Direct visualization of particle disposition in kaolin slurries undergoing high shear

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ABSTRACT *A novel approach has been developed to study the response of various kaolin slurries to high shear. A method was developed to instantaneously freeze slurries while they undergo high shear and to prepare them for viewing with high resolution electron microscopes. Several kaolin samples were evaluated using this technique, with rheologies ranging from apparent Newtonian to very dilatant (i.e., No. 1 fine clay and calcined clay, respectively). Dramatic results are presented which demonstrate the utility of the new device and reveal particle-particle and particle-fluid interactions not heretofore directly visualized.*

KEYWORDS
Dispersion
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Freezing
Kaolin
Particles
Rheology
Shear stress
Slurry
Suspended solids

Ultrarapid freezing is the only procedure currently available for arresting all motion of the particles in an aqueous suspension so that their instantaneous disposition in the suspending fluid can be directly observed (*1, 2*). The cryofixed sample can be placed under high vacuum and fractured. At that point, the fractured surface can be etched and then replicated for examination with a high-resolution electron microscope. The freeze-fracture-etch-replication technique has been widely applied by biologists to the study of cellular ultrastructure and increasingly it is being applied to the study of clays and other materials (*3, 4*). In this report, we describe its application to dynamic suspensions, to kaolin slurries undergoing high shear. The disposition of particles in a sheared suspension reflects not only the pattern of fluid motion but also particle-particle and particle-fluid interactions which bear directly upon the causes of dilatancy, pseudoplasticity, and thixotropy. These studies have high potential for yielding information leading to a more thorough understanding of the behavior of coating colors experiencing extremely high shear rates under the blade in a coating process. This report is only the beginning in a series of reports aimed toward this end. The initial work revolves solely around various dispersed slurries without any binders and coating additives. The ultimate goal is to visualize interactions taking place within the coating during abnormal coating behavior such as dewatering, whiskering, scratching, and streaking. Understanding the problem on a microscopic level will be the first step to a definitive solution.

Equipment and procedures

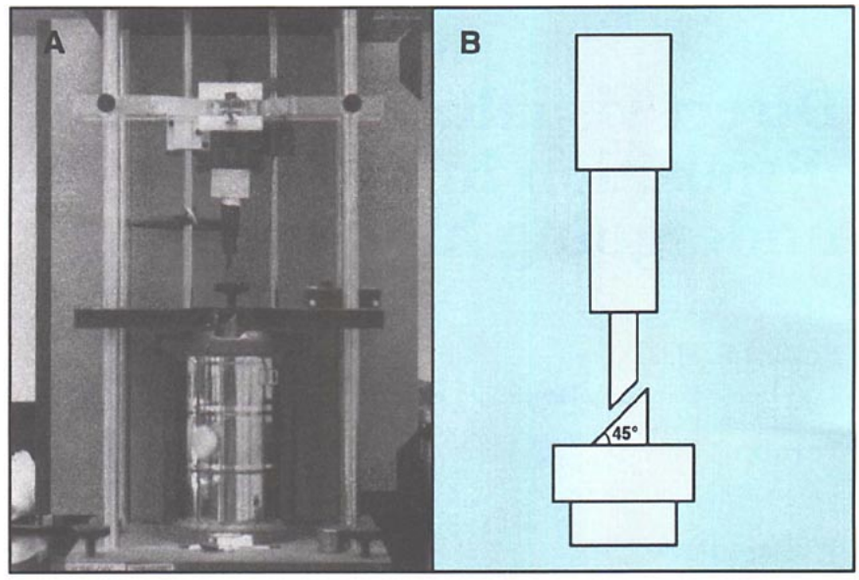
Two different devices have been used in this work for the ultrarapid freezing of an aqueous suspension while it is subjected to a high rate of shear. One device is a modification of a unit which currently exists called the "Gentleman Jim" (Pelco®) slam freezer. This unit has been used for some time in the biological field for rapid freezing. The other is a cone-in-cone microviscometer, being developed for this work. To the best of our knowledge, this is a completely new device for which patent applications have been filed.

Slam freezer

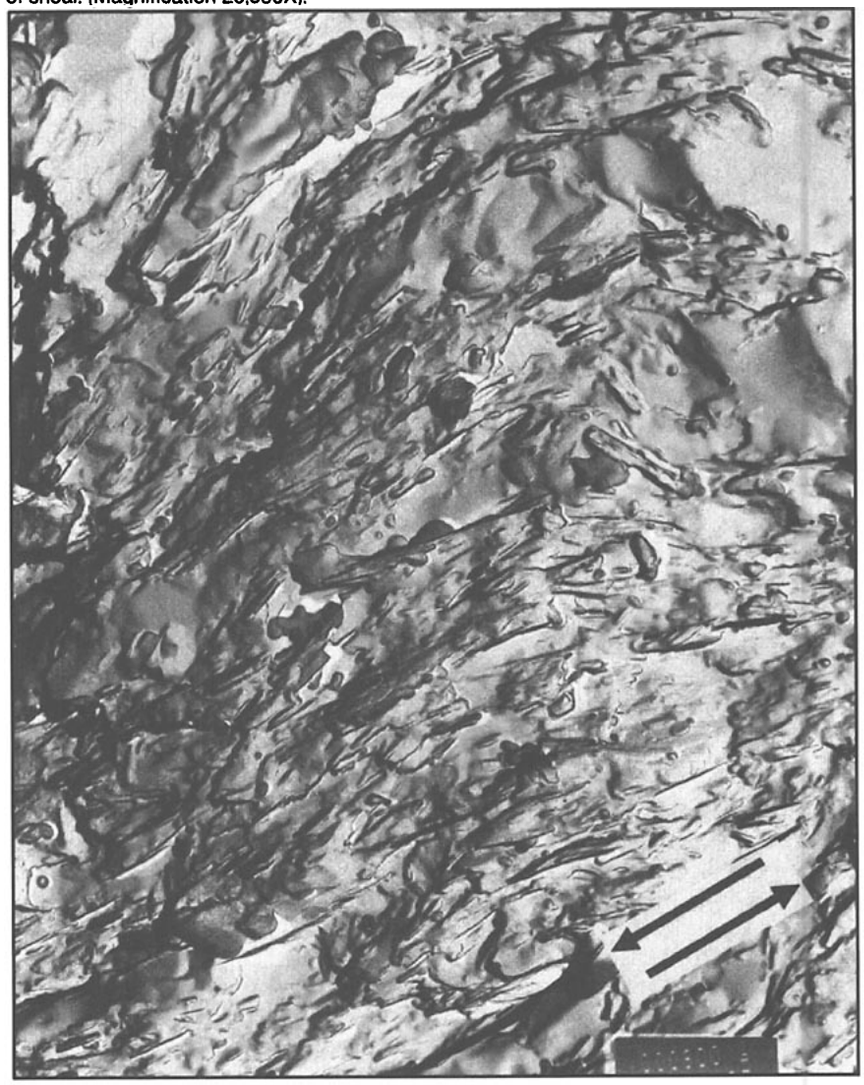
In the modified slam freezer, the specimen to be frozen is affixed to the underside of an upper, moveable platen, which is at room temperature. Approximately 17 cm directly below the upper platen is another fixed platen which is cooled to liquid nitrogen temperature. Upon release of the upper platen, it falls freely until it slams the specimen against the lower platen, where it is instantaneously frozen.

In the modified slam freezer (**Fig. 1**), the upper platen is made of Delrin®, the lower platen of copper, and their mating surfaces are inclined 45°, as shown in detail in Fig. 1B. When the upper platen is raised, it is 17 cm above the lower platen. To cryofix a suspension, the tank beneath the lower platen is filled with liquid nitrogen and the lower platen is allowed to cool to -190°C. At that time, a small droplet of suspension is placed on the underside of the upper platen, and the sliding mechanism that holds the upper platen is released. At the end of the upper platen's free fall, the droplet of suspension slams into the inclined surface of the lower platen at a velocity of about 1.82 m/s. The rate of freeze is approximately 10,000°K/sec at -190°C; therefore, immediately upon contact, the lowest part of the suspension freezes, while the suspension higher in the droplet begins to shear in the downslope direction. Resistance to further downward motion rapidly increases due to both the viscosity of the suspension and to the rapid freezing progressing upward. The upper platen moves not only downward but also a little to the left before the droplet completely freezes. Thus, maximum shear is at the top of the droplet. Relative shear directions

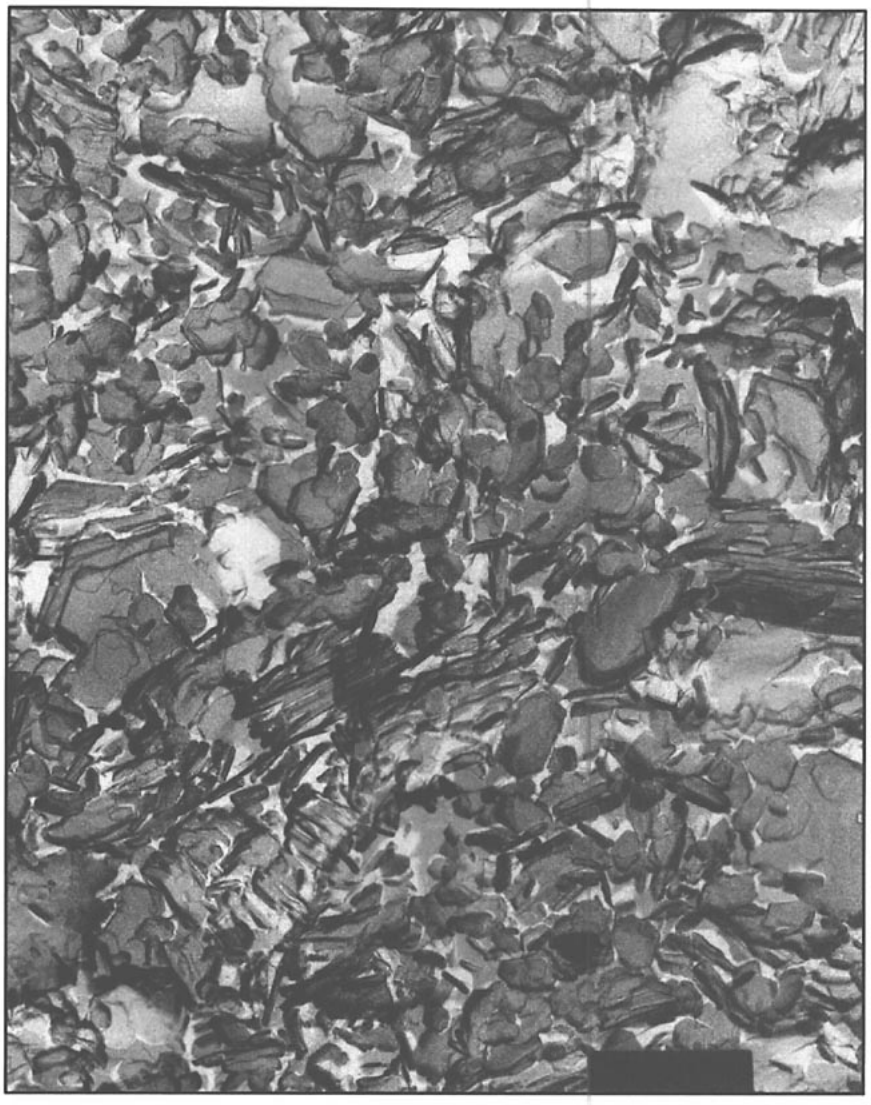
1. A: Photograph of the modified slam freezer. B: Detailed drawing of the upper and lower platen.



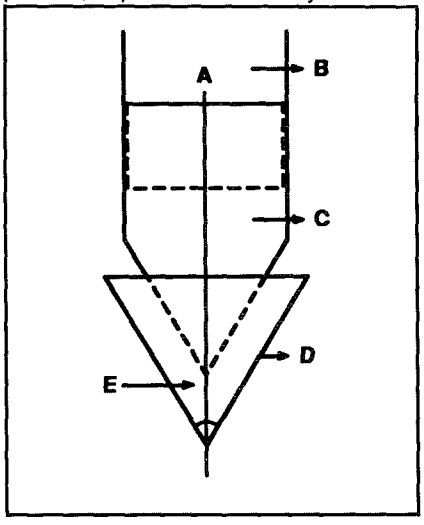
2. Electron micrograph of sample using the slam freeze technique. Arrows show the direction of shear. (Magnification 20,000X).



3. Electron micrograph of sample using a static freeze technique. (Magnification 20,000X).



4. Diagram of the cylinder-in-cylinder arrangement of the microviscometer. *A*: cone axis; *B*: rotor, 22 gauge brass tubing; *C*: inner cone, affixed to rotor 2 mm OD, made of gold; *D*: outer, stationary cone, 3 mm OD, made of platinum; *E*:space filled with slurry.



are indicated in Fig. 1B. When a suspension having little dilatancy is slam-frozen, the upper part of the droplet flattens noticeably and is sheared to a slightly elongated discoid before complete cryofixation. When the suspension is dilatant, elongation is minimal. Immediately after freezing, the specimen is stored in liquid nitrogen at -190°C until needed for subsequent processing.

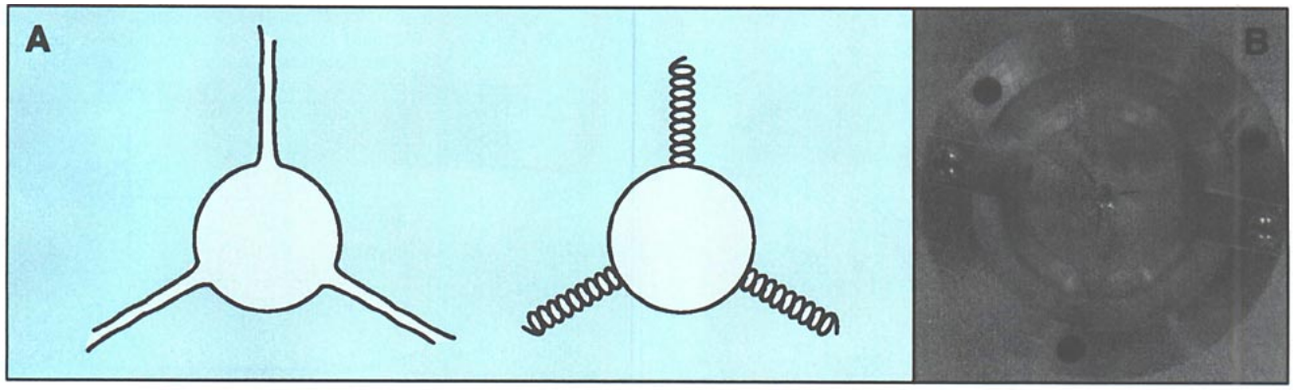
The modified slam freezer yields a cryofixed sample of sheared slurry that can be sectioned, etched, and replicated for electron microscopic examination. Rheologically useful information can be deduced from the size distribution and spatial disposition of the particles in relation to the direction of fluid motion. It is difficult to draw definitive conclusions when utilizing this method due to the inability to accurately define point-specific shear rates or magnitude of shear. A micrograph produced using the slam freezer is shown in **Fig. 2**. For comparison, **Fig. 3** shows a micrograph of a slurry frozen statically as is conventionally done.

Cone-in-cone microviscometer

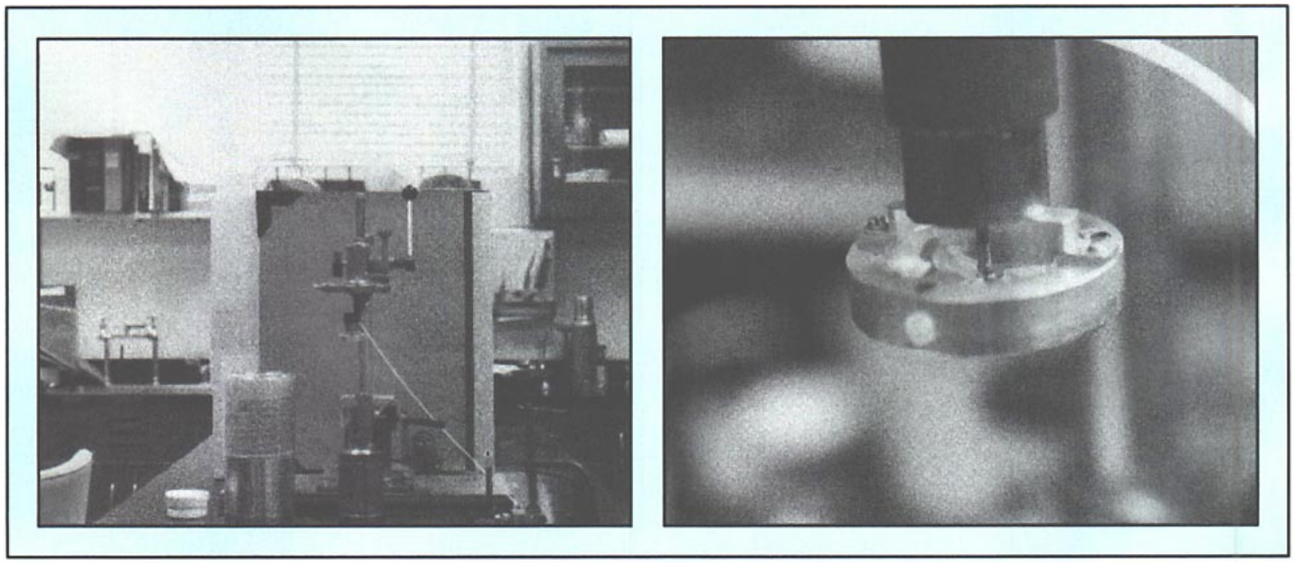
This device was designed to simulate a Hercules viscometer with respect to shearing action and rate of shear, but was drastically scaled down in size to operate with only a 10,000th of the slurry volume used in the Hercules cup. The scale-down was necessary in order to lower the mass of the slurry to a level that would enable instantaneous freezing. The cylinder-in-cylinder arrangement of the Hercules viscometer was replaced by the cone-in-cone arrangement in **Fig. 4**, to enable removal of the cryofixed sample from the viscometer. A cone angle of 60° was chosen because it gives better sample containment than a greater cone angle and gives a higher peripheral velocity than a smaller cone angle, for a given angular velocity. The design of the microviscometer was simplified by omitting any provision for directly measuring viscosity. The principal aim was to simulate on a microscale the shearing action and rate of shear of the Hercules viscometer so that interparticle and particle-fluid interactions might be directly visualized. The sample containment gap present in a Hercules viscometer using the A-bob is 0.5 mm. The gaps possible with the cone-in-cone viscometer are in the same range; therefore, the results from the cone-in-cone unit can be compared directly to what would occur in the Hercules unit.

The outer cone in Fig. 4 was fabricated from platinum foil 0.025 mm thick, with the shiny side of the platinum on the inside of the cone. The inner cone was fabricated from gold tubing and has the same wall thickness as the outer cone. The rotor to which the inner cone attaches is 22 gauge brass tubing. The rotor turns at a chosen rate between 800 and 5000 rpm when a slurry between the two cones is being sheared. Because the rotor and its attachments will stop

5. A: Wire spider arrangement—outer cone is placed here. B: Photograph of base holder assembly—wire spider is attached to the pegs with superglue.

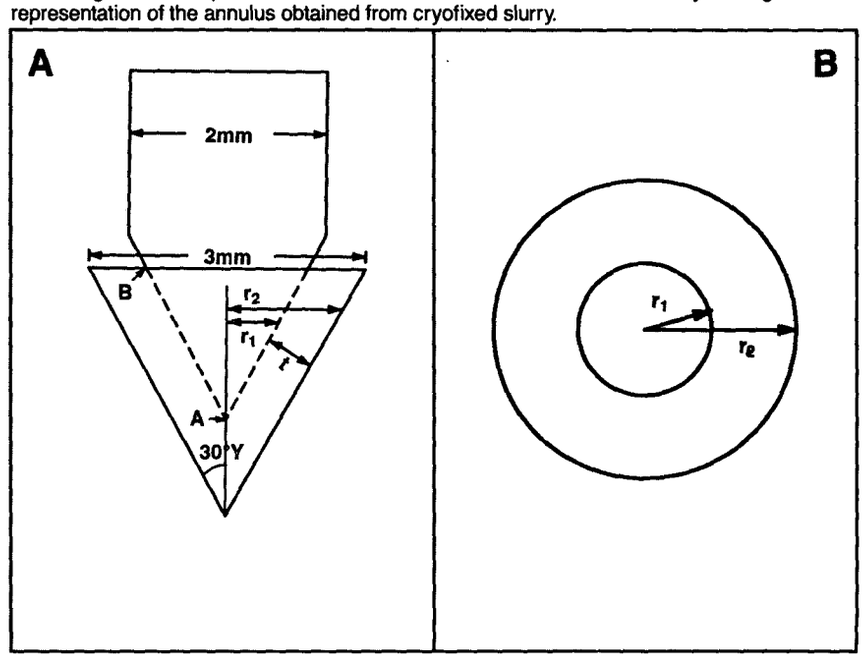


7. A: Microviscometry assembly. B: Base holder and cone assembly.

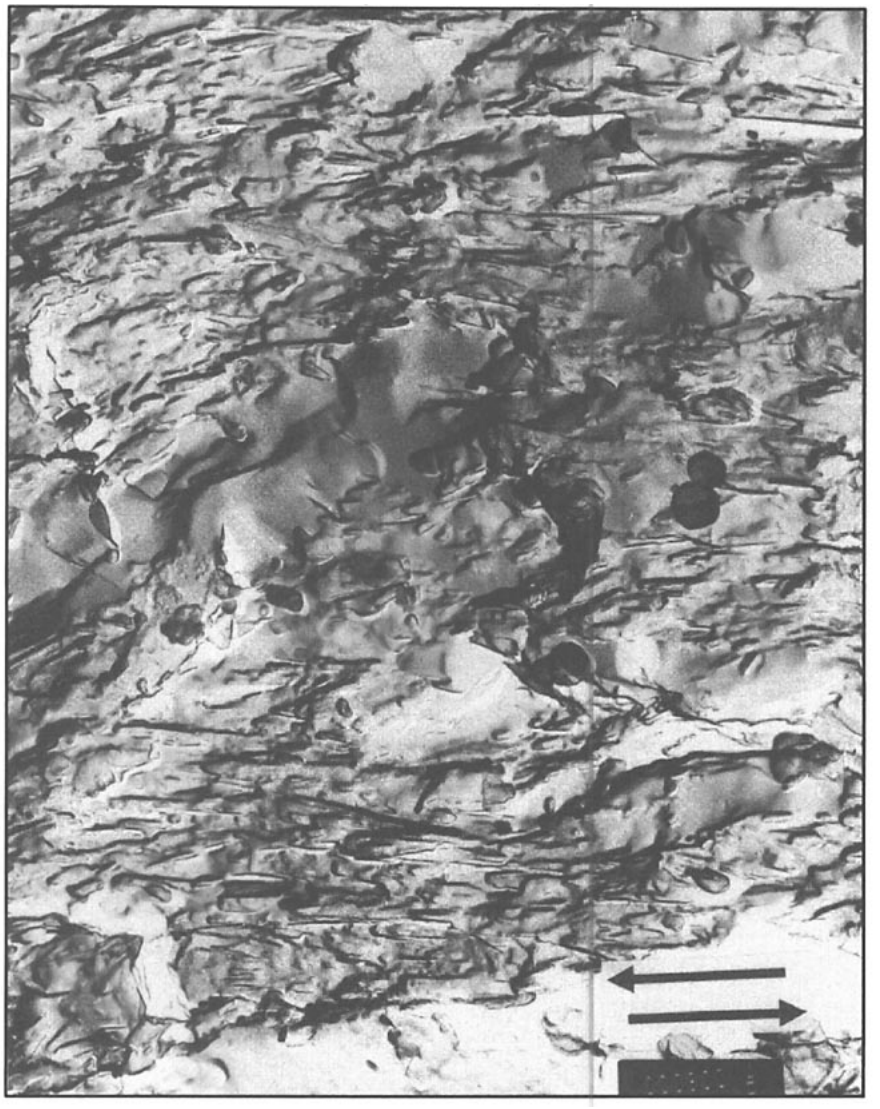


abruptly during cryofixation, considerable effort was given to reducing its weight. The outer cone is held in place by a wire spider (**Fig. 5**), which is affixed to 3 Lexan® pegs on the base holder (Fig. 5B). The wire spider is made from 3 short pieces of annealed copper wire 0.178 mm in diameter. In preparation for a run, the outer cone is placed in the wire spider and centered with respect to the inner cone. With the cones closely nested, the position of the outer cone and spider are fixed by touching a microdrop of super glue to each point of contact. Then the inner cone is raised the distance Y in **Fig. 6**. To make a run, the space between the inner and outer cones is filled with slurry using a micropipette. Compressed air is delivered through a needle valve to the vane at the top of the rotor. The rate of rotation is read with a Simpson phototachometer. When the rotation

6. A: Diagrammatic representation of the inner cone and outer cone assembly. B: Diagrammatic representation of the annulus obtained from cryofixed slurry.



8. Electron micrograph of slam frozen No.1 clay—70% solids by weight, 53% solids by volume. Arrows indicate direction of shear. (Magnification 20,000X).



rate of the inner cone has stabilized at the desired value, the base holder and cones are suddenly immersed in liquid nitrogen slush at a temperature of about -210°C, prepared as described by Umrath (*5*). The entire microviscometer assembly is shown in **Fig. 7**. Figure 7B is a closeup of the base holder and cone assembly. The liquid nitrogen slush being colder than regular liquid nitrogen facilitates the formation of vitreous ice void of any ice crystals. With the base assembly still immersed in liquid nitrogen, the inner cone is raised to free it from the conical mass of cryofixed suspension; the outer cone is separated with precooled tweezers and probe. The conical mass of cryofixed suspension is then stored in liquid nitrogen pending further processing.

Freeze-fracture-etch replication

Each cryofixed sample from the modified slam freezer and the cone-in-cone microviscometer was mounted on a special holder in a liquid nitrogen bath and then transferred to a Balzers 360M freeze-etch device, the interior of which was maintained at -100°C and a pressure of 3×10^{-6} torr or less. A supercooled knife was used to fracture the sample, and topographical relief was achieved by a gradual increase in temperature in the chamber, causing sublimation at the ice surface. A Balzers 445 K electron beam deposition gun, positioned at 45° 10 cm from the fracture surface, was used to deposit a layer 150 Å thick of 95%Pt/5%C. A Balzers QSG 301 quartz crystal film thickness monitor enabled control of film thickness. Following metal deposition, a strengthening layer of carbon was applied for 15 s from 90° with a resistance-type evaporator. The resulting replica was carefully floated onto distilled, deionized water, then transferred to concentrated hydrofluoric acid for digestion cleaning to remove residual clay material which may have adhered to the Pt/C film. After 24 h, the replica was given several washes with distilled, deionized water before mounting on Formvar®-coated grids for transmission electron miscroscopy (TEM) or carbon-coated stubs for the scanning electron microscope.

Rate of shear in the microviscometer

A diagram of the annulus obtained when a cryofixed cone of slurry from the microviscometer is sectioned and replicated is also shown in Fig. 6B. The greater diameter of the annulus, r_2, defines the position of the replicated plane with respect to the outer cone axis, (i.e., the greater r_2 is, the higher up on the frozen cone was the slice made). The smaller diameter of the annulus is r_1. The parameter z is $r_2 - r_1$. From measurements of r_1 and r_2, for right cones of known height and apical angle, all other parameters can be calculated. Likewise, for any given t, the thickness of the slurry between the cones and l, the distance between the top of the outer cone and the fracture plane to be replicated, all other parameters can be calculated.

The rate of shear in the cone-in-cone microviscometer varies not only with the rate of rotation of the inner cone but also with position along a line from A to B in Fig. 6A. It varies from zero at the tip of the inner cone to a maximum value near the top of the suspension. Additionally, it varies with t, the separation of the cones. As t decreases, for cones of a given size, rate of shear at point B increases. Rate of shear is approximately the peripheral speed of the inner cone divided by the clearance between the cones. It can be maximized by increasing the rate of rotation of the inner cone, decreasing the distance Y (i.e., by decreasing the thickness of the slurry) or by choosing the plane to be replicated normal to the cone axis and as far as possible from the tip of the inner cone. In short, one can select a particular shear rate regime in which to work.

Results and conclusions

Slam freezer

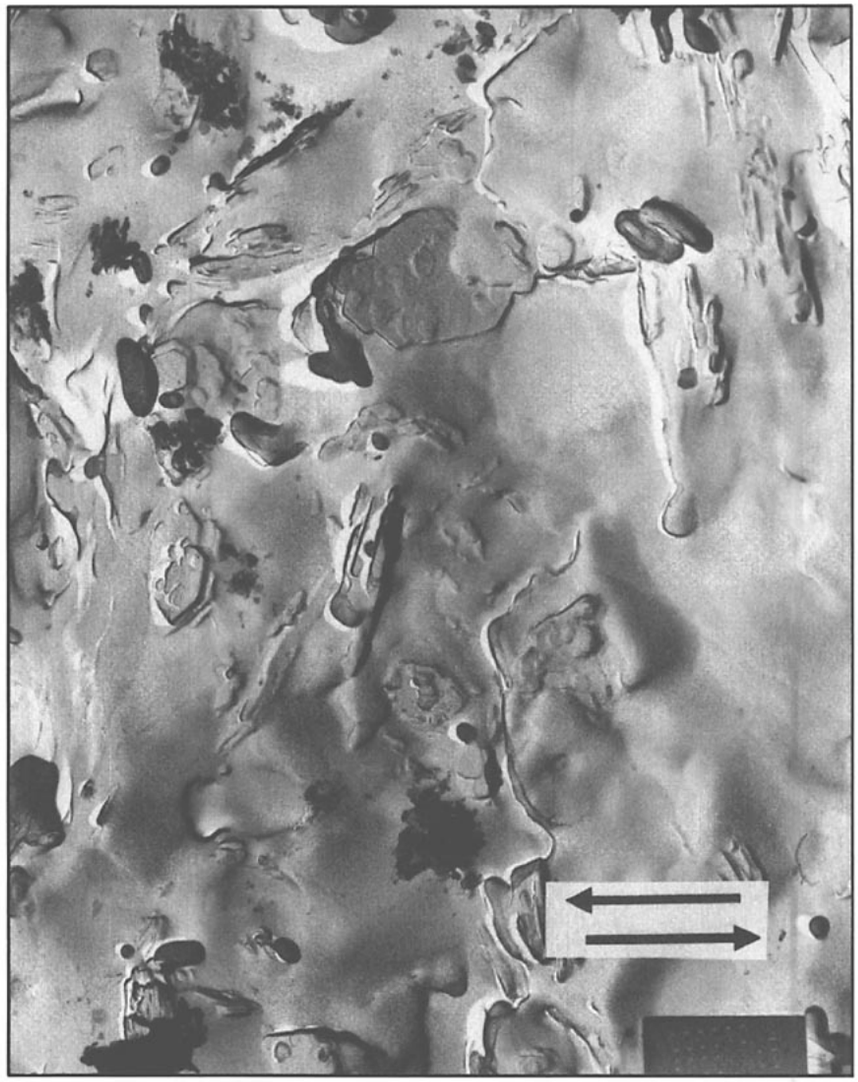
A small discoidal mass of a kaolin-water slurry, cryofixed during shear, is readily obtainable with the modified slam freezer. Replication of a fracture surface transecting the mass yields a high resolution image which reveals in detail how kaolinite platelets are distributed in the suspending fluid at the instant of cryofixation. Visualization is facilitated by preparing a montage of electron micrographs so that small-scale features like individual submicron particles can be observed simultaneously with large-scale features like lamellae and vestigial floccules. Unfortunately, it is not possible, due to limited illustration space available to reproduce a montage for a figure created from several glossy prints; therefore, only one print is shown in the following figures. These single micrographs will still reveal much of the information available in the entire montage. Seven different kaolin-water slurries ranging from 50% to 70% solids by weight and representing a wide range in particle size and viscosity have been treated by the slam-freeze procedure. The resulting replicas show that distinct lamellation, planar water-rich zones alternating with kaolinite-rich zones, may develop in slurries undergoing strong shear.

Shown in **Figs. 8 and 9** are two of the seven slurries tested. These were chosen because they represent a wide range of high shear viscosity values. Figure 8 is the micrograph of a slam frozen fine particle size No. 1 clay. The Hercules viscosity of this sample was 1.5 dynes or 26 cp* at 1100 rpm using the A-bob. The sample was tested at 70% solids. Figure 9 shows the micrograph of a slam frozen conventional calcined clay. This sample exhibited a viscosity of 18+/400 at 50% solids. This represents an apparent viscosity of 860 cp.

When one compares Figs. 8 and 9 there are striking differences in the appearance of the sheared sample. Figure 9 is the No. 1 fine kaolinite at 70% solids by weight, which is approximately 53% kaolinite by volume. Figure 9 is the calcined clay at 50% solids by weight which is only 28% kaolinite by volume. This difference in volume of water is evident when one examines Figs. 8 and 9. The extreme dilatancy of the calcined clay is difficult to explain especially because of the low volume fraction. The dilatancy of the calcined clay at low solids and low volume fraction implies that there is some sort of structuring effect on the bulk water. These observations are compatible with existing theories on vicinal water (*6, 7*). In this case, the layer of "vicinal" water is very large for a calcined clay sample.

With the slam-freeze-fracture procedure, it is relatively easy to observe the disposition and orientation of suspended particles in a slurry undergoing shear, and to map variations in relative rate of shear within the cryofixed mass, but the absolute rate of shear can hardly be evaluated. To overcome this shortcoming, the cone-in-cone microviscometer was developed.

9. Electron micrograph of slam frozen calcined clay—50% solids by weight, 28% solids by volume. Arrows indicate direction of shear. (Magnification 20,000X).



Cone-in-cone microviscometer

Though rate of shear varies within the slurry cone of the microviscometer, the variation is regular and can be evaluated from measurements made directly on the annular replication surface. Application of the microviscometer is considerably more demanding than the slam-freezer, even difficult. Several improvements are yet to be made, particularly with respect to better alignment of the

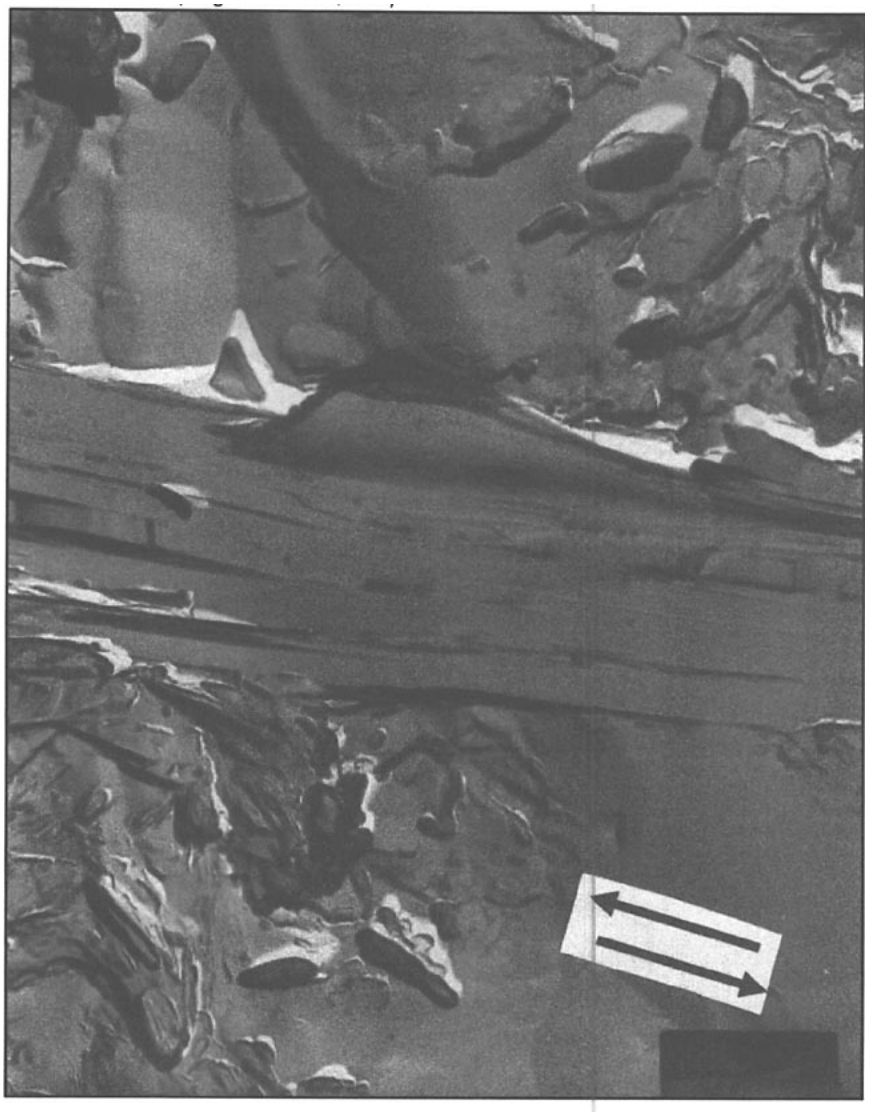
*The apparent viscosity in poise is calculated using the formula $\eta = 9.55\ sT/rpm$. Where s is the factor for the particular bob being employed. For the A-bob it is 0.0002. T is the torque, which is the spring constant times the horizontal pen displacement. For the example given,

$$\eta = 9.55 \cdot 2e^4 \cdot e^5 \cdot 1.5$$

where

$e = 10$.

10. Electron micrograph of slurry undergoing high shear in the microviscometer. Arrows show direction of shear. (Magnification 20,000X).



cones and better control of the rate of rotation of the inner cone. Still, the device and its operational procedures already are developed to the point that complete annular replications can be made.

Five kaolin slurries ranging from 50% to 70% solids by weight and representing a wide range in particle size and viscosity have been cryofixed while undergoing high shear in the microviscometer. Replicas of fracture sections across the cryofixed slurry cones have been made. Preliminary study of these replicas by high resolution electron microscopy reveals important new information about how the kaolin particles behave under high shear. **Figure 10** is a micrograph produced from one of these five conditions. This one was chosen because it shows several interesting physical phenomena taking place. The top of the micrograph is the part of the slurry closest to the inner cone, and the bottom is closest to the outer cone; therefore, the shear rate is maximum at the top of the micrograph and minimum at the bottom. At the top of the micrograph, one can see several sequestered clay regions oriented as if in a vortex. Note the water at the center of the vortex. This finding indicates that at high shear, clay particles do not always undergo strictly lamellar flow. Midway in the micrograph, there is a distinct zone of water devoid of pigment. This region is most probably a slip plane in the slurry at a transition area from high shear to very low shear. The area under the slip plane due to its random orientation shows no evidence of high shear. Other micrographs (not shown here) also indicate sequestering of particles and fluid. They appear to be roughly alternating zones of water and clay. Presently, a detailed study of this and other new data is under way.

Application

The examination of viscosity behavior in non-Newtonian fluids is an important area of study in many different industries. One of these areas, of course, is the paper industry, more specifically paper coatings. Paper coating "colors" are complicated mixtures containing various mineral pigments, organic binders, organic polymeric additives and, finally, water. They exhibit very complex rheological behavior at high shear rates. The interpretation of data can be difficult; moreover, the relationship of these data to performance on a paper coater can seem nonexistent. Rheology at lower shear rates is much more fully understood (i.e., regime of viscosity occurring during screening and pumping). These shear rates are several orders of magnitude lower than those encountered during the blade coating process. The shear rates under a coating blade exceed $1\times10^{6}s^{-1}$. A previously published article demonstrated how there is very little relationship between the high shear viscosity of a clay slurry and the high shear viscosity of the resultant coating (*8*). In short, finding a tool with which one can predict coating performance and runnability is difficult. Problems that continue to plague coating personnel are scratching, streaks, whiskers, and stalactite formation on the backside of the blade. The slam freezer and cone-in-cone viscometer will be utilized to visualize specific microscopic interactions taking place in coating colors, and these observations will be correlated to runnability phenomena on the coater.

Conclusions

Two methods have been presented that allow one for the first time to actually view the interactions taking place in a kaolin slurry undergoing controlled high shear. The slam freeze method, while comparatively simple in concept and apparatus, produces both interesting and enlightening cryofixed preparations for observation. As mentioned before, however, quantification of causative forces

producing the observed phenomena is desirable. The cone-in-cone microviscometer, though much more complex, affords the luxury of accurately attributing or choosing specific shear for analysis of particle interactions. While the results seen thus far have been predicted at times, at other times the results have been unexpected. The relatively even distribution of particles and fluid in a static, well-dispersed slurry vanishes rapidly when the slurry is subjected to a high rate of shear. If displacement at high shear are by lamellar flow, then particle-rich and fluid-rich lamellar zones tend to develop, with most of the displacement taking place in the fluid-rich zones. If displacement is not by lamellar flow, then displacements lead to particle bridging and clotting and to the development of transient planes of shear or tear. Sometimes microvortexing is conspicuous. Turbulent flow appears to be associated with high dilatancy.□

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