Transport Characteristics of Suspensions

VII. Relation of Hindered-Settling Floc Characteristics to Rheological Parameters

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Both the rheological and the hindered-settling characteristics of small particle size suspensions (0.1 to 50 μ) are primarily determined by the degree of flocculation and the concentration of the suspension. Previous studies have shown that when the laminar shear diagrams are fitted by the Bingham plastic model, the parameters τ_y/ϕ^3 and ϕ^{-1} ln η/μ are constants which are proportional to the degree of flocculation.

The present study showed that these rheological parameters were proportional to the value of α determined from the hindered-settling measurements (α is defined as the ratio of the volume of fluid immobilized by the floc structure to the volume of solids in the floc structure). The materials studied included suspensions of thorium oxide in water and methanol and of titania, kaolin, alumina, and graphite in water. The particle size range was from 0.40 to 17.0 μ.

Values of the attractive force between particles calculated from the rheological and hindered-settling data were in good agreement with each other and with the theoretical values calculated from the Derjaguin-Verwey-Overbeek theory of colloid stability. The good agreement among the different values suggests that the present approach may be generally applicable to a variety of different systems.

The mechanics of the interaction of solids dispersed in liquids have long been studied both theoretically and experimentally (*1*). The results of these studies show that both the laminar viscosity and the settling rate (*2*) of symmetrically shaped solid particles, sufficiently large to eliminate all but hydrodynamic forces, can be expressed as the product of simple functions of the volume fraction solids and either the viscosity of the suspending medium or the Stokes' law settling rate of a single particle.

As one or more dimensions of lyophobic particles are reduced to near colloidal size, physicochemical forces become important and may result in increased particle-particle interaction (*3*). An attractive force may cause a clustering of particles into flocs or agglomerates. In this situation the theoretical evaluation of the mechanics of the particle-particle and particle-fluid interaction of flocculated suspensions is complicated by several factors. The attractive forces must be accounted for since they are often the same order of magnitude as the shear forces of interest, and perhaps more important there is an uncertainty in the effective volume fraction solids due to the variable amount of water incorporated in the three-dimensional network of particles which comprise the floc.

The object of the present study was first to determine the characteristics of flocs or agglomerates of particles by making a systematic study of the settling behavior of a variety of suspensions; second to relate the floc characteristics to the previously determined laminar flow properties of the suspensions (*4*); and third to estimate the attractive forces between particles from both the settling rate and the laminar flow data.

BASIC CONCEPTS

Forces of a colloidal nature become important as one or more dimensions of a particle are reduced below 20 to 50 μ (*3*). In the absence of a stabilizing electrolyte, liquid suspensions of such particles are observed to agglomerate into flocs. A floc may be considered as a loose, irregular, three-dimensional cluster of particles in contact in which the original particles can still be recognized. The attractive force between particles markedly modifies the laminar flow properties of suspensions and the formation of flocs increases the settling rate of dilute suspensions by a factor of 10 to 100 over the Stokes' law rate for a single particle.

Suspension Settling Rate

The Stokes' law settling rate for a single spherical particle is given by

$$U_o = \frac{g_L\,(\rho_p - \rho)\,D_p^2}{18\,\mu} \qquad (1)$$

The presence of additional nonflocculated particles affects a reduction in the settling rate due to hydrodynamic factors which may be accounted for by an expression of the form (*2*)

$$\frac{U}{U_o} = f(\phi) \leq 1 \qquad (2)$$

Although there is agreement about the general form of Equation (2), different semitheoretical and experimental expressions give a range of values for $f(\phi)$. The extent of this range is illustrated in Figure 1, which shows results for different experimental studies (*5, 6, 7, 8, 9, 10*).

Suspensions of flocculated particles also follow Equation (2) except that the volume fraction solids must be increased to account for the floc structure. That water within a rigid porous structure can be considered immobilized by the network has been demonstrated by experiments of Eirich, Mark, and Huber (*11*). Their studies showed that the drag coefficients of slowly moving perforated spheres and ellipsoids were substantially the same as those for the unperforated bodies. This means that the liquid inside the bodies was dragged along in spite of the free communication and strongly supports the belief that the floc, consisting of a network of solid particles enclosing water, must be considered as an integral unit. Estimates of the relative velocity through and around the floc show that for the suspensions used in the present study the velocity through the floc was always <5% of the velocity around the floc.* The belief that the floc and enclosed water may be considered as an integral unit is further supported by the tests of Reich and Vold (*12*) which show that although the floc structure is a function of the rate of shear, the floc characteristics

* Personal communication, R. N. Lyon, Oak Ridge National Laboratory, July 24, 1962.

were reproducible at any given shear rate and were reversible as the shear rate was varied.

On this basis the increase in volume fraction solids of flocculated suspensions may be accounted for by a parameter α, the ratio of immobilized water volume to solid volume (*5, 13*). The volume fraction solids and density of the floc are then given by

$$\phi_f = (1 + \alpha)\,\phi \qquad (3)$$

$$\rho_f = \frac{\rho_p + \alpha p}{1 + \alpha} \qquad (4)$$

The floc diameter may be calculated from Stokes' law [Equation (1)] and Equation (4) with a settling rate determined by extrapolation of the hindered-settling data to zero concentration. Care must be used in applying Equations (1) to (4) to data in which g_L is varied because sedimentation studies in a centrifuge have shown that floc characteristics are a complicated function of the centrifugal force (*14*).

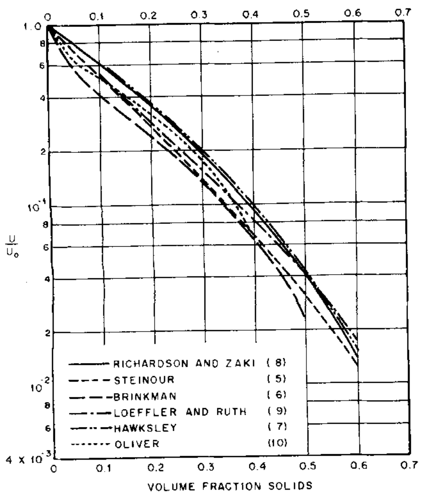

Fig. 1. Effect of concentration on the hindered-settling rate of noninteracting spherical particles.

Laminar-Flow Characteristics

Flocculated suspensions possess non-Newtonian laminar-flow characteristics (*3*) which have been shown to be primarily a function of the true volume fraction solids and the mean particle size (*4*). Alternatively, the rheological properties of flocculated suspensions may be correlated in terms of the floc characteristics, and, in fact, rather good agreement has been obtained between floc characteristics determined from settling rate studies (*15*) and from flow measurements (*16*) with suspensions of plate-shaped kaolin particles.

In the present study the Bingham plastic equation

$$\frac{du}{dr} = \frac{g_c}{\eta}(\tau - \tau_y), \quad \tau > \tau_y \qquad (5a)$$

$$\frac{du}{dr} = 0, \qquad \tau \leq \tau_y \qquad (5b)$$

was selected for the laminar-flow data analysis. Although care must be used in applying this model (*17*), concurrent studies have shown that the present techniques of measurement and analysis produce physical property values which successfully correlate data for a variety of suspensions flowing under laminar and turbulent conditions in tubes from ⅛ to 4 in. in diameter (*18, 19*). With these models used, the laminar flow properties were shown to be related to the suspension characteristics by the following empirical expressions:

$$\tau_y = 2.27 \times 10^{-9}\,\psi_1\,\phi^3/D_p^{\,2} \qquad (6)$$

with a mean deviation of ±20% and

$$\eta/\mu = \exp\,(2.5 + 14\,\psi_2/\sqrt{D_p'})\,(\phi) \qquad (7)$$

with a mean deviation of ±15%.

EXPERIMENTAL MATERIALS AND TECHNIQUES

Solids Properties

A necessary prerequisite for the study of suspension characteristics is a source of solid particles having a wide range of sizes. Procedures were developed (*20*) for preparing thorium oxide powders having such a wide range of physical properties. Consequently the major emphasis in these studies was on the factors affecting aqueous thorium oxide suspensions. In addition to the aqueous suspensions two series of tests were made with different thorium oxide powders suspended in chemically pure methanol; no particular precautions were taken to dry either the thorium oxide or the methanol. Finally a limited number of suspensions of commercially available materials, such as titanium dioxide, kaolin, and graphite, were studied in order to verify the general applicability of the thorium oxide data.

Particle sizes were determined either by sedimentation with a modified Andreisen method (*21*) or by particle count from electron micrographs. The sedimentation procedure was used for powders having a mean size of 0.5 μ or larger and had a lower limit of 0.2 μ. The electron micrographs were used to verify the distribution of material smaller than 0.5 μ and by shadowcasting to verify the shape of the particles. In all cases where the size range overlapped, the results of both particle size analyses were in substantial agreement. The size distributions were closely approximated by the logarithmic normal expression (*22*) and thus could be characterized by two terms, the mean diameter D_p and the logarithmic standard deviation σ. In all cases the mean diameters are given on a weight basis. The properties of the powders used in this study are given in Table 1, and shadowcast electron micrographs of representative powders are shown in Figure 2.

Settling Rates

Studies of the phenomenology of the settling of flocculated suspensions have shown (*16, 23*) that dilute suspensions frequently possess an incubation period due to slow coagulation. After this initial period, a more rapid settling rate is observed. The data reported in the present paper correspond to this rapid settling-rate period and thus represent conditions in which flocculation was substantially completed.

Care must be used in conducting the setttling-rate measurements to distinguish between naturally slow settling and slow settling due to bridging of flocs between tube walls (*16*). The effect of container diameter on the tendency for flocs to bridge is illustrated in Figure 3 for a typical thorium oxide suspension. For this particular suspension the concentration at which bridging occurred increased from 0.037 to 0.062 volume fraction solids as the container diameter was increased from 0.053 to 0.340 ft. From the limited data available the concentration at which bridging will occur may be estimated from the empirical relation:

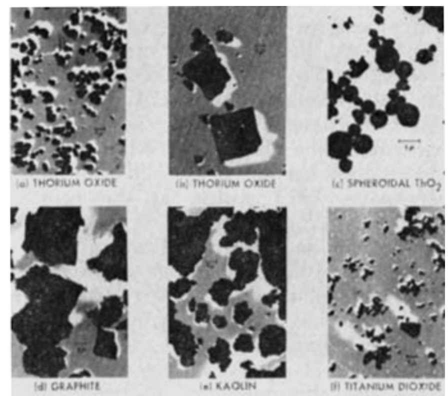

Fig. 2. Electron micrographs of particulate matter used in study of suspension properties.

$$\frac{\phi\,(\rho_p - \rho)\,g_L\,L^{1/8}\,D^{2/8}}{g_c\,\tau_y} = \frac{g_L\,(\rho_p - \rho)\,L^{1/8}\,D^{2/8}}{g_c\,k\phi^8} = 220 \qquad (8)$$

with a mean deviation of ±12%. This differs from the relation proposed by Michaels and Bolger (*15*) in the value of the numerical constant and in the term $L^{1/8}$, which accounts for the support given the floc structure by the container bottom.

Values of α were calculated by application of Equation (3) to the initial linear portion of the settling rate—concentration curve; for example for the suspension shown in Figure 3 the data for true volume fraction solids ϕ are less than 0.025. It is essential to consider only this extremely dilute region for only with dilute suspensions can interference between flocs be minimized, thus giving a unique characterization of floc properties. The apparent volume fraction solids ϕ_f

TABLE 1. PROPERTIES OF POWDERS USED IN SUSPENSION STUDIES

Material	Particle density, (g./cc.)	Range of size distribution Mean diameter, (μ)	Logarithmic standard deviation (σ)
ThO_2-Granular	10.0	0.71-11.7	1.4-2.2
ThO_2-Spheroidal	10.0	1.4-17.0	1.8-1.9
Kaolin	2.65	1.2-4.7	4.7-4.8
Graphite	2.2	2.7-6.0	2.4-2.9
TiO_2	4.2	0.40	1.6
Al_2O_3	4.0	2.0	3.8

was estimated from an average line through the curves of Figure 1 given by

$$\ln \frac{U}{U_o} = -5.9\phi_f \qquad (9)$$

Rheological Measurements

A detailed description of the equipment and procedure has been given previously (*4*). Briefly, the equipment consisted of a horizontal-tube capillary viscometer with an inside diameter of 0.124 in. and a length-to-diameter ratio of 1,000. These particular tube dimensions were selected to minimize kinetic energy and wall effect corrections (*17*) which, at the present state-of-the-art, are rather uncertain for non-Newtonian suspensions. In any event it is believed that the maximum correction in the present study amounted to less than 3.5%, so that the uncertainty is some value less than this.

No attempt was made to control the electrolyte atmosphere of the suspension particles; that is in some cases the suspensions were prepared by mixing as received powder directly with the suspending medium, while in other cases the suspension has been pumped for times up to 2,000 hr. in a stainless steel loop and hence would contain normal corrosion products. In all cases the pH of the suspension was between 4 and 10. Tests (*4*) in which the pH was adjusted over this range by the addition of either chromic or sulfuric acids or of sodium hydroxide showed that the rheological parameters varied less than ±20% for a suspension of a given particle size and concentration. Consequently pH variations within the range of 4 to 10 apparently were of secondary importance to the other independent variables.

EXPERIMENTAL RESULTS

For any given suspension the value of τ_y/ϕ^3 is a constant independent of concentration [Equation (6)] and thus is a measure of the degree of flocculation. Similarly the value α determined from settling-rate measurements is also a measure of the degree of flocculation. The data in Figure 4 show, not surprisingly, that these two factors are indeed uniquely related. Contrary to previous correlations (*4*) of the rheological data in terms of the concentration and particle size it is no longer necessary to account for the effect of particle shape (that is spheroidal, symmetrical-granular, or platelike) on the degree of flocculation. Instead the value of α from the settling-rate measurements provides the same direct measure of the flocculation as does the value τ_y/ϕ^3 from the rheological measurements. The relation between the two factors is

$$\tau_y/\phi^3 = k_1\,\alpha^4 \qquad (10)$$

where $k = 1.55 \times 10^{-2}$ lb.$_f$/ft. with a mean deviation for the numerical constant of ±60%. The accuracy of the value of the exponent of Equation (10) is assured by the 10^4-range in values of τ_y/ϕ^3. The precision of the value of the numerical constant is undoubtedly affected by the obvious difficulties of obtaining the precise values of slopes and intercepts which are required for the calculation of both τ_y/ϕ^3 and α. Under these circumstances the agreement of the data shown in Figure 4 is quite satisfactory.

The value of the other rheological coefficient η is a constant for any given suspension when expressed as $(\ln \eta/\mu)/\phi$. This parameter is shown as a function of α in Figure 5. The simplest expression which fits the data and which is consistent with the Einstein relation (*1*) for the viscosity of nonflocculated suspension is:

$$\frac{\ln \eta/\mu}{\phi} = 2.5 + \alpha \qquad (10a)$$

The data scatter somewhat on the upper side of the line; however the mean deviation is only ±15%. In view of the fact that the parameters $(\ln \eta/\mu)/\phi$ and α are each obtained as the product of slopes determined from the experimental data, the agreement is again quite satisfactory.

The primary factor affecting the degree of flocculation was found to be the particle size. This is shown in Figure 6 in which D_f/D_{app} is plotted vs. $(1+\alpha)$. The apparent diameter D_{app} was calculated from

$$D_{app} = D_p\,(S_o/S)\,\exp\,(-1/2\ln^2\sigma) \qquad (11)$$

and thus accounts for both the particle size distribution and for nonsymmetrical (that is platelike) particle shape. When the particle diameter is calculated in this way, it is inversely proportional to the total external surface area of the particles and would logically be expected to be one of the major factors affecting the degree of flocculation. The data of Figure 6 are fitted by the expression

$$D_f/D_{app} = (1+\alpha)^2 \qquad (12)$$

with a mean deviation of ±30%. Note that as α goes to zero in Equation (12), the floc diameter and the particle diameter become equal as required by the original definition of α.

Finally, the hindered-settling rate of dilute flocculated suspensions may be obtained by combining Equations (1), (3), (4), and (9) to give

$$U = U_o\,(1+\alpha)^3\,e^{-5.9\,(1+\alpha)\,\phi} \qquad (13)$$

It must be emphasized that this expression applies only to dilute suspensions (for example for the particular data of Figure 3, only for concentrations less than 0.025 volume fraction solids). Equation (13) establishes the upper limit on the settling rate of very dilute flocculated suspensions, namely the settling rate of a dispersed particle times the factor $(1+\alpha)^3$.

PHENOMENOLOGICAL ANALYSIS

The results of this study show that the rheological coefficients of flocculated suspensions, evaluated in a particular way (*4*), may be estimated to within better than an order of magnitude from a series of hindered-settling rate measurements. In the strictest sense the present results are applicable only to the suspensions used in this study; however the fact that a total of twenty different suspensions prepared from five different solids in two different liquids gave substantially the same correlation suggests that the empirical relations [Equations (10) to (13)] may be of a more general nature. The extent of the possible generality can be indicated qualitatively by means of a greatly simplified model of the floc structure.

Particle-Particle Interactions

Hoskin and Levine (*24*) have shown that an approximate expression derived by Derjaguin (*25*) gives the interaction of two spherical particles to within 10% provided the potential at the surface of the particles is of the order of 50 mv. or less and the thickness of the double layers $1/\kappa$ is not less than about one-fifth of the particle radius. Both of these criteria are met by flocculated suspensions of particles of the size range used in the present study.

Derjaguin showed that the force of interaction F of two spherical particles could be calculated from the expression

$$F = \frac{A\ r}{12\ h^2} \qquad (14)$$

Application of Equation (14) to calculations of the attractive force between particles can only give at best an order of magnitude estimate because of several factors. First there is evidence (26) that the interaction between particles of radii greater than 500 Å. is overestimated, when the particle radius is used in the calculations, and that in reality the radius of curvature of protuberances should be used instead. Second the distance separating the two surfaces cannot be determined accurately; usually the particles are assumed to be in contact (27), although distances up to 40 Å. have been used in some calculations (28). Another major uncertainty is in the value of A, the attraction constant. Theoretically A can be estimated (29) from

$$A = \frac{3}{4} \pi^2 h' \nu' q^2 \alpha_o^2 \qquad (15)$$

where $h'\nu' = 2.05 \times 10^{-11}$ erg. The effect of the suspending medium on the value of A is given by

$$A = (A_p^{1/2} - A_m^{1/2})^2 \qquad (16)$$

A qualitative estimate of the effect (30) of the medium may be obtained by dividing the constant A by the square of the refractive index since the Van der Waals force is essentially of an electric nature. Because of the uncertainties in the theory as well as in the values for α_o, Equations (15) and (16) will only give an order of magnitude estimate for A, with the most probable value for suspensions of metallic oxides [in which oxygen makes the major contribution to the polarisability (31)] in water falling between 5×10^{-13} and 5×10^{-12} erg. It has not been possible to obtain direct experimental verification of these values (32), although indirect experimental evidence (26) confirms that the value is in the range 2×10^{-14} to 10^{-12} erg. for particles in the size range 0.03 to 0.2 μ. In the following calculations a value for A of 10^{-12} erg. will be used.

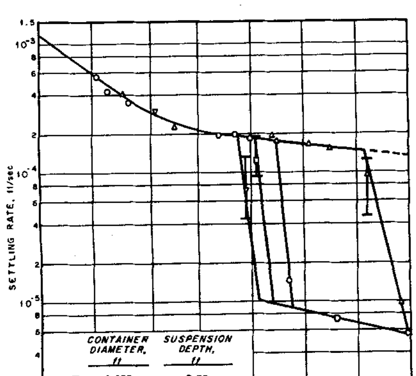

Fig. 3. Effect of concentration on the hindered-settling rate of a typical flocculated suspension.

Floc Model

The major assumption in the development of a floc model involves the substitution of a square potential well link for the Van der Waals attractive force. The link is assumed to be formed on contact, and the force required to rupture this link is assumed to be that given by Equation (14). It will further be assumed that the protuberances on the particles [that is the correct value for the r term in Equation (14)] have a radius of the order of 0.1 μ, a value consistent with those observed in the electron micrographs of Figure 2. Finally it will be assumed that the particles approach to within a distance of twice the Van der Waals radius of the oxygen atom. Again this is consistent with values assumed by others in similar calculations (33). With these general assumptions, the floc model can be used to calculate some of the physical properties of flocculated suspensions.

Yield Stress

The yield stress τ_y in Equation (5a) is just the force required to initiate flow on a macroscopic scale. On a microscopic scale τ_y may be related to the floc characteristics with arguments similar to those originally advanced by Goodeve (34, 35). However a considerable simplification is afforded because the particles used in this study were sufficiently large to minimize the effects of Brownian motion (12). This means that thermal motion had a negligible effect on either the formation or rupture of the floc structure.

The yield stress may be related to the particle and suspension characteristics as follows. The number of particle-particle contacts n_c per unit volume of floc is

$$n_c = \nu N = \nu \frac{6\ \phi}{\pi D_p^3} \qquad (17)$$

In a three-dimensional floc a structure composed of symmetrically shaped particles, a fraction a (where a is a number less than 1 with a most probable value between 1/3 and 1/2) of the particle contacts are broken in simple shear. The number of particles per unit area in a layer one particle thick is D_pN, and the number of particle contacts per unit area that are

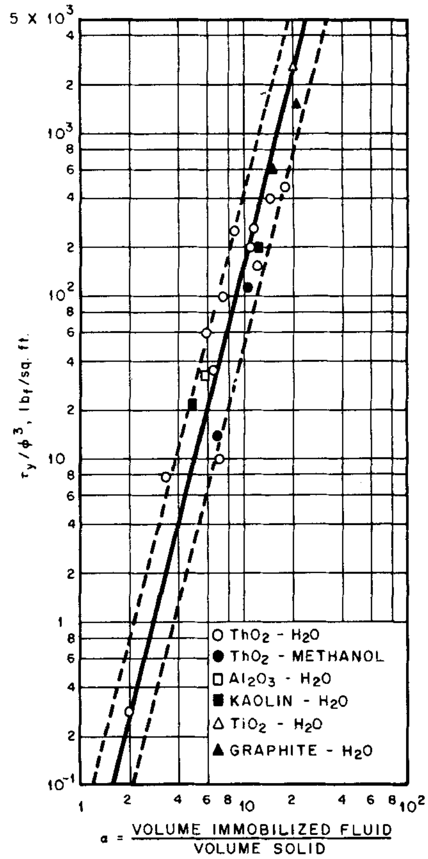

Fig. 4. Effect of suspension flocculation characteristics on the yield stress.

broken as the suspension is sheared is $a\nu ND_p$. If the attractive force between particles is F [Equation (14)], the yield stress is

$$\tau_y = a\ \nu\ F\ N\ D_p = a\ F\ n_c\ D_p \qquad (18)$$

The rate of formation of particle-particle contacts is a second-order process, since two particles are necessarily involved while the rate of destruction of contacts is simply proportional to the number of contacts n_c:

$$\frac{dn_c}{dt} = K N^2 - \beta n_c \qquad (19)$$

At steady state the rate of formation and breaking of contacts is equal; hence

$$n_c = \frac{K N^2}{\beta} \qquad (20)$$

Manley and Mason (36) have proved experimentally the theoretical results of Smoluchowskii (37) that the rate of collision of particles is

$$K = \frac{1}{12} D_p^3 \frac{du}{dr} \qquad (21)$$

The rate of breakage of contacts β is somewhat more difficult to arrive at, but it is approximately given by the time of contact t_c. Bartok and Mason (38) have shown that the mean time of contact of two isolated spheres in a laminar velocity gradient is given by

$$t_c = \frac{5\ \pi}{6\ du/dr} \qquad (22)$$

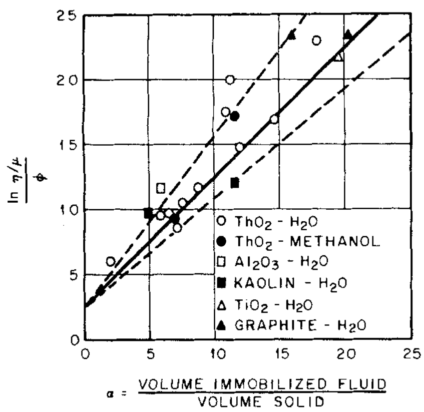

Fig. 5. Effect of suspension flocculation characteristics on coefficient of rigidity.

The effect of additional neighboring spheres on the contact time can be estimated as follows. During the period that the two spheres are in contact, the doublet rotates as a rigid dumbbell. Burgers (*39*) has shown that the relative viscosity of suspensions of rigid rods is directly proportional to the volume fraction solids for a fixed axial ratio. This means that as the volume fraction solids is increased at constant shear stress, the effective velocity gradient is decreased. Combining Burgers results with those of Bartok and Mason for an isolated pair of spheres one obtains

$$t_c = \frac{5\,\pi\, B\, \phi}{6\, du/dr} \approx 1/\beta \qquad (23)$$

where B is a constant in Burgers theory which is between 1 and 10 for the present case. Combining Equations (18), (20), (21), and (23) and writing N in terms of ϕ one obtains

$$\tau_y = \left(\frac{5\,a\,B}{2\pi}\right) F \frac{\phi^3}{D_p^2} \qquad (24)$$

Evaluation of the constants in Equation (24) with the mean of the range of values cited above gives 2.77×10^{-9} lb.$_f$ which is to be compared with the the value of 2.27×10^{-9} lb.$_f$ determined empirically.

Hindered-Settling Characteristics

As the floc settles through the suspending medium, drag forces at the surface are too small to shear off clumps of particles (that is, the surface shear is always less than 0.1 of the yield stress); therefore it will be assumed that at steady state the attractive forces holding individual particles to the floc are balanced by the hydrodynamic forces tending to shear them off. The hydrodynamic forces are exerted tangent to the surface of the floc; hence it will also be assumed that particles are removed by rupture of a rigid link. This is consistent with the observation that particles adhere on contact and the hypothesis that the contacts are primarily protuberance on the surface with a radius of curvature of 0.1 μ.

If the drag force on a floc is considered to be exerted primarily on the semirigid floc structure, then the drag force exerted on a single particle adhering to a particle which is fixed in the floc structure is given to a first approximation by

$$F_d = 12\,\pi\,(1 + \alpha)\,\mu\, U_f\, D_p/g_c \qquad (25)$$

This force is exerted tangent to the surface so the torque tending to remove a single particle from the surface is approximately

$$T_1 = (D_p/2)\, F_d \qquad (26)$$

In order to maintain a stable position, while in contact, particles must touch on at least three points. If the average distance separating these points of contact is assumed to be one-tenth particle diameter, then the torque due to the interparticle attractive force is

$$T_1 = 0.1\, D_p\, F_1 \qquad (27)$$

Combining Equations (25) to (27) one gets

$$F_1 = 60\,\pi\,(1 + \alpha)\mu\, U_f D_p/g_c \qquad (28)$$

With data for particles sufficiently large for gravitational forces to be of the same order as the attractive forces excluded, the ratio of the attractive force calculated from the Derjaguin-Verwey-Overbeek theory [Equation (14)], with the same constants as in the previous calculation, to the attractive force calculated from settling-rate data [Equation (28)] has an average value of 1.20 with a mean deviation of ±60%.

DISCUSSION OF RESULTS

By definition a floc is a rather porous and formless structure. However flocs can be identified as entities in dilute suspensions, and in fact good agreement was found between the diameter calculated from settling-rate measurements and the diameter obtained by direct observation (*12, 15*) of dilute suspensions. The present study showed that it was possible to characterize the floc structure from settling-rate measurements (via the parameter α) without making assumptions about the size and shape of the floc. It was further shown that α was directly related to the rheological parameters τ_y/ϕ^3 and $(\ln \eta/\mu)/\phi$, which are also constants characteristic of the degree of flocculation.

It should be particularly noted that τ_y/ϕ^3 may be calculated both from the value of α and from the data for critical concentration for compaction [Equation (8)]. For instance for the data shown in Figure 3 the value for τ_y/ϕ^3 from α is 240 lb.$_f$/sq.ft., the mean for the data for the critical concentration is 290 lb.$_f$/sq.ft., and the combined mean is 280 ±25% lb.$_f$/sq. ft. This is quite good agreement with the value of 260 lb.$_f$/sq.ft. determined from the rheological data alone.

When the equations for the rheological parameters [Equations (10) and (10*a*)] are substituted into the Bingham plastic equation [Equation (5*a*)], it is seen that in the limit as α goes to zero and for low concentrations the Bingham plastic equation goes over to the form for noninteracting suspensions required by the Einstein equation (*1*). At the other extreme, for highly flocculated suspensions, α is much greater than 1. Under these circumstances Equations (10), (10*a*), and (13) can be combined to give

$$\frac{\tau_y}{\phi^3} = k_1 \left(\frac{D_f}{D_{app}}\right)^2 \qquad (29)$$

and

$$\frac{\ln \eta/\mu}{\phi} = 2.5 + \sqrt{D_f/D_{app}} \qquad (30)$$

With only the symmetrically shaped particles considered, the floc diameters were in the range of 40 to 115 μ with an average of 86 μ and a mean deviation of ±22%. If the floc diameter were assumed to be essentially a constant, then Equations (29) and (30) have the same particle size dependence as determined from rheological data alone; however the particle shape factor enters in a different way so the numerical constants cannot be compared directly.

The object of the phenomenological analysis was not to demonstrate that

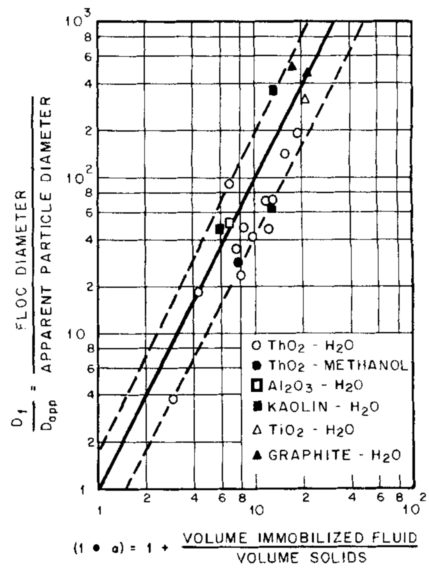

Fig. 6. Effect of particle diameter on suspension flocculation characteristics.

good agreement of the numerical coefficients could be obtained, but rather to clarify the manner in which varying the chemical composition of the solid or the suspending medium affects the flocculation characteristics. The absolute value of each of the individual geometric terms in Equations (14) and (24) is relatively unimportant in discussions of chemical effects as long as reasonable assumptions for their value produce order of magnitude agreement with the experimental data. Such agreement was obtained which supports the belief that the principal attraction between particles is due to London-Van der Waals forces [Equation (14)] as predicted by the Derjaguin-Verwey-Overbeek theory (*3*, *25*). The chemical composition of the solid and suspending medium enter their theory through the value of the interaction constant *A*, which was discussed above in the section on particle-particle interactions. The principal factors which affect the magnitude of *A* are the number of atoms per cubic centimeter and the polarisability which is the coefficient relating the magnitude of the induced dipole moment to the external field strength. In the present study the oxygen atoms made the principal contribution to the polarisability of the solids (*31*), and contribution due to the liquids was approximately the same and significantly less than the solids. Verwey and Overbeek have pointed out (*30*) that the effect of the liquid can be accounted for in an approximate way by dividing by the square of the refractive index.

CONCLUSIONS

It has been shown that the rheological parameters of flocculated suspensions may be estimated by making a series of hindered-settling rate measurements at different concentrations. If the flow data are arbitrarily fitted by the Bingham plastic model, then the ratio τ_y/ϕ^3 can be determined by evaluating either the volume of water immobilized by the solid phase [Equation (10)] or from the concentration at the onset of compaction [Equation (8)]. Similarly the value $(\ln \eta/\mu)/\phi$ may be determined by evaluating the volume of water immobilized by the solid phase [Equation (10*a*)].

Comparison of the present results for thorium oxide suspended in methanol and water and for kaolin, titania, alumina, and graphite suspended in water with the qualitative predictions of the Hamaker theory of the attractive forces between particles and the Derjaguin-Verwey-Overbeek theory of colloid stability support the belief that the present results will permit a somewhat better than order-of-magnitude estimate of the rheological parameters of a wide variety of flocculated suspensions. That is the internal consistency of the present results for many different systems is in good agreement with the theoretical predictions that the composition of the solid phase and the nature of the electrolyte double layer play only a second-order role in the behavior of flocculated systems. However it must be emphasized that since the choice of the Bingham plastic model to describe the rheological data is purely arbitrary (see discussion in reference *17*), the numerical constants given in the present paper will apply only for the experimental conditions specified in the present series of papers. However this is not a serious limitation, since the present results have been shown to be satisfactory for correlation of turbulent heat and momentum transport data (*18*) and for correlation of minimum transport velocity data (*19*) in tubes from 1/8 to 4 in. in diameter.

NOTATION

- a = constant, dimensionless
- A = Hamaker interaction constant, ft. lb.$_f$
- B = constant, dimensionless
- D = diameter, ft.
- D_{app} = apparent diameter, ft.
- D_p' = particle diameter, μ
- F, F_1 = attractive force, lb.$_f$
- F_d = drag force, lb.$_f$
- g_c = conversion factor, (lb.$_m$/lb.$_f$) (ft./sec.^{2})
- g_L = gravitational acceleration, ft./sec.)^2
- h' = Planck's constant
- h = interparticle distance, ft.
- k = constant in Equation (8), τ_y/ϕ^3, lb.$_f$
- k_1 = constant in Equation (10), 1.55×10^{-2} lb.$_f$/sq.ft.
- K = rate constant
- L = length, ft.
- n_c = number of contacts per unit volume, ft.$^{-3}$
- N = number of particles per unit volume, ft.$^{-3}$
- N_p = number of particles
- q = atoms/cc.
- r = particle radius, ft.
- S/S_o = platelike particle surface area per equiaxial particle surface area, dimensionless
- t_c = time of contact, sec.
- T_1 = torque, ft. lb.$_f$
- U = hindered-settling rate, ft./sec.
- du/dr = velocity gradient, sec.$^{-1}$

Greek Letters

- α = volume immobilized water per volume of solid, dimensionless
- α_o = polarizability, cc.
- β = rate constant
- η = coefficient of rigidity, lb.$_m$/ft. sec.
- μ = fluid viscosity, lb.$_m$/ft. sec or $\mu = 10^{-4}$ cm.
- ν = number of contacts per particle, dimensionless
- ν' = London's characteristic frequency
- π = 3.1415. . . .
- ρ = fluid density, lb.$_m$/cu. ft.
- σ = logarithmic standard deviation, dimensionless
- τ = shear stress, lb.$_f$/sq.ft.
- τ_y = yield stress, lb.$_f$/sq.ft.
- ϕ = volume fraction solids, dimensionless
- ψ_1 = shape factor, exp 0.7 $(S/S_o - 1)$, dimensionless
- ψ_2 = shape factor, $\sqrt{S/S_o}$, dimensionless

Subscripts

- f = floc
- p = particle
- m = suspending medium

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Semifluidization in Solid-Gas Systems

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A new type of solid-fluid contacting device consisting of the features of both fixed and fluidized beds has been proposed (*2, 3*). The expansion of a fluidized bed is partially restricted by placing a porous plate or screen on top of the bed. Thus a packed section is formed beneath the top porous plate while the particles underneath remain fluidized. Such an operation is called *semifluidization* (*2, 3*).

A semifluidized bed has the advantages of both a fluidized and fixed bed. By adjusting the position of the top sieve plate a semifluidized bed can be made to suit any particular chemical reaction.

The mechanics of semifluidization of single size particles has been reported, and the data for solid-liquid systems were correlated (*2*). It is the purpose of the present investigation to extend the study to solid-gas systems and to present a unified correlation for both solid-liquid and solid-gas systems.

By means of a material balance between the fully fluidized and partially expanded states of the suspension, Fan, Yang, and Wen (*3*) derived the following equation, assuming that the particles in a column behave independently and uniformly and that the voidage of the packed section is constant:

$$h_{pa} = (h_f - h)(1 - \epsilon_f)/(\epsilon_f - \epsilon_{pa}) \quad (1)$$

Fan and Wen (*2*) showed that Equation (1) is valid for any particle shape provided that the particles can be represented by the same characteristic dimensions. Their experimental data substantiated the validity of Equation (1) for large-and-irregular-size particles of benzoic acid in liquid systems.

The total pressure drop across a semifluidized bed can be considered to be equal to the algebraic sum of the pressure drops across the packed section and the fluidized section.

Accordingly

$$\Delta P_t = \Delta P_f + \Delta P_{pa} = (\Delta P/L)_f\,(h - h_{pa}) + (\Delta P/L)_{pa}\,h_{pa} \quad (2)$$

When one employs the Ergun equation (*1*) for the pressure drop in the packed section, the following equation is obtained for the total pressure drop across a semifluidized bed:

$$\Delta P_t = (1-\epsilon_f)(\rho_s - \rho_f)\left[h_f - \frac{(1-\epsilon_{pa})(h_f - h)}{(\epsilon_f - \epsilon_{pa})}\right] + \left[150\frac{(1-\epsilon_{pa})^2}{\epsilon^3_{pa}}\frac{\mu u}{D^2_p} + 1.75\frac{1-\epsilon_{pa}}{\epsilon^3_{pa}}\frac{Gu}{D_p}\right]\cdot\left[(h_f - h)\frac{1-\epsilon_f}{\epsilon_f - \epsilon_{pa}}\right]\cdot\frac{1}{g_c} \quad (3)$$

In order to evaluate the total pressure drop in a semifluidized bed by Equation (3), accurate knowledge of fluidized bed porosity as well as fixed bed porosity at the given condition is necessary.

EXPERIMENTAL

The experiments were carried out with the equipment shown schematically in

TABLE 1. PROPERTIES OF SOLID PARTICLES USED IN THE EXPERIMENTS

Particles	D_p, in. (geometrical mean)	Shape	Sphericity ϕ	Absolute density, ρ_s lb./cu. ft.	Porosity of least dense static bed ϵ_o
80- to 100-mesh glass beads	0.0061	Sphere	1.00	156.0	0.4386
High-density polyethylene	0.0663	Sphere segment (diameter 0.1042 in. thickness 0.04218 in.)	0.770	57.87	0.4893
High-density polyethylene	0.1145	Cylinder (diameter 0.1077 in., length 0.1222 in.)	0.867	57.87	0.4448

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