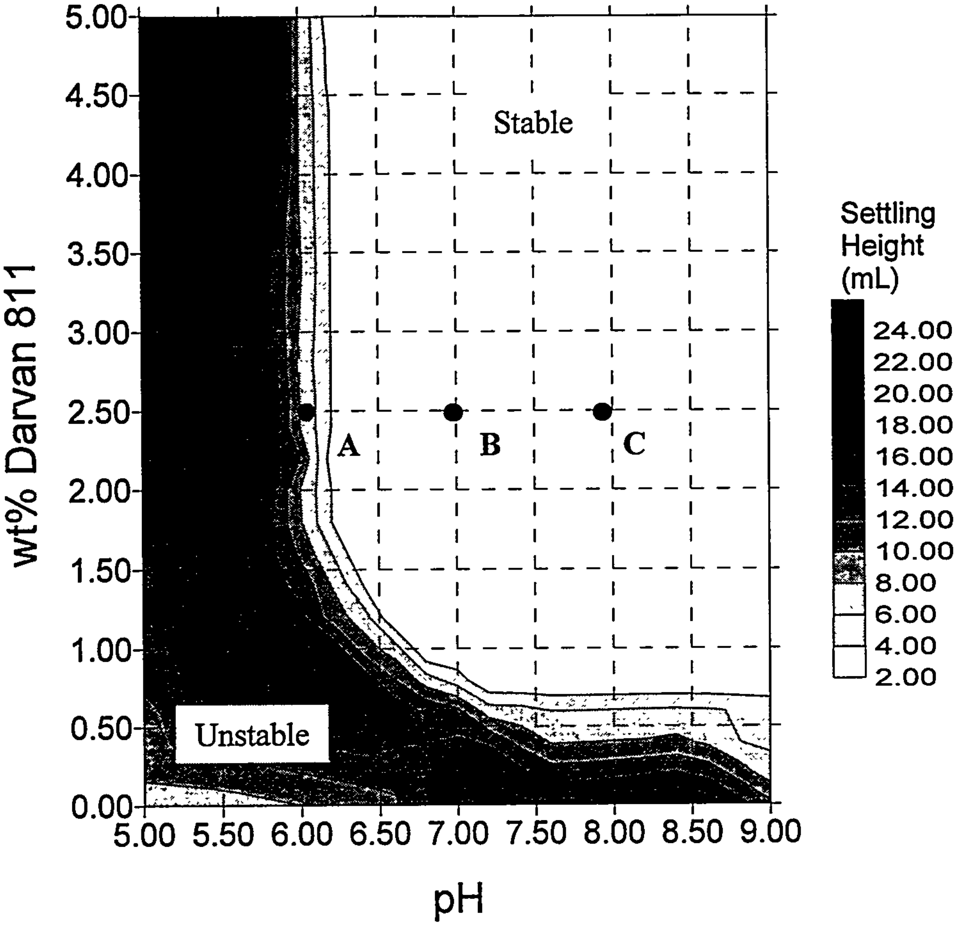

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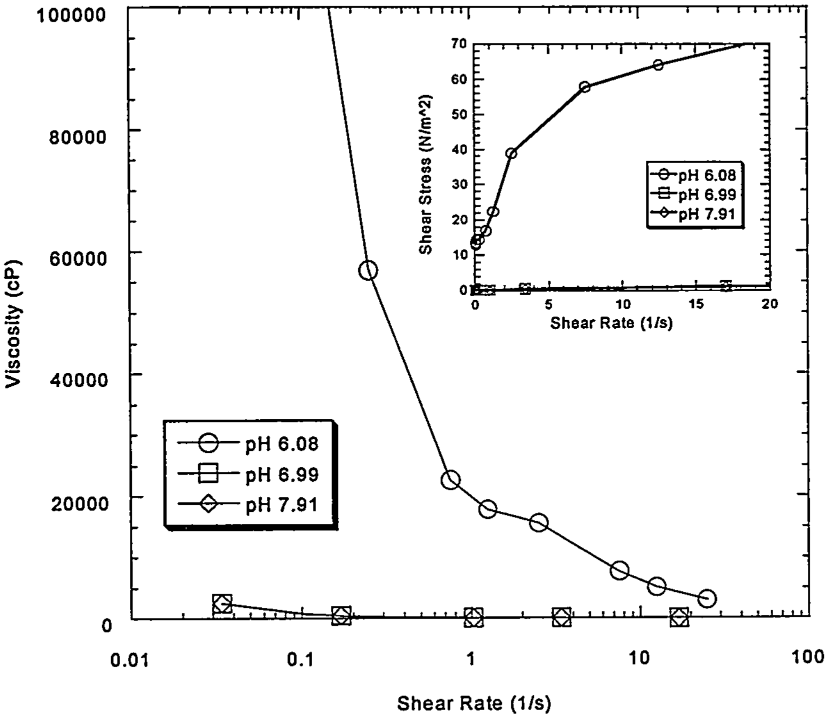

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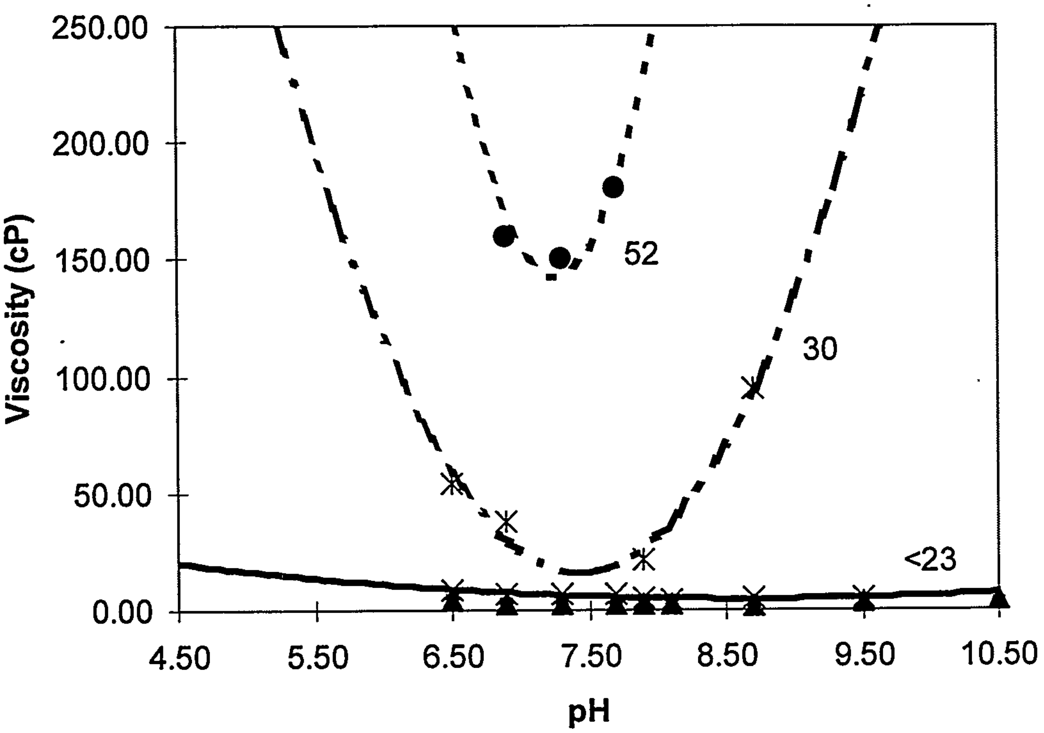

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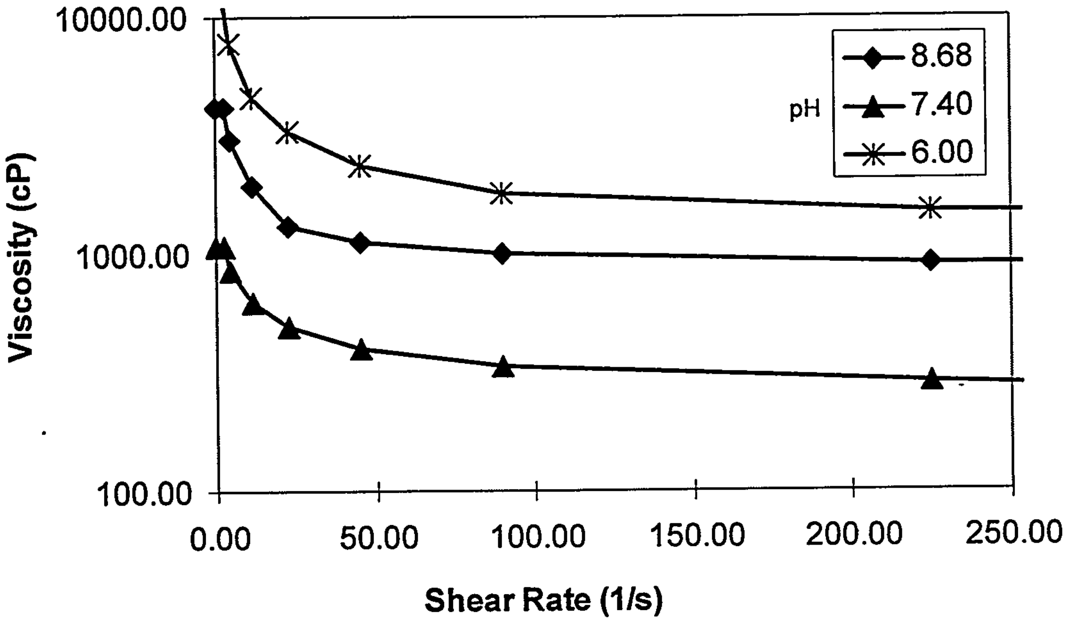

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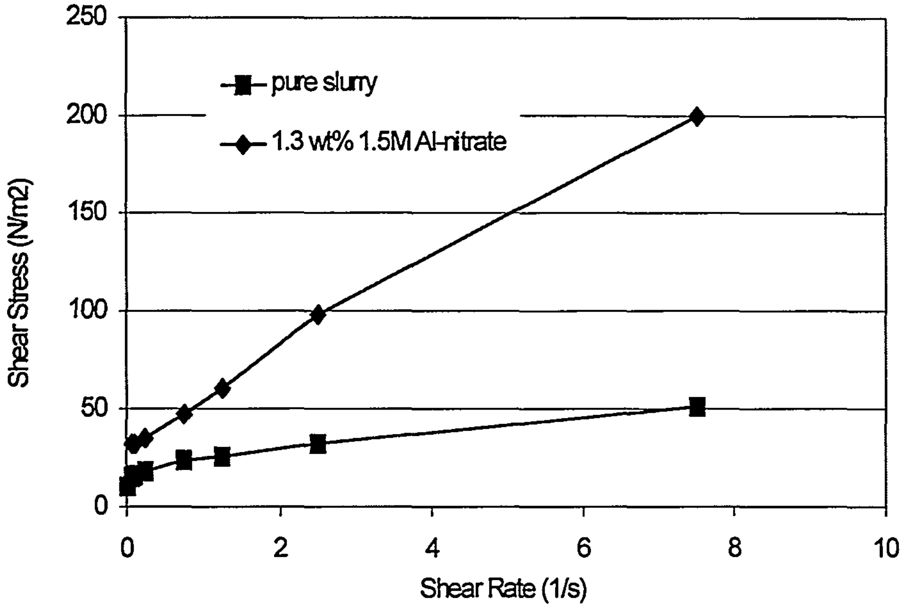

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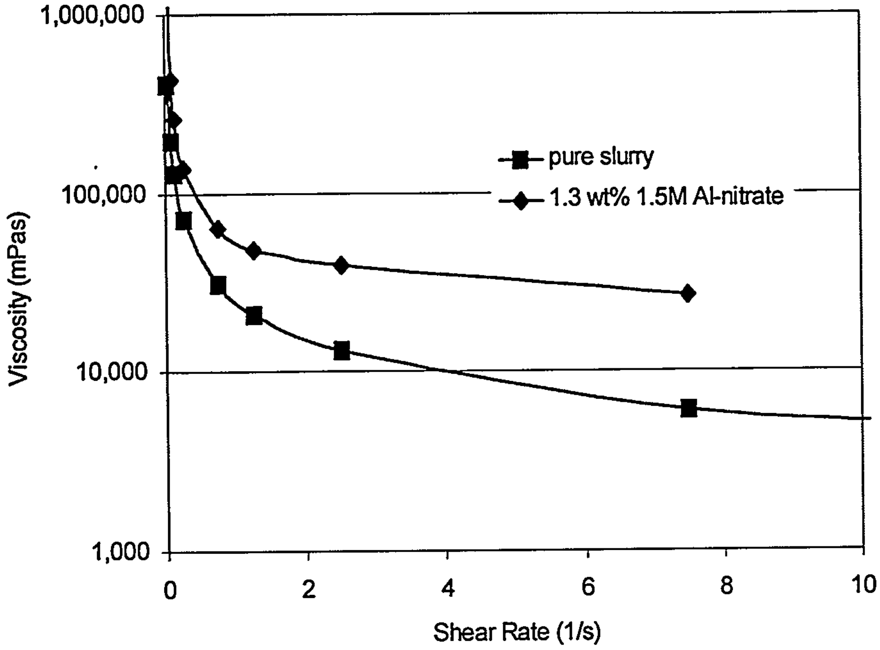

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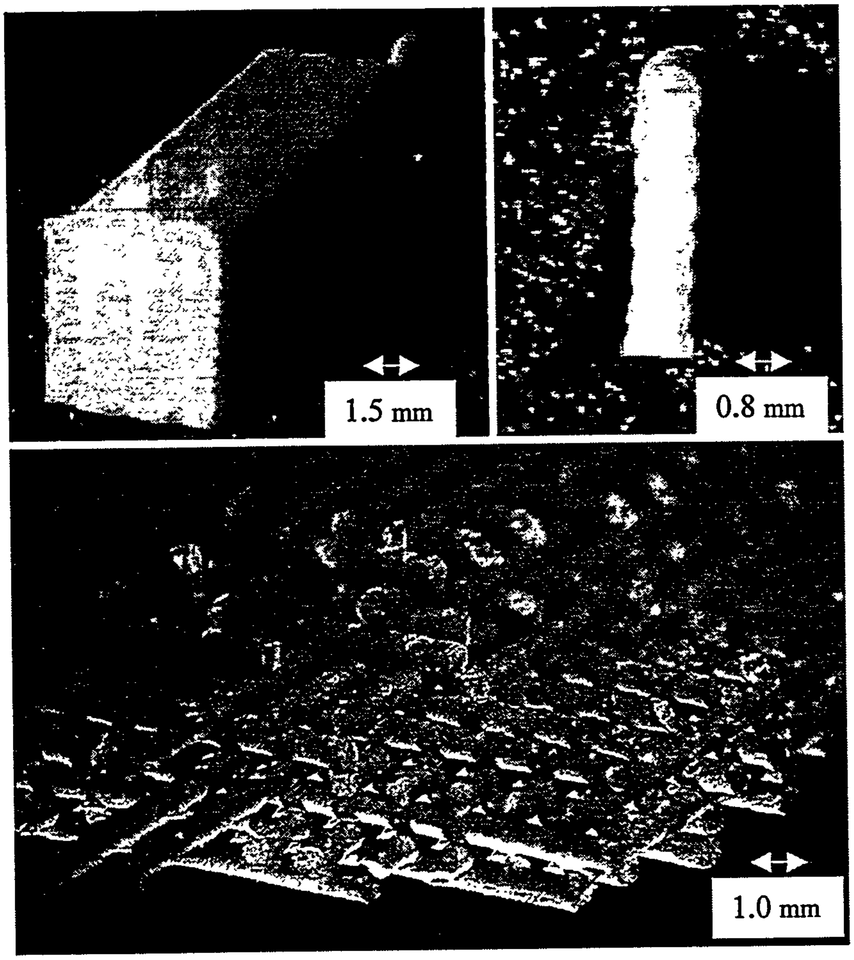

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