III. Laminar-Flow Properties of Flocculated Suspensions

The turbulent heat, mass, and momentum transport characteristics of suspensions of particles with near-colloidal dimensions have previously been shown to be related to the non-Newtonian laminar-flow properties of the suspension. However the laminar-flow properties were not studied systematically. The present study showed that the principal factors affecting the magnitude of the laminar-flow properties of flocculated suspensions were the concentration and particle diameter of the solid phase. The range of variables included concentrations from 0.02 to 0.23 volume fraction solids and particle sizes from 0.35 to 13 μ. Materials tested included thorium oxide, kaolin, titanium oxide, aluminum oxide, graphite, magnesium, and uranium dioxide.

At high rates of shear the data were fitted satisfactorily with the Bingham plastic model. With the use of this model, the yield stress was directly proportional to the cube of the volume fraction solids and inversely proportional to the first or second power of the particle diameter, depending on the particle shape. The logarithm of the ratio of the coefficient of rigidity of the suspension to the viscosity of the suspending medium was directly proportional to the volume fraction solids over the complete range of concentrations studied. Although specific electrolytes (such as oxalate or pyrophosphate) deflocculated the suspensions even at low concentrations, the suspensions remained flocculated both in the presence of up to 0.1 *M* of 1:1 electrolyte and over a *p*H range of 4 to 12. This is consistent with present theories of the stability of colloidal and near-colloidal particles.

Although the concentration-dependence relationships of the yield stress and coefficient of rigidity have been proposed previously and have been shown to apply to specific systems, this is the first time they have been shown to apply to a broad class of materials. In addition it is the first time that the laminar-flow properties used in the particle-size and concentration correlations have been determined over a shear-rate range which permits application of the results in correlations of turbulent heat, mass, and momentum transfer data obtained in systems of commercial interest.

The determination of the heat, mass, and momentum transport characteristics of flocculated suspensions requires a detailed knowledge of their non-Newtonian laminar-flow properties (1 to 4). However no systematic study has been made which would permit the prediction of the behavior of a suspension from the physical properties of its constituents. The object of the present study was to determine the principal factors (that is concentration of the solid phase, particle size, and shape) affecting the laminar-flow properties of flocculated suspensions. In addition it was necessary to establish an experimental procedure which would yield physical properties equivalent to those used in the previous correlations of turbulent-flow data taken in pipes with diameters in the range of ⅜ to 1 in.

Most investigators have not been concerned with both of these objectives but have concentrated on one or the other. For instance Norton et al. (*5*) have studied the factors affecting the properties of kaolin suspensions using a rotational viscometer. The data were fitted with a Bingham plastic model. Although the shear-rate range was too low to permit application to pipeline design, their results showed that the yield stress was roughly proportional to the cube of the concentration. On the other hand Alves et al. (*6*) have demonstrated the applicability of capillary tube viscometer results to the determination of pressure drop in large-scale systems transporting a variety of different suspensions, but they did not systematically investigate the suspension characteristics.

BASIC CONCEPTS

Suspensions of liquids and solids having near-colloidal dimensions often belong to the general class of non-Newtonian materials whose consistency decreases as the rate of shear is increased. More specifically at low rates of shear the effective viscosity of such suspensions is large and does not vary appreciably as the rate of shear is decreased. At intermediate rates of shear the effective viscosity changes rapidly with shear rate, decreasing as the shear rate is increased. At high rates of shear the effective viscosity is again almost constant, approaching a limiting value. This limiting value is always greater than that of the suspending medium.

Because of this complicated variation of viscosity with shear rate no general relation is available which adequately describes the data over the complete shear-rate range of interest. Previous studies (*3*, *4*) have shown that application of the Bingham plastic model gives suitable parameters for correlating data where processes occurring at high-shear rates are controlling, that is heat and momentum transfer at the pipe walls. This model has the following desirable features:

1. It fits the data sufficiently well at high-shear rates to allow accurate effective viscosities and laminar velocity gradients at the wall to be calculated from the experimentally determined flow parameters.
2. It extrapolates to give a limiting value of the viscosity at high rates of shear that is always greater than the viscosity of the suspending medium.

The two parameters that characterize the Bingham plastic model are the yield stress and the coefficient of rigidity. It is recognized that there are some doubts as to the existence of a true yield stress as required by the Bingham plastic model, and no claim is made that the suspensions used in the present study are Bingham plastics. Nevertheless within the limitations prescribed above this model has proved entirely adequate in correlating data taken with flocculated suspensions in turbulent flow and, in addition, has proved to be extremely useful in visualizing the physical processes that are occurring (*3*, *4*).

Particle-Particle Interaction in Flocculated Suspensions

Suspensions of particles having near-colloidal dimensions derive many of their properties from the same forces that are important in the stability of true colloid systems (*7*). Thus it is believed that attraction between particles is largely a result of van der Waals' forces and that repulsion arises in the electrolyte double layer surrounding the particles (*8*, *9*). The relative magnitude of these forces determines whether the net force on the particles is attractive or repulsive. Since the attractive forces originate within the solid, little can be done to modify them. However the repulsive forces are dependent on the amount and nature of the electrolyte in the suspension, and thus changes in these variables are responsible for the drastic changes in physical properties often observed with suspensions of small particle size material.

One of the most striking aspects of the electrolyte double layer is that its basic structure is fixed by the so-called "potential determining ions," with other ions contributing only to the details of the charge distribution. The potential determining ions for a broad class of materials (which include such solids as oxides, hydroxides, and materials which may act as a reversible gas electrode, that is noble metals and graphite) are hydrogen, and hydroxyl ions. This means that suspensions prepared with materials from any of the above categories should exhibit the same general behavior with regard to changes in hydrogen and hydroxyl ion concentration. An exception to this is that extremely small quantities of organic complexing agents, such as oxalic acid, and of inorganic polymers, such as sodium silicate and sodium pyrophosphate, are powerful deflocculating agents not only for thorium oxide suspensions (*20*), but also for a wide variety of clays used in the ceramic industry (*22*).

EXPERIMENTAL PROCEDURE

Selection of Viscometer Tube

Particular attention must be given the selection of the capillary tube dimensions for use with suspensions in order to minimize the relative magnitude of entrance and wall effects. Since these corrections are not thoroughly understood, it is desirable to reduce the correction term to the smallest practicable value so as to minimize possible errors. Entrance effect corrections may be reduced by increasing the length-to-diameter ratio of the tube (*10*) while wall effects may be reduced by increasing the tube diameter (*11* to *14*). On the other hand it is advantageous to select as small a tube diameter as possible in order to achieve high-shear rates before transition from laminar to turbulent flow.

Laminar flow entrance effects for shear-rate-thinning (*15*) non-Newtonian fluids have been shown (*10*) to decrease regularly from the value for Newtonian fluids as the non-Newtonian character is increased. For tubes with a length-to-diameter ratio of 1,000 the maximum entrance correction for Newtonian fluids at the transition Reynolds number is about 3.5%. It is always smaller than this value for lower flow rates and for more non-Newtonian behavior (*10*). However in another study which utilized highly flocculated titanium oxide and magnesium suspensions the entrance correction was shown to be substantially the same as for Newtonian fluids, independent of the non-Newtonian characteristics (*16*).

Wall effects in the laminar flow of suspensions have been attributed (*11* to *14*) to a layer of dispersion medium adjacent to the tube walls. Two approaches have been followed in attempting to determine the nature of the wall correction. In the first, the rheological equations are written incorporating a slip coefficient which must be evaluated for each suspension with viscometer tubes of different diameter (*11, 12*). In the second approach, the wall effect is related directly to the diameter of the particles. Not only does this limit the results to nonflocculated suspension of solid spherical particles, but as yet the agreement between theory and experiment is only approximate.

With the semiempirical approach of the first procedure it has been shown (*3*) that laminar wall effects are negligible for flocculated suspensions of particles in the micron size range flowing through tubes from ⅛ to 1 in. in diameter. However a pronounced wall effect has been observed with similar material flowing through capillaries of 0.038- and 0.057-in. I.D. As an example of the magnitude of the effect to be expected, data were obtained for a suspension having a mean particle diameter of 1.35 μ flowing through tubes of 0.038- and 0.124-in. diameter. In this particular case the values of yield stress differed by 22%, the coefficient of rigidities differed by 56%, and the data did not coincide for any of the shear stress values. In contrast to this, data taken with tubes of 0.124-, 0.138-, and 1.024-in. diameter coincided over the complete laminar-flow range with no observable effect of tube diameter (*3*). In the particular case cited above the transition from laminar flow occured at values of $8V/g_cD$ of 580 and 140 (lb.$_f$/lb.$_m$) (sec./ft.) respectively, for the 0.038- and 0.124-in. diameter tubes. However until the wall correction is better understood, full advantage cannot be taken of this fact.

Experimental Equipment

In the present study the laminar flow rheological properties were determined with a horizontal tube viscometer of stainless steel with a tube of 0.124-in. I.D. and a length-to-diameter ratio of 1,000. The tube protruded 1 diam. into the vessel, and both ends of the tube were cut off perpendicular to the axis. The suspension was agitated by two 1½-in. diameter marine type of impellers spaced 4 in. apart on a single shaft connected to a 1,750-rev./min. motor. Pressure was applied to the system with compressed air and was adjusted to the desired value with a pressure controlling valve; the air pressure was measured with water or mercury manometers or with calibrated pressure gauges. The total pressure at the tube inlet was obtained by adding a small correction for the static head of slurry remaining in the reservoir to the observed overpressure of compressed air.

Operational Precautions

During experimental operation care was taken to insure that data were obtained well into the turbulent-flow region. The necessity for this is illustrated in Figure 1 which shows that as the concentration was increased from 0.069 to 0.154 volume fraction solids, the value of the term ($8V/g_cD$) at the transition increased from 115 to 350, representing a more than threefold increase in the transition velocity. The locus of the transition points remains substantially the same for any given tube diameter and material and tends to increase as the particle density is decreased. For instance with the viscometer used in the present study the locus of the transition values for kaolin suspensions was parallel to and 10 to 25% greater than the locus for thorium oxide. This is shown by the dotted line on Figure 1. These two loci can be used as a general guide for the range of data that must be covered to obtain useful physical property data, it being obvious that the data should be extended to as low a flow rate as possible.

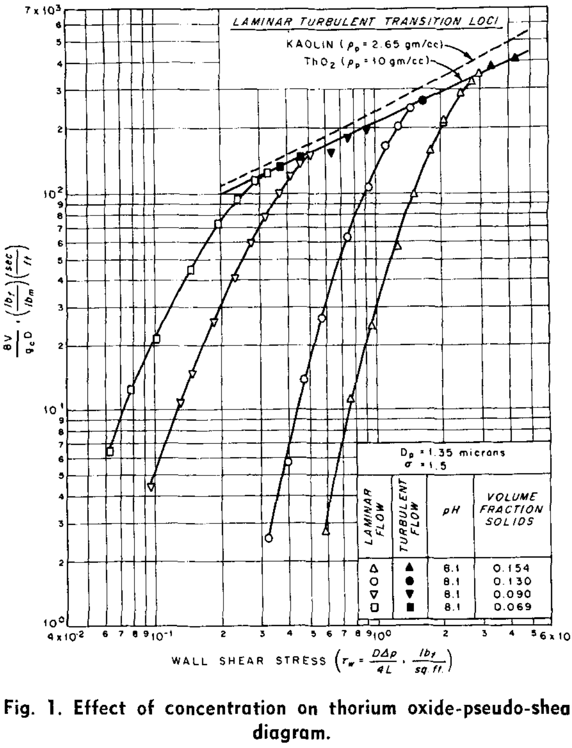


Fig. 1. Effect of concentration on thorium oxide-pseudo-shear diagram.

Data Treatment

The coefficients of the Bingham plastic model were determined by fitting the high-shear rate portion of the data with the Bingham plastic equation integrated for flow through tubes of circular cross section, Equation (*1*):

$$\frac{8V}{g_c D} = \frac{1}{\eta}\left[\tau_w - \frac{4}{3}\tau_y + \frac{1}{3}\frac{\tau_y^4}{\tau_w^3}\right] \quad (1)$$

If only the high-shear data are considered, the last term on the right may be neglected. Then after fitting the high-shear rate data with a straight line one can obtain the yield stress, by taking three-fourths of the intercept at zero flow rate. The coefficient of rigidity is given by the reciprocal of the slope. These are commonly accepted techniques, and further details may be obtained from readily available sources (*1, 2, 6*).

Particle Size Determination

Particle sizes were determined either by sedimentation with a modified Andreisen method (*17*) or by particle count from electron micrographs. The sedimentation procedure was used for powders having a mean size of 0.7 μ or larger, while the electron micrographs were most useful for sizes less than 1 μ. The size distributions generally were closely approximated by the logarithmic normal expression (*18*) and thus could be characterized by two terms, the mean diameter and the logarithmic standard deviation. In all cases the mean diameters are given on a weight basis.

EXPERIMENTAL RESULTS

A powder having a wide range of sizes is a necessary prerequisite for the study of the factors affecting the physical properties of suspensions of solids in liquids. Procedures were developed (*19, 20*) for preparing thorium oxide powders having a wide range of physical properties. Thus the major emphasis in this study was on the factors affecting the laminar-flow shear diagrams of aqueous thorium oxide suspensions.* The results of the correlation of thorium oxide suspension data were then compared with physical-property measurements of a variety of suspensions prepared from commercially available materials, such as titanium oxide and kaolin, in order to determine the general applicability of the thorium oxide results.

Concentration Dependence

Numerous data taken with suspensions prepared from a wide variety of thorium oxide powders showed that, for any given preparation, the yield stress was proportional to the cube of the volume fraction solids

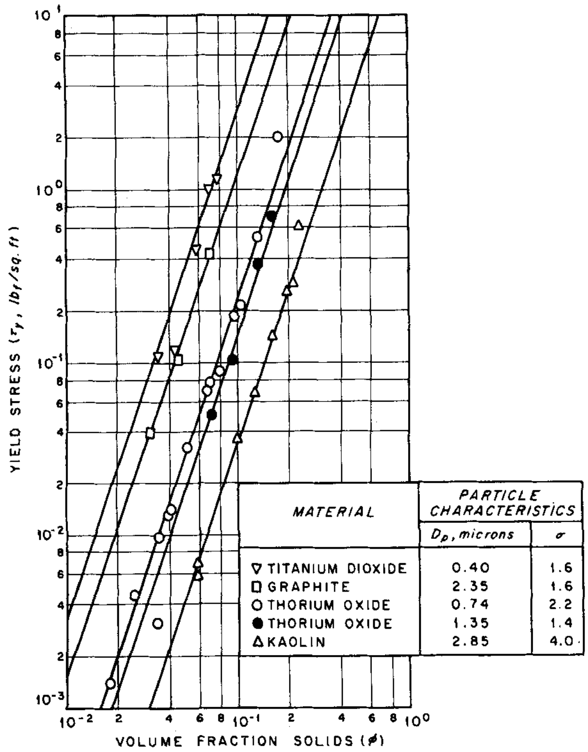
$$\tau_y = k_1 \phi^3 \quad (2)$$

and that the logarithm of the ratio of the coefficient of rigidity to the viscosity of the suspending medium was directly proportional to the volume fraction solids:

$$\frac{\eta}{\mu} = \exp\,(k_2 \phi) \quad (3)$$

These relations were valid for concentrations of thorium oxide from 0.02 to 0.15 volume fraction solids, for oxides that had been calcined at temperatures from 1,202° to 2,912°F. (650° to 1,600°C.), for pure oxides, and for oxides containing corrosion products accumulated during circulation of oxygenated suspensions for up to 4,000 hr. in stainless steel loops at temperatures of 482° to 572°F. (250° to 300°C.). Typical data taken with two different samples of thorium oxide are shown in Figures 2 and 3. The data for the 0.74-μ mean diameter material (calcined at 850°C.) were obtained over an interval of 6 mo. during an investigation of the transport characteristics of flocculated suspensions (*4*). In spite of the fact that the material was being constantly recirculated in an essentially all steel loop open to the air (hence with a slowly increasing iron pickup and possible carbon dioxide contamination), the cubic relationship was followed remarkably well. The scatter at the low-concentration end is believed to be due to experimental difficulties in measuring the very small yield values. On the other hand the data for the 1.35-μ mean diameter material (also shown in Figure 1) were obtained with a suspension prepared by simply mixing a 1,400°C. calcined powder with water. Typical data for graphite, titanium oxide, and kaolin suspensions are also shown on Figures 2 and 3. These suspensions, as well as all other suspensions tested, followed the general relations given by Equations (2) and (3). This is in accord with qualitative predictions of similarity of behavior of oxides, noble metals, and hydrogen electrodes based on present concepts of the double layer (*7*). Both Equations (2) and (3) have been proposed previously (*5, 21*) and have been shown to apply to specific systems. However this is the first time they have been shown to apply to a broad class of materials, and it is also the first time that the physical properties used in the correlations have been determined over a shear-rate range useful for correlating turbulent heat, mass, and momentum transfer data obtained in systems of commercial interest (*3, 4*).

The terms k_1 and k_2 of Equations (2) and (3) are constants which characterize each particular suspension, independent of concentration. Succeeding sections will show the relative importance of such factors as electrolyte concentration, particle size,



MATERIAL	PARTICLE CHARACTERISTICS	
	D_p, microns	σ
▽ TITANIUM DIOXIDE	0.40	1.6
□ GRAPHITE	2.35	1.6
○ THORIUM OXIDE	0.74	2.2
● THORIUM OXIDE	1.35	1.4
△ KAOLIN	2.85	4.0

Fig. 2. Effect of volume fraction solids on suspension yield stress.

---

* Portions of the data given in this paper originally appeared in Homogeneous Reactor Project Progress Reports during the interval October 31, 1956, to July 31, 1960.

and particle shape on the value of these constants.

ELECTROLYTE EFFECTS

Hydrogen- and Hydroxyl-ions

The suspension *p*H was measured by immersing glass and calomel electrodes in the suspension and recording the *p*H value given by a vacuum tube potentiometer. This procedure was adopted as the simplest and most expedient in view of the fact that there is no entirely satisfactory theoretical interpretation of the phenomena observed in detailed studies of suspension *p*H (*7, 23*).

The effect of *p*H on the yield stress and coefficient of rigidity of a suspension of 1.35 μ thorium oxide particles is shown in Figure 4 for *p*H values from 1.6 to 12.0 The *p*H of the suspension in the absence of additives was 8.1 over a range of concentrations from 0.069 to 0.154 volume fraction solids. All of the data in Figure 4 were obtained at 0.090 volume fraction solids. The acidic suspensions were obtained by the addition of sulfuric or chromic acid, and the more basic suspensions were obtained by the addition of sodium hydroxide. Sulfuric acid was chosen as one acid because the HSO_4^- ion has been shown to be strongly adsorbed by the thorium oxide, whereas chromate ion is virtually not adsorbed at all (*24*). As can be seen there was very little difference in the effect of the two anions on the physical properties for *p*H values greater than 4. Of more practical significance is the observation that all of the physical property values determined in the *p*H range from 4 to 12 were within ±20%. This lack of dependency of the physical properties on *p*H seemed to be characteristic of almost all thorium oxide suspensions studied, regardless of the physical or geometrical properties of the particles. It means that a scatter of less than ±20% was introduced into the following correlations, even though the suspensions used in the laminar-flow measurements had *p*H values which usually ranged from 6 to 10. (This represents the range of *p*H values observed with different suspensions as received for measurement; no attempt was made to adjust the acidity to a preselected value.)

Neutral Salts

Although van der Waals' forces are the primary attractive forces between particles, under some circumstances electrostatic forces may occur as a result of separation of ionic charges on different crystal faces. Charge separation has been experimentally verified with special kaolin preparations (*25*), and it might be expected with thorium oxide powders having the relic plate structure of the oxalate from which it was prepared. Electrostatic charge separation effects are eliminated in the presence of concentrated electrolytes (*25*). A 1:1 electrolyte, potassium nitrate, was selected for addition to the suspension, since monovalent ions have the least effect on the double layer.

Laminar flow shear diagrams were obtained with several different thorium oxide and kaolin suspensions before and after addition of potassium nitrate. For concentrations of salt up to 1 molar, there was less than 5% change in the yield stress. Although there was a noticeable increase in the coefficient of rigidity, the ratio η/μ was essentially constant if the effect of salt on the viscosity of the suspending medium was taken into account. On the basis of these preliminary studies it was concluded that electrostatic charge separation did not contribute significantly to the flocculation characteristics of the suspension medium in the present study. However the existence of such effects should always be borne in mind as a possibility in case unusual flocculation effects are observed.

Particle Size Effects

The rheology of liquid-solid suspensions involves two different aspects of the exterior surface (as opposed to the internal surface consisting of pores and fissures) of the particles. The chemistry of the double layer at the surface determines the nature of the interaction of single particles, while the exterior surface per unit volume determines the total attraction between particles for any given suspension concentration. As pointed out above the net attractive force between particles is remarkably constant provided the suspension pH is between 4 and 12. Thus the greatest surface effects may be expected owing to variations in the extent of subdivision of a given quantity of material, the greater the subdivision the greater the total macroscopic attraction (that is the greater the subdivision the greater the degree of flocculation). For regularly shaped particles, such as cubes and spheres, the surface per unit volume is given by

$$S_o = \frac{6}{D_p} \qquad (4)$$

As one or more of the dimensions are reduced so that the particles resemble plates or needles, the surface per unit volume is increased over that given by Equation (4). This means that if a single dimension is to be used to characterize the particles, a shape factor must be introduced in order to account for the increased surface per unit volume.

Effect of Particle Characteristics on the Yield Stress

The coefficient k_1 of Equation (2) is a constant for any given suspension which gives a measure of the magnitude of the suspension yield stress independent of the concentration. Data for a wide variety of thorium oxide powders are shown in Figure 5 plotted as $k_1 = \tau_y/\phi^3$ *vs.* the mean particle diameter on a weight basis. The mean particle sizes ranged from 0.35 to 13 μ; this 37-fold variation in diameter was accompanied by an over 200-fold variation in τ_y/ϕ^3. The internal consistency of the data shown in the figure is quite remarkable in view of the variations in powder characteristics and in the procedure for preparing the suspensions. These included:

1. The oxides were prepared by calcination at temperatures from 1,202° to 2,912°F. (650° to 1,600°C.).
2. The particle size distribution had an average logarithmic standard deviation of 2.0 and the range was from 1.3 to 3.9.
3. The suspension pH was between 4 and 12.
4. The suspensions were prepared either by simply mixing the freshly prepared powder with water, or by circulating as an aqueous suspension in stainless steel loops at temperatures from 482° to 572°F. (250° to 300°C.) under oxygen atmosphere.

In some of the elevated temperature circulation tests particle degradation occurred. Although this was accompanied by the production of fine particles and appreciable corrosion products, τ_y/ϕ^3 values for the degraded material were in good agreement with those for an unpumped material of the same mean particle size as the pumped material. As an indication of the variation observed with one of the above factors, the oxide calcination temperature is identified on the figure.

For suspensions prepared from powders having mean particle diameters in the range 0.35 to 1.5 to 2.0 μ, Figure 5 shows that τ_y/ϕ^3 was inversely proportional to the square of the particle diameter. For particle diameters greater than 1.5 to 2.0 μ, τ_y/ϕ^3 was more nearly inversely proportional to the first power of the particle diameter. The rather abrupt change in slope at a particle diameter of 1.5 to 2.0 μ corresponds almost exactly with the change in morphology of the oxide powder reported previously (*19*). Particles smaller than 1 to 2 μ are essentially equiaxial, closely approximating cubes, whereas particles greater than 1 to 2 μ become more and more platelike as the particle size is increased with edge to thickness ratios of as much as 6:1 observed for 6- to 7-μ particles. It is believed that the break in the curve in Figure 5 is due to the increase in surface area per unit volume accompanying the change in particle shape from equiaxial to platelike.

The rheological shape factor may be evaluated by assigning a value of unity to the shape factor for equiaxial

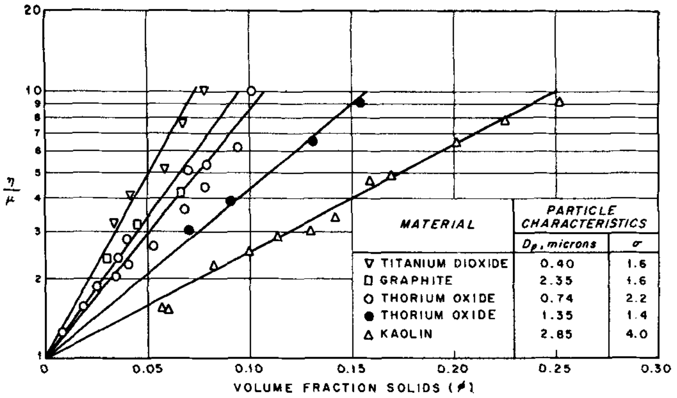


Fig. 3. Effect of volume fraction solids on suspension coefficient of rigidity.

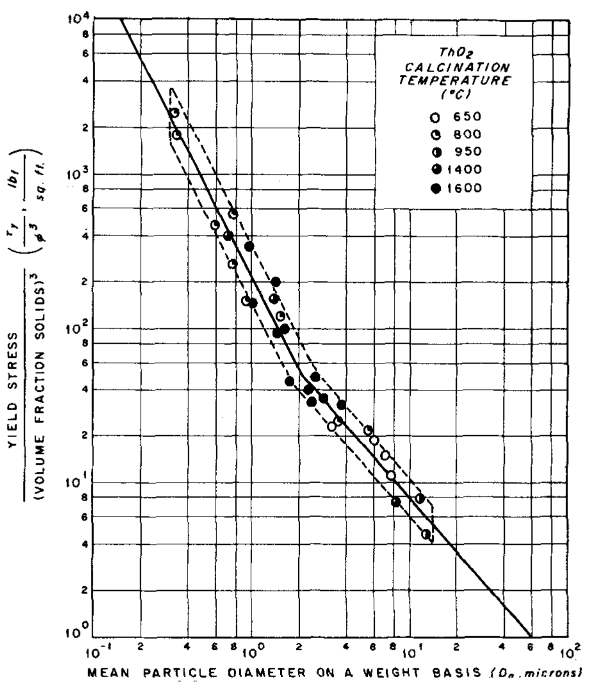


Fig. 5. Effect of particle diameter on thorium oxide suspension yield stress.

particles and assuming that this value applies to the present data in the 0.35- to 1.5-μ size range. On this basis the expression for the yield stress becomes

$$\tau_y = \frac{A\,\psi_1\,\phi^3}{D_p^2} \tag{5}$$

where the coefficient and the shape factor have yet to be determined. The shape factor was introduced to account for the increase in surface area due to particle asymmetry. This suggest that the shape factor should be a function of the ratio of platelike particle surface area to equiaxial particle surface area. In order to verify this, particle dimensions were determined from shadowcast electron micrographs, and surface areas per unit volume were calculated as a function of the edge to thickness ratio, L/x, with the expression

$$S = \frac{2\left(1 + \frac{2x}{L}\right)}{x} \tag{6}$$

Values of the shape factor were determined by application of Equation (5) to the data for Figure 5. A plot of the logarithm of the shape factor vs. the relative surface areas S/S_o gave a straight line with a maximum deviation of ±10%.

Comparison of Thorium Oxide Yield Stress Results with Data for Other Materials

Values of τ_y/ϕ^3 for a variety of materials are shown on Figure 6 as a function of particle diameter. In addition to results for aluminum oxide, titanium oxide, magnesium, uranium dioxide, uranium trioxide, and kaolin, data are given for graphite and for suspensions prepared from spherical thorium oxide particles. The points for the uranium trioxide (*26*) and the 14-μ (*27*) graphite suspensions are the only data from the literature for which several shear diagrams were determined which covered shear rate ranges comparable to those of the present study and for which particle size information was available. Except for the graphite and spherical-thorium oxide data, the results are in good general agreement with the thorium oxide data previously presented, the range of which is shown as the cross-hatched area in Figure 6.

An explanation for the general good agreement as well as the differences observed for the spherical thorium oxide and the graphite suspension data can be given on the basis of the chemistry of the particle surface and on the particle morphology. Langmuir (*28*) has shown that the force between plates immersed in an aqueous medium is a function of the osmotic pressure at the centerline between the plates. It was also shown that the centerline osmotic pressure was almost independent of the surface potential of the plates. This means that differences in the surface potential of the solid phase [which is determined by the work function of the solid phase (*7*)] are not primary factors in determining the attractive force between particles. Hence the degree of flocculation of suspensions should not be markedly affected by differences in the work function of the solid phase. It should also be recalled that the potential distribution in the vicinity of the surface of both metallic oxides and graphite is determined primarily by H^+ and OH^- ions. Combining this with Langmuir's observation one would expect that the flocculation characteristics of the different materials shown in Figure 6 (all of which belong to the same general class of materials which possess the same potential determining ions) should be quite similar.*

Examination of electron micrographs showed that the titanium oxide, magnesium, uranium trioxide, and the

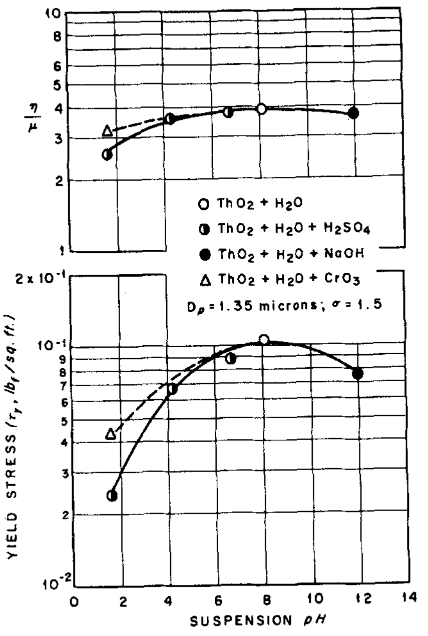


Fig. 4. Effect of suspension pH on yield stress and coefficient of rigidity. (Volume fraction solids = 0.090.)

---

* This was suggested to the author by Samuel Levine of the University of Manchester, Manchester, England.

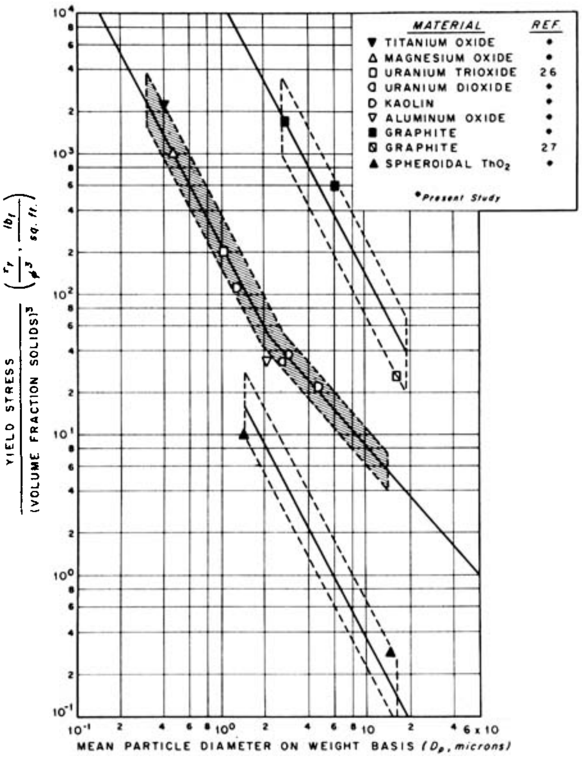


Fig. 6. Effect of particle diameter on yield stress of suspensions.

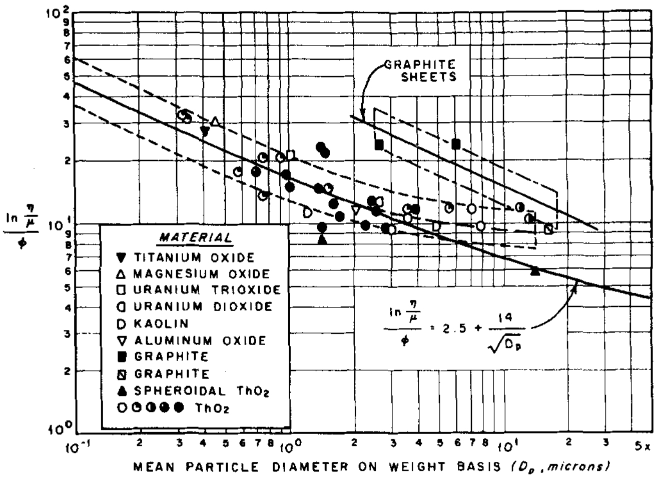


Fig. 7. Effect of particle diameter on coefficient of rigidity showing shape factor effect observed in using large particles.

1.25-μ kaolin were regularly shaped, equiaxial particles, whereas the larger kaolin and the aluminum oxide particles were more platelike. This is the same general trend of shape with particle size that was observed with the thorium oxide data. It follows that values of the shape factor for these oxides should also agree with those for the thorium oxide data. On the other hand the graphite particles were more nearly sheets than plates, having L/x values of 10, 20, or higher, instead of values generally less than 10 observed with the oxides. Shape factors for all of these materials agreed to within ±10% with the line determined for the thorium oxide particles, the graphite data merely extending the shape factor curve to larger values of L/x.

Although the data for spheroidal particles are quite meager, they are the only ones known in this size range which could be used to estimate the reduction of yield stress possible in going from irregularly crystalline to spheroidal particles. As can be seen, as much as a tenfold reduction might be expected.

Combining the results for all the oxide and graphite suspension data one gets a value for the dimensional constant in Equation (5) of $A = 2.27 \times 10^{-10}$ lb.$_f$ with a mean deviation of ±20%. If the particle diameter is given in microns, the coefficient becomes $A = 210$ lb.$_f$ μ/sq. ft. The shape factor in Equation (5) is given by

$$\psi_1 = \exp 0.7 \left(\frac{S}{S_o} - 1\right) \qquad (7)$$

with the exception that for spheroidal particles the values of the shape factor may be as small as 0.1, instead of the value of unity for equiaxial granular materials.

Effect of Particle Characteristics on Coefficient of Rigidity

The coefficient k_2 of Equation (3) is a constant for any given suspension which gives a measure of the magnitude of the coefficient of rigidity independent of the concentration. Data for all of the materials used in the present study are shown in Figure 7 plotted as $k_2 = [\ln (\eta/\mu)/\phi]$ vs. the mean particle diameter on a weight basis. As with the τ_y/ϕ^3 data the values of $(\ln \eta/\mu)/\phi$ were divided into two groups depending on the particle size. The results for the smaller particle size material were inversely proportional to the square root of the particle diameter. For larger size particles $(\ln \eta/\mu)/\phi$ was almost independent of particle diameter. The divergence of the results for larger particle size material is believed to be due to geometrical factors as was the case with the yield stress results.

Although the results shown in Figure 7 indicate a significant effect of particle size on the coefficient of rigidity, both theoretical and experimental investigations show that the relative viscosity of suspensions of noninteracting particles is only a function of the volume fraction solids independent of the particle diameter. The reason for the difference in particle size dependence of the viscosity of flocculated and nonflocculated suspensions is that the apparent volume fraction solids of the flocculated suspensions is increased owing to the incorporation of water in the floc. Since the degree of flocculation increases as the particle size decreases, the effective volume fraction solids would be expected to follow the same trend. This means that although the coefficient k_2 of Equation (3) was inversely proportional to the square root of the particle diameter in the small particle size range, it must asymptotically approach the theoretical (29) value of 2.5 for large particle size, dilute suspensions. The simplest expression, compatible with the theoretical and experimental results, is

$$k_2 = 2.5 + \frac{14}{\sqrt{D_p}} \psi_2 \qquad (8)$$

where D_p is given in microns. This equation is shown on Figure 7. For the smaller particle size material the agreement with the data is quite good with $\psi_2 = 1$. A log-log plot of the shape factor for the larger particle size material as a function of the relative surface area gave a straight line of slope one-half with a maximum deviation of ±15%, so that the value of the shape factor for use in Equation (8) is given by

$$\psi_2 = \sqrt{\frac{S}{S_o}} \qquad (9)$$

Within the accuracy of the present

data the shape factor for spheroidal material is unity.

NOTATION

A = coefficient, lb.$_f$
D = tube diameter, ft.
D_p = particle diameter, ft.
g_c = conversion factor, (lb.$_m$/lb.$_f$) (ft./sec.^{2})
k_1 = coefficient, lb.$_f$/sq. ft.
k_2 = coefficient, dimensionless
ln = logarithm to base e
L/x = particle edge to thickness ratio, dimensionless
S/S_o = platelike particle surface area/equiaxial particle surface area, dimensionless
V = mean velocity, ft./sec.

Greek Letters

η = coefficient of rigidity, lb.$_m$/ft. sec.
μ = viscosity of suspending medium, lb.$_m$/ft. sec.
σ = logarithmic standard deviation, dimensionless
τ_y = yield stress, lb.$_f$/sq. ft.
τ_w = wall shear stress, lb.$_f$/sq. ft.
ϕ = volume fraction solids, dimensionless
ψ = shape factor, dimensionless

LITERATURE CITED

1. Metzner, A. B., in "Advances in Chemical Engineering," T. B. Drew and J. W. Hooper, Jr., ed., Academic Press, New York (1956).
2. Wilkinson, W. L., "Non-Newtonian Fluids," Pergamon Press, London (1960).
3. Thomas, D. G., *A.I.Ch.E. Journal*, **6**, No. 4, p. 631 (1960).
4. *Ibid.*, **7**, No. 3, p. 423 (1961).
5. Norton, F. H., A. L. Johnson, and W. G. Lawrence, *J. Am. Ceramic Soc.*, **27**, 149-164 (1944).
6. Alves, G. E., D. F. Boucher, and R. L. Pigford, *Chem. Eng. Progr.*, **48**, 385-393 (1952).
7. Kruyt, H. R., ed., "Colloid Science," Vol. I, Elsevier, Amsterdam (1952).
8. Verwey, E. J. W., and J. Th. G. Overbeek, "Theory of Stability of Lyophobic Colloids," Elsevier, Amsterdam (1948).
9. Hoskin, N. E., and Samuel Levine, *Phil. Trans. Roy. Soc. London*, **A248**, 449-466 (1956).
10. Bogue, D. C., *Ind. Eng. Chem.*, **51**, 874-878 (1959).
11. Mooney, Melvin, *J. Rheology*, **2**, 210-222 (1931).
12. Reiner, Markus, "Deformation, Strain, and Flow," 2 ed., Interscience, New York (1960).
13. Vand, V., *J. Phys. Colloid Chem.*, **52**, 300-314 (1948).
14. Maude, A. D., and R. L. Whitmore, *Brit. J. Appl. Phys.*, **7**, 98-102 (1956).
15. Burgers, J. M., and G. W. Scott Blair, *Proc. Int. Rheological Cong.*, Holland (1948).
16. Weltman, R. N., and T. A. Keller, *Natl. Advisory Comm. Aeronaut. Tech. Note 3889* (Jan., 1957).
17. Boyd, C. M., et al., *Oak Ridge Natl. Lab. Rept., ORNL-2345* (Aug. 5, 1957).
18. Herdan, G., "Small Particle Statistics," Elsevier, Amsterdam (1953).
19. Allred, V. D., S. R. Buxton, and J. P. McBride, *J. Phys. Chem.*, **61**, 117-120 (1957).
20. McBride, J. P., and D. G. Thomas, in "Fluid Fuel Reactors," J. A. Lane et al., ed., Addison-Wesley, Reading, Mass. (1958).
21. Arrhenius, S., *Z. physik. Chem.*, **1**, 287 (1887).
22. Searle, A. B., and R. W. Grimshaw, "The Chemistry and Physics of Clays," 3 ed., Interscience, New York (1959).
23. Overbeek, J. Th. G., *J. Colloid Sci.*, **8**, 593-605 (1953).
24. Wadsworth, M. E., et al., "Progress Reports," Institute for the Study of Rate Processes, University of Utah, Salt Lake City, Utah (Feb. 15, 1958, to Jan. 11, 1960).
25. Schofield, R. K., and H. R. Samson, *Discussions Faraday Soc.*, No. 18, 135-145 (1954).
26. Dudgeon, E. H., and W. C. Michie, *Natl. Research Lab. Canada Rept., MT-36* (Nov., 1957).
27. Orr, Clyde, Ph.D. thesis, Georgia Inst. Technol., Atlanta, Georgia (Dec., 1952).
28. Langmuir, Irving, *J. Chem. Phys.*, **6**, 893 (1938).
29. Einstein, Albert, *Kolloid Z.*, **27**, 137 1920).

Manuscript received September 19, 1960; revision received November 7, 1960; paper accepted November 9, 1960.

Laminar Boundary Layer Flow and Heat Transfer Past a Flat Plate For a Liquid of Variable Viscosity

O. T. HANNA and J. E. MYERS
Purdue University, Lafayette, Indiana

A solution for the problem of incompressible laminar boundary-layer flow and heat transfer with variable viscosity is presented. Because of the variation of viscosity with temperature the velocity and temperature fields interact mutually. This necessitates the simultaneous solution of the momentum and energy equations. The analysis is carried out for the case where heating begins at the leading edge of the plate. The results show the effect of the important variable property parameters on the friction factor and the heat transfer coefficient. These parameters are seen to be the temperature difference between wall and free stream, the viscosity temperature variation law, and the Prandtl number at the wall. The results are applicable to liquids.

The laminar boundary-layer equations for incompressible flow and heat transfer past a flat plate maintained at a constant temperature have been solved exactly for constant properties (*1*). In addition Eckert (*2*) has given a useful approximate solution for flow with constant properties, which accounts for the effect of an unheated starting length on heat transfer. When heating starts at the leading edge, the Eckert solution reduces to a form which is in agreement with the exact solution. These relations are useful in many cases, but there is doubt concerning their validity in the case of

---

O. T. Hanna is with the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.