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Suspensions and Sediments. Part II. Behavior of Concentrated Suspensions

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REVIEW

Suspensions and Sediments. Part II. Behavior of Concentrated Suspensions

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Abstract

The behavior of concentrated suspension, the phenomenon of hindered settling, and structural characteristics of the settling suspensions are described.

The use of interface sedimentation rate and the settled volume in calculating the volume of associated fluid carried down on sedimenting particles is outlined by employing a theory which assumes that particle-particle association is the factor responsible for variation of sedimentation behavior from one suspension system to another.

INTRODUCTION

The settling of individual particles in a very dilute suspension can be regarded as "free" until at higher concentration where the fall of any particle is observed to be hindered by the presence of other particles in its path. The concentration at which the suspension starts to exhibit hindrance is not sharply defined experimentally, yet it is assumed that hindrance depends upon the physicochemical properties of the solid powder and the liquid. At this concentration a transition in behavior is observed from a system of dilute conditions (where it should obey Stokes' law) to a system of concentrated conditions in which the suspension should settle "en block" with a well-defined interface, above which is a clear supernatant liquid and below which is the settling sediment.

THE PHENOMENON OF HINDERED SETTLING

Davies et al. (1) defined hindered settling as a process of sedimentation in which a clear suspension-supernatant interface forms early and in which the interface settles at a linear rate for a considerable portion of the period during which sedimentation occurs.

The determination of a sharp break between the free settling conditions and those of hindered settling has not been clearly described in the studies reported by Kermack et al. (2), Power (3), Steinour (4-6), Richardson and Zaki (7, 8), Shannon and Tory (9, 10), and Dollimore and McBride (11). Davies et al. (1), however, identified a function ϵ_1 as the initial liquid volume fraction (initial porosity) of a suspension at which hindered settling commences. Parameter ϵ_1 corresponds to the maximum sedimentation mass transfer for a given suspension. Bhatti (12) identified values of ϵ_1 for model systems of glass ballotinis in aqueous glycerol. Figures 1 and 2 show the variation of function $Q(1 - \epsilon)$ with suspensions of equisized and polysized glass ballotinis in aqueous glycerol, respectively; ϵ_1 here is the value at which $Q(1 - \epsilon)$ has a maximum value. Various values for ϵ_1 are given in Table 1. Parameter Q is the interface settling rate of the settling suspension.

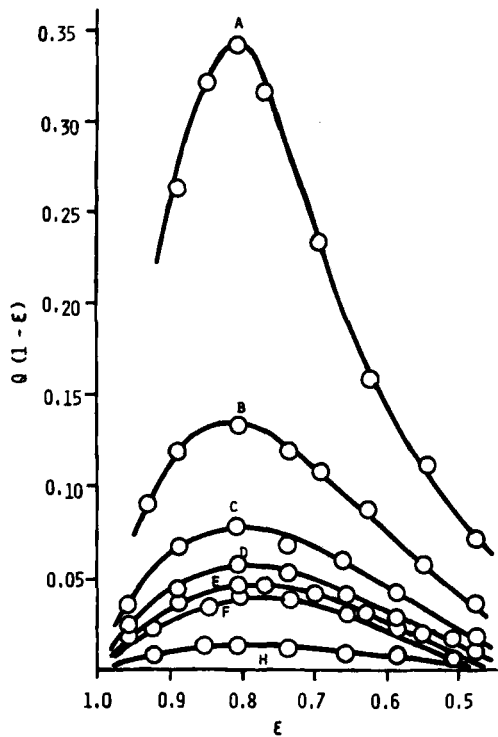


FIG. 1. Variation in the function $Q(1 - \epsilon)$ with ϵ for suspensions of equisized glass ballotini in aqueous glycerol.

TABLE 1
Values of ϵ_1 for Various Mixtures of Glass Ballotini in Equisized and Polysized Glass Ballotini Suspensions in 75% Aqueous Glycerol

<i>Equisized Suspension</i>							
Grades	A	B	C	D	E	F	H
ϵ_1	0.78	0.80	0.79	0.79	0.78	0.77	0.78

<i>Polysized Suspensions</i>						
Mixtures	I	II	III	IV	V	VI
ϵ_1	0.77	0.79	0.79	0.79	0.74	0.74

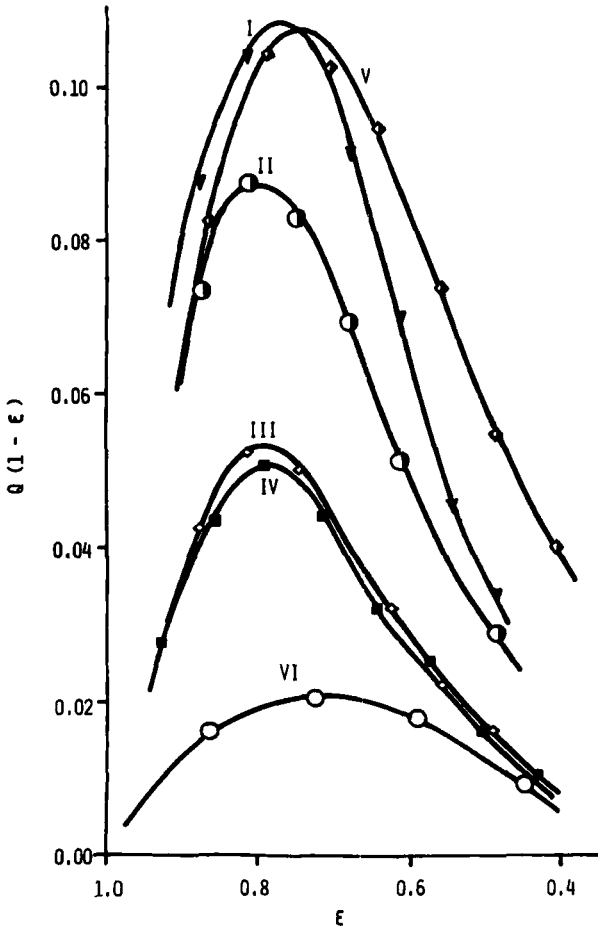


FIG. 2. Variation in the function $Q(1 - \epsilon)$ with ϵ for suspensions of mixtures of glass ballotini in aqueous glycerol.

Parameter ϵ_1 is a useful indication of the tendency of a system to show hinderance, and it has been suggested that the more nearly ϵ_1 approaches its theoretical maximum value of unity, the more the sedimentation process is self-hinderance. Suspensions for which ϵ_1 is close to unity are named "highly hindered systems."

Dollimore (13) carried out preliminary studies on sedimentation and stated that the mode of settling of a suspension is effected by general factors such as particle size, shape and density of the particles,

concentration of the suspensions, physical and chemical properties of the suspending liquids, and chemical constitution and surface properties of the solid.

Michaels and Bolger (*14*) reported three types of sedimentation curves (plots of interface height vs time) for suspensions with increasing solid concentrations. They are shown in Fig. 3. For a very dilute suspension a straight-line plot (with a higher settling rate) is obtained (A in Fig. 3). During the settling of a suspension with an intermediate concentration, the aggregates settle as a coherent network and the settling plot has the shape of Curve B in Fig. 3. This could also be true for the sedimentation of flocculated suspensions. The initial portion of Curve B is explained as an equilibration period where reflocculation is believed to be taking place. The initial settling rate is, therefore, very low. The straight-line

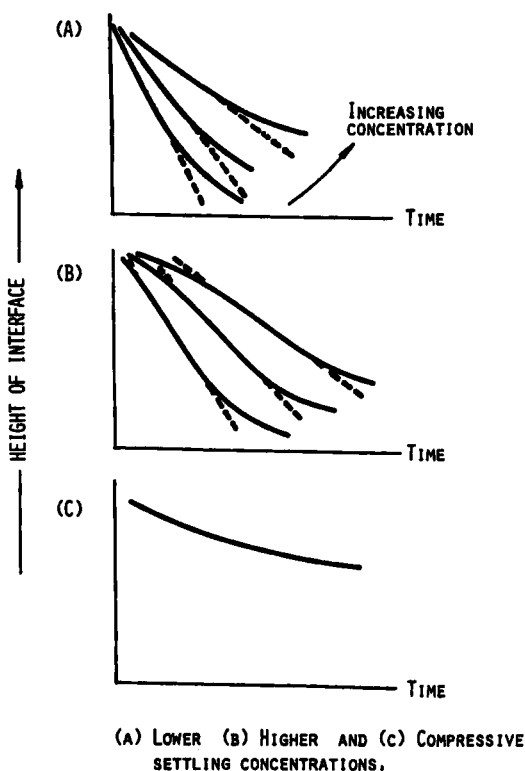


FIG. 3. Three general types of settling plots.

portion of this curve is considered to be a region of uniformly hindered settling from which the uniform settling rate of the suspension-supernatant interface Q (cm/s) can be calculated. On further increasing the concentration of the suspension, the settling rate of the interface subsides slowly at an ever-decreasing rate so that the settling plot resembles Curve C in Fig. 3, also known as compressed settling.

STRUCTURAL CHARACTERISTICS OF SETTLING SUSPENSIONS

Coe and Clevenger (15) and Michaels and Bolger (14) showed that a dilute suspension settles at a constant rate until it nears its final settled volume, whereas a concentrated suspension exhibits continuous settling (i.e., compressive settling).

Coe and Clevenger proposed that in the settling of solid pulp, the flocs containing the liquid pass downward at known rates. The pulp column could thus be divided into various layers, and this enabled the calculation of the solid content passing out of the upper layer into the middle layer and then to the lower layer. For pulps settling at a constant rate, the solid consistency was found to be good, but the pulp became thicker in the lower layers. Similar results were found for concentrated pulps which settle at continuous settling rates.

Studies on the relative movement of solid and liquid during settling and consolidation in suspensions have also been carried out by Gaudin, Fuerstenau, and Mitchell (16-18), who confirmed the observation described earlier by Coe and Clevenger. They, in fact, used an x-ray adsorption technique to measure the local solid concentration in settling beds as a function of time and position of the settling interface. Their observations revealed that the displaced supernatant fluid leaves the bed through pores of comparatively large size in the early part of settling and later is expelled via much smaller tubules in the compressive phase of sediment consolidation. They showed that during the early free-settling period a region exists, extending from the interface downward, where the density is constant and equal to that of the original suspension at the start, as shown in Fig. 4.

Tory and Shannon (19) and Bhatti (12) reported similar observations on concentration profiles of settling sludges of aqueous suspensions of calcium carbonates, calcium fluoride, and clay minerals. Some of the results on clay/water suspensions are shown in Fig. 5.

Michaels and Bolger (14) characterized the microstructure of settling sediments and found that initially the aggregates are interconnected,

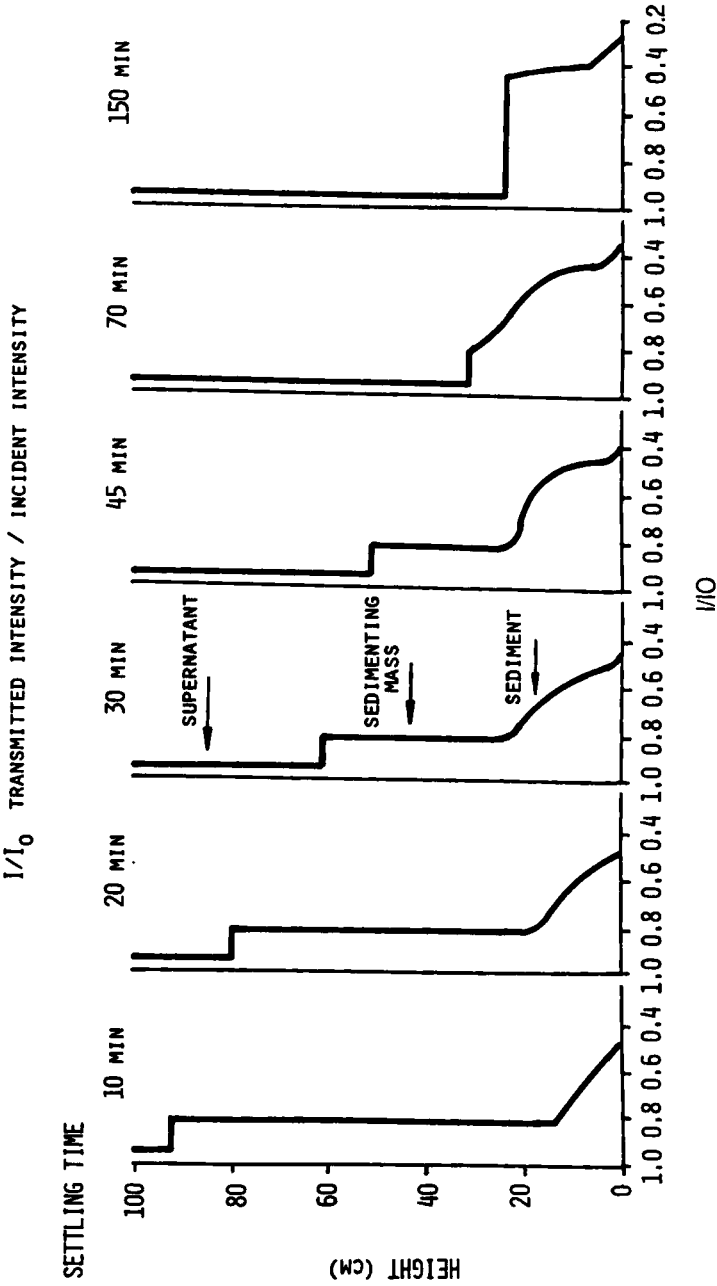


FIG. 4. Transmission of x-ray through sedimenting clay suspensions as a function of time.

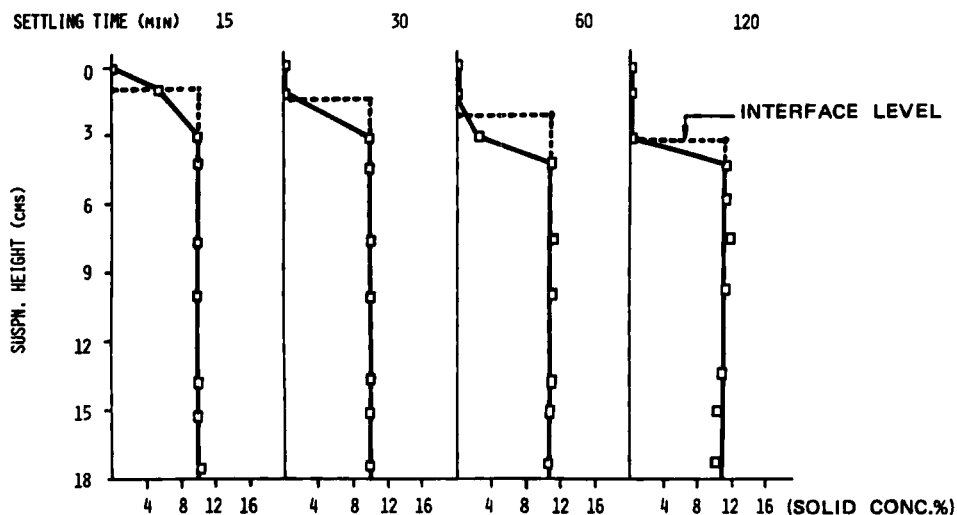


FIG. 5. Concentration vs suspension height plots for clay/water suspensions ($20 \text{ g}/200 \text{ cm}^3$ total suspensions).

irregular spheres, and that the fluid flow paths go up between the aggregates and are tortuous and contain many expansions and contractions. Drag forces are strong and the initial settling rates are low. As settling proceeds, the aggregates tend to coalesce and line up into vertical rows, and the flow paths straighten out. Plastic deformation of the aggregates occurs whenever the viscous shear forces exceed the aggregate yield stress. Contractions and sharp bends are smoothed out. Given enough time, the liquid paths in a vessel of infinite extent would tend to approach the configuration of smooth vertical tubes rising through the continuous aggregate region, and the settling rate would increase to its maximum.

Another important factor in the study of the mode of sedimentation is the ratio of interparticle forces to particle size. With large particles the significance of adhesion between particle is reduced, and the system packs down until there are sufficient points of contact to bear the load. With small particles the forces of adhesion are significantly large at the points of contact so a system with large voidage is produced; larger particles tend to make weaker contact and counteract this with more points of contact, leading to a reduction of voidage.

Gregg and Hill (20), Gregg and Stephens (21), and Dollimore and

McBride (22) demonstrated similar relationships between particle size and bulk density while working with different solid materials.

It therefore seems that suspensions undergoing hindered settling have some form of persistently ordered structure which develops when the components are mixed. The supernatant fluid corresponds to the liquid forced out of the sedimenting material on compaction into settled sediment.

In the data of Gaudin et al., as mentioned earlier, it was pointed out that the bulk density of the sediment is not uniform with respect to height and consists of a lower zone of higher solid concentration and an upper zone of decreasing solid concentration. In the upper zone of lower solid concentration, the number of pores per unit volume is more, which in turn leads to an increase in the proportion of liquid in these pores. This liquid is assumed to be expelled from the lower zones of the sediment.

Gregg, Hill, and Stephens (20, 21) and McKay (23, 24) demonstrated certain important aspects of the relationship between pore size and bulk density of the sediment. These are that the volume of the sediment is much greater than that predicted from the solid weight and density, which is due to an increase in the porosity of the bed and a high proportion of associated "immobile" liquid which stays with individual solid particles in the sediment.

FLUID RETENTION IN SUSPENSIONS AND SEDIMENTS

McKay (23, 24), while working on various dispersions of organic pigments, pointed out the presence of a considerable proportion of liquid which appeared to be associated with the dispersed particles. As a result of this, the effective density of the dispersed particles is far less than that of the solid pigment and can lead to considerable error in measuring sedimentation parameters. The association of liquid with the particles must also reduce the volume of free liquid through which the sedimenting material can settle; this then becomes another factor that reduces the tendency to sedimentation.

Gaudin and Fuerstenau (25), in their studies on clay suspensions, had already pointed out that during the early stages of sedimentation, i.e., the linear settling zone, the displaced supernatant fluid leaves the bed through pores of comparatively large diameter, whereas in the later stages of sedimentation the fluid is expelled via much smaller tubules in the consolidating sediments, thus making the upward flow of fluid leaving the tortuous bed the effective length of the settling bed, L_e , in a

suspension, as mentioned by La Mer and Smellie (26) in their theory of filtration, the effective path length of the upward flow of liquid through the bed. This is shown in Fig. 6. In a stabilized suspension the increase in L_e is interpreted as an increase of tortuosity to flow, causing increased hindrance to sedimentation. This hindrance was interpreted earlier in terms of the Kozeny-Carman theory (27-30) as being due to tortuosity.

La Mer and Smellie based their theory on the Kozeny-Carman expression:

$$U = \frac{g}{2\eta\rho_l^2 S_w^2} \frac{L}{L_e} \frac{\nabla\rho}{L} \frac{\epsilon_b^3}{(1 - \epsilon_b)^2} \quad (1)$$

where U = filtration rate

g = acceleration due to gravity

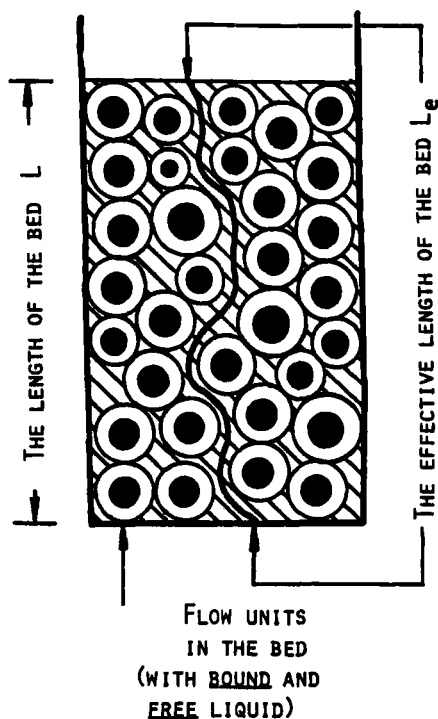


FIG. 6. The effective path length (L_e) of the upward liquid flow through the bed (schematic).

η = viscosity of the liquid

ρ_l = density of the liquid

S_w = surface area of the bed

L = length of the bed

L_e = effective length of the bed

$\nabla\rho/L$ = pressure drop across the bed

ϵ_b = voidage of the bed (as distinct from the porosity of the total system)

La Mer and Smellie assumed that the volume of the filter bed and the floc structure are not affected by the pressure applied to the bed to assist filtration. However, the experimental evidence by Bhatt \bar{y} (12) is in disagreement with this view that claims that the filter beds are, in fact, formed by the settling process and not by the applied pressure. In spite of the doubtful assumptions of La Mer and Smellie, an equation of form similar to Eq. (1) might hold, but its application could be difficult.

These observations represent an important contribution to knowledge of the relative movement of solids in liquid. However, the part played by the liquid associated with the sedimenting solid species in these phenomena is still not very clear.

CONCEPT OF "IMMOBILE" ASSOCIATED LIQUID

A particle settling through a fluid appears to carry a layer of associated liquid with it. McKay (23, 24) has termed these sedimenting species "flow units" capable of carrying a large proportion of "immobile" liquid. The solid of the plug in which particles of different masses fall at a uniform rate presumably has a proportion of associated liquid which is intrinsic to a particular suspension under the conditions of the experiment, and the presence of this liquid is one factor determining the sedimentation behavior of the suspension.

The final settled volume is usually greater than that predicted from the solid weight and density, even after allowing for possible packing of the particles. Dollimore et al. (11, 13, 22) and McKay (23, 24) presented their results on the sedimentation of certain inorganic powders and pigments, respectively, and they suggested that the retention of liquid with flow units is due to the physicochemical characteristics of the solid species. Surface morphology, distribution of surface charge, and packing coordination of the flow units in a settling sediment are to be regarded as factors contributing toward the retention of liquid with solids.

TABLE 2
Calculated Values of Sediment Volume Fraction v and Parameter p for Suspensions of Glass Ballotini in Water, Clay in Water, and Clay in Water and Gum Tragacanth

Glass ballotini-water suspensions				Clay-water suspensions		Clay-water-gum suspensions	
Mass of glass ballotini (g)	Sediment volume fraction v	Value of p	Mass of clay (g)	Sediment volume fraction v	Value of p	Sediment volume fraction v	Value of p
75	0.34 } 0.45 }	0.651	10	0.25	1.25	0.24	0.83
100							
125	0.56 } 0.68 }	0.670	15	0.35	1.27	0.40	1.0
150			20	0.44			
175	0.79 } 0.90 }	0.625	25	0.51	1.25	0.435	1.05
200			30	0.59			
Average p values				= 1.27		= 0.96	
				i.e., $p > 1$		i.e., $p < 1$	

As a first approximation, the final settled volume may be used to estimate the quantity of associated liquid. McKay, however, proposed a packing factor p to account for the liquid associated with flow units in a settling suspension. He attempted to calculate the proportion of this liquid by correlating the setting rate Q (cm/s) with the sediment volume fraction v . Packing factor p accounts for the proportion of liquid in the sediment that is not associated with and immobilized by the flow units in the linear settling zone. Mathematically, p is the ratio of the total flow units volume to the settled sediment volume.

Bhatty et al. (12, 31-33) and Bhatti et al. (34) utilized McKay's approach to examine the degree of liquid retention in various model systems including glass ballotini-water, china clay-water, china clay-water-gum tragacanth, and cellulose-water-polymer, and suggested a relationship between p and v :

$$p = \frac{1 - \epsilon''}{v} \quad (2)$$

where $1 - \epsilon''$ is the volume fraction of the flow units in a uniformly mixed suspension. Values of v and p for these systems are given in Table 2. According to Bhatty et al. (33), McKay's theory, if valid, means that a suspension with $p > 1$ (clay-water system) results in sediment by a process in which the associated liquid is forced off the sedimenting flow units as they settle into sediments. While working on calcium carbonate suspensions in various liquids, Davies (35) stated that values of $p > 1$ are associated with less compressible and less flocculated sediments, suggesting that the associated liquid is stripped from around the flow units rather than from within them. For suspensions with $p < 1$ (glass ballotini-water system), a sediment of compressible nature is commonly formed since the total flow units volume is less than the settled sediment volume and an amount of free liquid stays between the flow units in the sediments. The glass ballotini gives a very low value of p , which is consistent with close packing of incompressible spheres with a minor proportion of associated liquid.

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