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LAYERING PHENOMENA IN COLLOIDAL SUSPENSIONS

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Abstract—Aged suspensions of microspheres and two kaolinites exhibit several horizontal layers. Particle concentration is greater at the top of a layer; lower layer tops have increasing particle concentrations. Lower layers also settle more rapidly than upper layers; however, an increase in original suspension concentration results in a proportional increase in the particle concentration of comparable layers and causes comparable layers to settle at a slower rate. The average equivalent diameter of particles within and between kaolinite layers is identical. The maximum measured diameters are also identical. Microsphere layers show similar uniformity of average and maximum diameters. Ultimate settling of layers in suspension does not result in observable layers in the sediment. Data are interpreted as indicating that, in a colloidal suspension, particles interact to become observable as definite horizontal layers. A sequence of mechanisms is proposed for layer formation.

INTRODUCTION

EXPECTED sedimentation behavior of particles in suspension is that the particles will settle according to Stokes law, i.e. as a function of their mass and the viscosity of the suspending medium. Aged suspensions frequently show one or more horizontal layers suspended in the column of liquid. The suspension within each layer appears to be very dense at the top, becoming nearly clear at the bottom. Layer formation, therefore, appears to contradict expected settling behavior.

Ramann and Krauss (1927) observed layering in suspensions of quartz particles and suggested the following conditions for layer formation: (i) a particle size below 1μ; (ii) a particle concentration which would lead to an interparticle distance reflecting equilibrium conditions between particle repulsion and attraction forces; and (iii) an electrolyte concentration below the flocculation value. Nutting (1929) proposed that a gradient in kinetic pressure opposes gravity settling of fine particles. Elton and Hirschler (1954) suggested that an appreciable part of the total resistance to motion of settling particles is due to the potential gradient which is generated by particles falling through a liquid. Larger particles undergo a greater "electroviscous retarding force" due to their larger total surface charge and therefore the rate of separation of sizes by sedimentation is decreased.

Recently Tobias and Ruotsala (1966) observed layering in suspensions of clay-sized materials and noted that: (i) no layers form below 10°C; (ii) there is an increase in both the time required for layers to develop and the number of layers formed with an increase in particle concentration in the original suspension; and (iii) the sediment from a kaolinite suspension has a "varved" appearance. They also suggested that the upper layers consist of smaller particles since the upper layers settle less rapidly than lower layers.

The purpose of this investigation was: (i) to study some of the conditions necessary for layers to form and be observed; (ii) to describe quantitatively some layer parameters; and (iii) to discuss the data in terms of layer formation.

EXPERIMENTAL PROCEDURE

Materials

Two well-crystallized kaolinites and a sample of microspheres were chosen for detailed investigation. The kaolinites were obtained from the Thiele Kaolin Company and are Kaobrite and CH Air-floated. In this study these are referred to as Thiele No. 1 and Thiele No. 4, respectively. The microspheres were prepared from a kaolinite by a spheroidization technique described by Joshi and Rosauer (1969). Properties are given in Table 1 and representative electron micrographs of the materials are shown in Fig. 1.

Preparation of suspensions

The two kaolinites were first converted to the sodium ion form by repeated washings with a 6N solution of $Na_4P_2O_7$ and Na_2CO_3 (3 : 1 by wt). The pH of the suspensions was then adjusted to 7 at a solids concentration of 5 g/l by further addition of the above solution. The microspheres received no

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Table 1. Properties of kaolinites and microspheres

	pH	Density (g/cm³)	Particle size (wt. %)			
			$< 0{\cdot}5\mu$	$0{\cdot}5$–$2{\cdot}0\mu$	2–10μ	$> 10\mu$
Thiele No. 1*	7·2	2·58–2·63	12–14	67–69	19	0
Thiele No. 4*	4·5	2·58–2·63	30–35	45–50	19	0
Microspheres	6·7	2·6†	0·2‡	4·2‡	95·6‡	0

*Data supplied by Thiele Kaolin Co.
†Pycnometer method.
‡Converted from electron microscope measurements.

chemical treatment. Suspension preparation followed the ASTM method D 422-63 (1968) using the high-speed mechanical stirrer; however, no additional dispersing agent was added. Prepared suspensions were allowed to settle undisturbed in a constant temperature room in standard glass hydrometer cylinders and in specially-prepared Plexiglas cylinders described below. Various solids concentrations were prepared and are indicated where appropriate.

Methods of analysis

A millimeter scale was placed on all suspension cylinders to allow measurements of settling rates and layer widths to be made. Samples were obtained from suspensions in specially-prepared Plexiglas cylinders using a hypodermic syringe. The cylinders were constructed from 48·0 cm lengths of 6·4 cm OD Plexiglas tubing cemented to a flat base. A 0·3 cm vertical slit was milled along one side of the cylinder. Surgical rubber tubing with a 0·3 cm wall thickness was split lengthwise and cemented to the cylinder over the slit (Fig. 2).

Two milliliter samples were taken from the suspension with a hypodermic syringe fitted with a No. 27 needle. Particle concentration measurements were obtained by evaporating 2 ml samples until dry and weighing on a balance accurate to 0·00005 g.

A Siemens Elmiskop I electron microscope was used to obtain information about the particle size and morphology of particles. A drop of suspension taken with the syringe was placed on a carbon-coated copper grid. The dried specimen was then shadowed with 50 Å of germanium to increase contrast and aid in particle thickness measurement. The fluorescent screen of the microscope was imaged on the monitor of a closed-circuit television system for rapid particle size measurement. Magnification on the monitor was 100,000× and size measurements were accurate to $\pm 0{\cdot}005\mu$. A sample of 500 particles was randomly measured for each specimen to reduce the standard error of

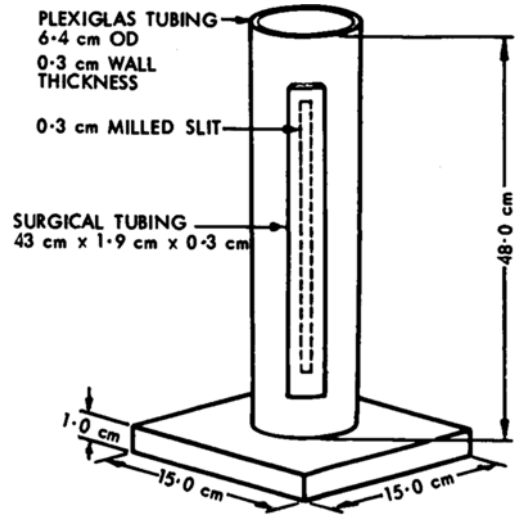


Fig. 2. Plexiglas sampling cylinder (not to scale).

the mean particle size. Since the clay particles had a preferred orientation on the carbon film, a value for the average thickness was obtained by measuring the shadow cast by the particle. This value, corrected for the film thickness using the method described by Rosauer and Wagner (1966), was found to be 200 Å with a maximum variation of ±9 Å. The clay particles exhibited excellent hexagonal habit and therefore the plate diameter could be obtained by use of Feret's statistical diameter.

A Thelco constant temperature oven was used to observe the influence of temperature on layering. The oven temperature could be varied from 20 to 100°C ± 2°C. The sedimentation potential of 5 g/l suspensions was measured in millivolts with a Keithley electrometer Model No. 610B. Two 20 ml platinum wires were inserted through the surgical tubing attached to the cylinders and placed 5 and 20 cm from the bottom of the cylinder. Electrical leads from the electrometer were

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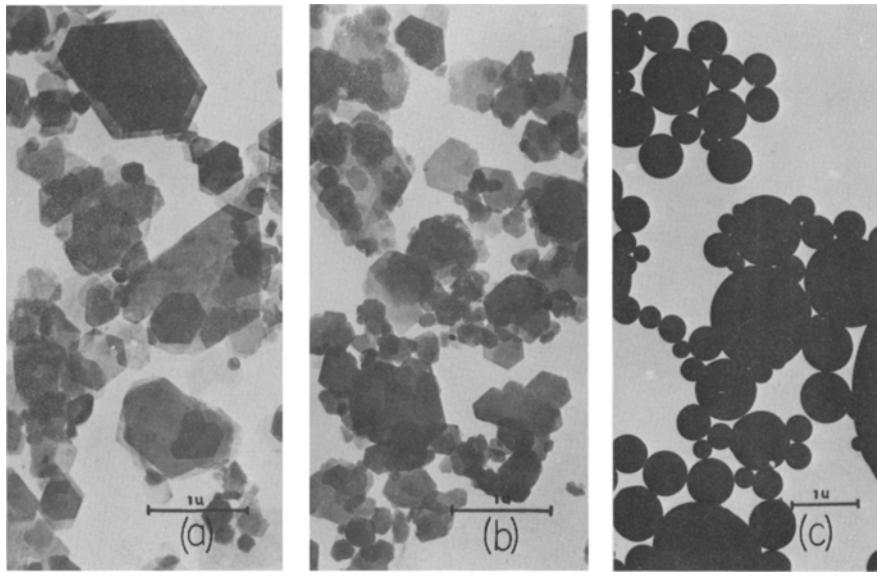


Fig. 1. Representative electron micrographs of materials used. (a) Thiele No. 1; (b) Thiele No. 4; (c) Microspheres.

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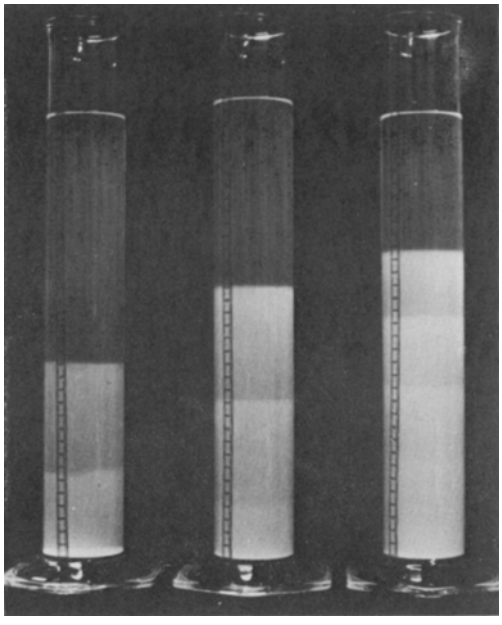


Fig. 3. Thiele No. 1 after 60 days of settling (left to right: 1·0, 2·5, and 5·0 g/l).

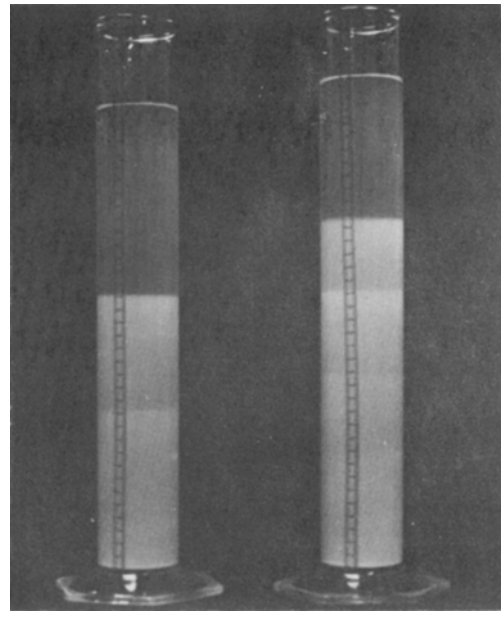


Fig. 4. Thiele No. 1 and No. 4 at 2·5 g/l after 60 days of settling (left, Thiele No. 1; right, Thiele No. 4).

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attached to a Bausch and Lomb strip chart recorder Model VOM 7. The measurements were made immediately upon dispersing the materials in the cylinders and continued for a period of 24 hr.

RESULTS

Effect of concentration on some layer parameters

The following suspensions of all three materials were prepared: 0·1, 0·25, 1·0, 2·5, and 5·0 g/l. Layering was observed in all kaolinite suspensions and in the 2·5 and 5·0 g/l microsphere suspensions. Photographs of typical, aged suspensions are shown in Figs. 3 and 4.

Layer settling rates. The fifteen suspensions indicated above were inspected periodically and, as layers were observed, their position in the column was plotted on graph paper (Fig. 5). Lower layers settle more rapidly than upper layers. This has the apparent effect of increasing the width of the remaining layers with time. A least squares treatment of the plots in Fig. 5 gives values for the settling rates of layers (Table 2). An increase in concentration of the same material significantly reduces the settling rate of comparable layers.

Observations of layers. The ability to plot layer settling rates tacitly assumes that the layers are definitely observable. A review of the data suggested use of the term "time of first observation," i.e. the time required for at least one layer to be clearly recognizable (Table 3). The data show that as the g/l concentration increases more time is required to observe at least one layer. It should be noted that the time of first observation for the kaolinite samples was a period of days, whereas for the microspheres it was a matter of a few hours.

The term "time of first observation" was chosen to avoid specific reference to time of layer formation. In fact, it was impossible to pinpoint the specific time of layer formation due to the masking effect of other particles, and/or the indistinctness of the layers, and/or the long time periods involved. The plots of layer settling rates (Fig. 5) also show that after a certain period of time a given suspension will exhibit a maximum number of layers. The maximum number of layers observed and the time period involved are the values in parentheses in Table 3. Again the masking effect of settling particles may conceal other layers possibly present in the lower part of the suspension. This is particularly true for the 2·5 and 5·0 g/l suspensions of Thiele No. 4 (Fig. 5).

Several suspensions of Thiele No. 1 were observed while aging at elevated temperatures. Concentrations of 0·25 and 0·50 g/l were chosen since they form distinct layers within a reasonable period of time. The data are given in Table 4. Layers were observed sooner in suspensions aged at elevated temperatures. No layering was observed at temperatures of 50°C or above. A constant number of three layers was observed in the 0·25 g/l suspensions regardless of aging temperature. In the 0·50 g/l suspensions more layers appear to form at 30–35°C than at other

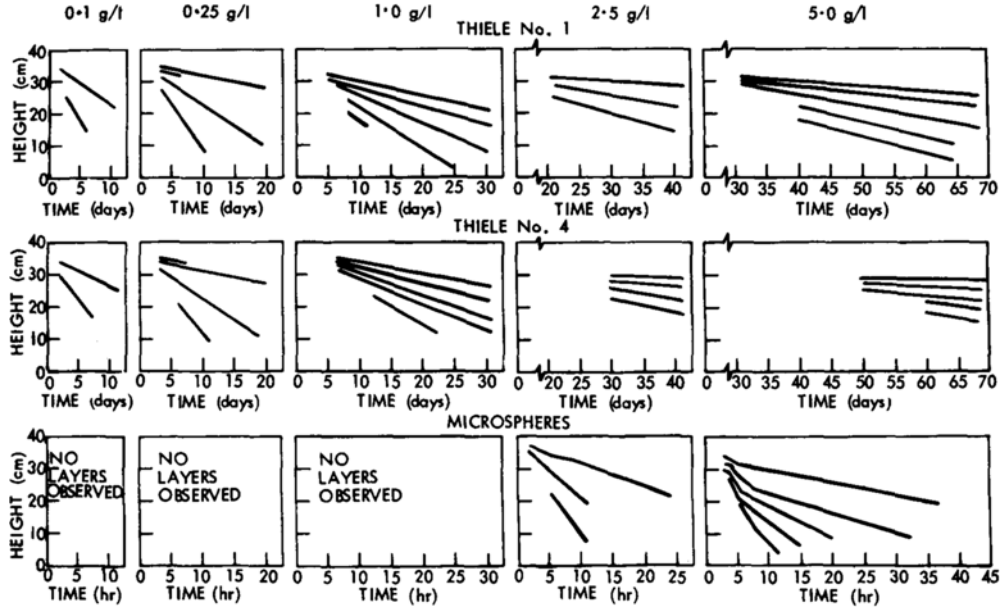


Fig. 5. Effect of suspension concentration on layer settling rates (lines indicate layer tops).

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Table 2. Layer settling rates

Conc (g/l)	Layer number	Settling rate (cm/day) Thiele No. 1	Thiele No. 4	Microspheres
0·1	1	1·73	1·39	
	2	4·90	3·71	
0·25	1	0·74	0·57	
	2	0·66	0·57	
	3	1·26	1·30	
	4	2·86	2·55	
1·0	1	0·39	0·30	
	2	0·55	0·76	
	3	0·83	0·70	
	4	1·23	0·83	
	5	2·07	1·02	
2·5	1	0·25	0·08	17·52
	2	0·34	0·19	40·08
	3	0·50	0·30	115·20
	4		0·39	
5·0	1	0·14	0·02	10·08
	2	0·25	0·09	15·36
	3	0·38	0·18	61·92
	4	0·41	0·28	63·12
	5	0·48	0·36	67·20

Table 3. Effect of g/l concentration on observation of layers and number of layers

Conc (g/l)	Time of first observation (time required to observe max. no. of layers) days	No. layers observed (max. no. layers observed)
Thiele No. 1		
0·1	2 (2)	2 (2)
0·25	3 (3)	4 (4)
1·0	6 (8)	2 (5)
2·5	21 (21)	3 (3)
5·0	31 (40)	3 (5)
Thiele No. 4		
0·1	2 (3)	1 (2)
0·25	3 (5)	3 (4)
1·0	7 (13)	4 (5)
2·5	31 (31)	4 (4)
5·0	50 (60)	3 (5)
Microspheres		
0·1	– (–)	None observed
0·25	– (–)	None observed
1·0	– (–)	None observed
2·5	$\frac{2}{24}$ ($\frac{5}{24}$)	2 (3)
5·0	$\frac{3}{24}$ ($\frac{5}{24}$)	3 (5)

temperatures, suggesting this to be an optimum temperature range for maximum number of layers.

Particle concentration within and between layers

Syringe samples for particle concentration measurements within and between layers were taken from the top, middle and bottom areas of layers formed in 1·0 and 5·0 g/l suspensions of Thiele No. 1 and a 1·0 g/l suspension of Thiele No. 4. Samples were taken when the layer width had become sufficiently large so that syringe samples could be obtained from different, definite

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Table 4. Effect of temperature on layer formation (data obtained from suspensions of Thiele No. 1)

	Conc (g/l)	Max. no. layers observed	Time required to observe max. no. of layers (days)
20°C	0·25	3	3
	0·5	4	5
30°C	0·25	3	3
	0·5	5	5
35°C	0·25	3	3
	0·5	5	4
40°C	0·25	3	2
	0·5	4	3
50°C	0·25	None observed	
	0·5	None observed	

and therefore meaningful depths. The data obtained are given in Table 5 and plotted in Fig. 6. The following observations may be made from the data:

(i) The concentration of particles was higher at the top of any given layer than at its bottom. Exceptions to this are believed due to sampling error, i.e. the volume sampled at layer boundaries may have inadvertently included some material from neighboring layers due to the width of the volume withdrawn.

(ii) Lower layer tops had increasing solids concentrations. The average solids concentration values show this same trend.

(iii) At the same original concentration, e.g. 1·0 g/l, layers in Thiele No. 4 had higher solids concentrations than comparable layers in Thiele No. 1.

(iv) Layer tops in the 5·0 g/l Thiele No. 1 suspension had slightly more than five times the number of particles than did layer tops in the 1·0 g/l Thiele No. 1 suspension. This is remarkable in view of the fact that there was a period of 40 days between sampling dates.

Particle size within and between layers

Syringe samples for particle size measurements were taken from the top, middle, and bottom areas of the upper two layers formed in 1·0 g/l suspensions of Thiele No. 1 and No. 4 and a 5·0 g/l suspension of microspheres. Again, samples were taken after layer widths had become sufficiently large. The electron microscopic size data for the Thiele samples were converted to equivalent diameters. The mean and the maximum equivalent

Table 5. Particle concentration within and between layers

	Original conc (g/l)	Layer no.	Particle conc observed in layers after settling (g/l)			
			Top	Middle	Bottom	Average
Thiele No. 1	5·0*	1	0·40	0·32	0·39‡	0·37
		2	1·60	1·25	1·10	1·32
		3	1·75	1·70	1·60	1·68
		4	1·90	—	—	—
Thiele No. 1	1·0†	1	0·07	0·07	0·27‡	0·13
		2	0·30	0·23	0·30‡	0·28
		3	0·32	0·30	0·24	0·29
Thiele No. 4	1·0†	1	0·20	—	0·16	0·18
		2	0·58	—	0·40	0·49
		3	0·74	—	0·60	0·67
		4	0·77	0·61	0·49	0·93

*After 57 days of settling.
†After 17 days of settling.
‡Possible sampling error.

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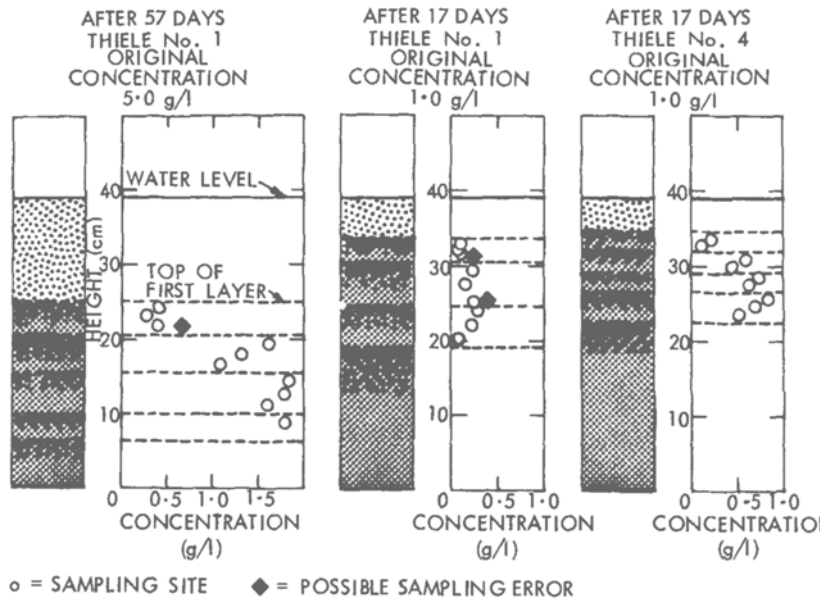


Fig. 6. Particle concentrations within and between layers.

diameters are presented in Table 6. The data for all Thiele samples display a remarkable uniformity in both mean and maximum equivalent diameters. This is even more significant since the samples were obtained from different depths in the suspension, e.g. the distance between the top of the first layer and the bottom of the second layer in the Thiele No. 1 suspension is 7·3 cm. The mean and maximum diameters of the microspheres are also fairly uniform over a depth of 6·6 cm. The microsphere diameters are larger than the Thiele diameters due to the shorter sampling time.

Sedimentation potential

The results of sedimentation potential measurements are given in Fig. 7 for 5·0 g/l suspensions. All samples showed an initial sedimentation potential of >100 mV which decreased to constant values in 1–2 hr.

DISCUSSION

Particle size

Observations of all suspensions indicate that Stokesian sedimentation occurs, i.e. particle

Table 6. Equivalent diameters of layer particles in suspensions of Thiele No. 1 and No. 4 and microspheres

	Thiele No. 1*		Thiele No. 4*		Microspheres†	
	Mean μ	Maximum μ	Mean μ	Maximum μ	Mean μ	Maximum μ
First layer						
Top	0·10 ± 0·01	0·28	0·11 ± 0·01	0·27	0·51 ± 0·05	1·70
Middle	0·10 ± 0·01	0·27	0·11 ± 0·02	0·26	0·61 ± 0·06	2·00
Bottom	0·10 ± 0·01‡	0·27	0·10 ± 0·01	0·27	0·65 ± 0·08	2·00
Second layer						
Top	0·10 ± 0·01	0·28	0·11 ± 0·01	0·27	0·68 ± 0·06	1·70
Middle	0·11 ± 0·01	0·27	0·10 ± 0·01	0·27	0·56 ± 0·06	2·40
Bottom	0·09 ± 0·01‡	0·26	0·11 ± 0·01	0·27	0·53 ± 0·05	2·10

*1·0 g/l after 17 days of settling.
†5·0 g/l after 5·5 hr of settling.
‡Possible sampling error.

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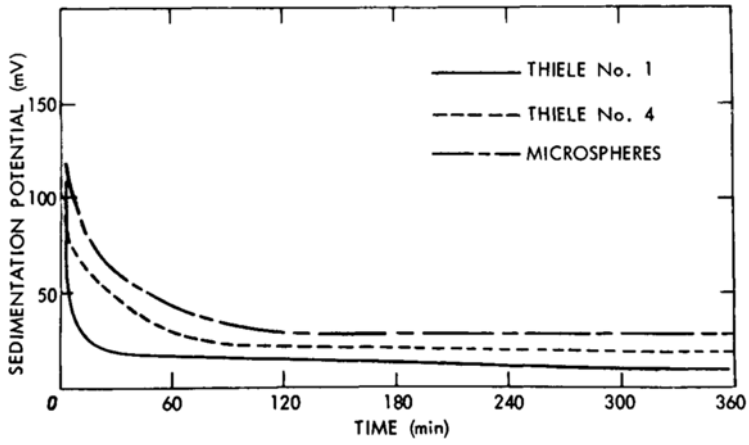


Fig. 7. Sedimentation potential of 5·0 g/l suspensions.

concentration increases toward the bottom of the suspension. The observed layers appear superimposed on this normal particle concentration gradient. The question arises if the maximum sizes of the particles measured in the layers are within the limits defined by Stokes law. Table 7 gives the Stokes diameters for particles which would be present at the same suspension depth where the maximum measured particles are found. Table 7 also presents particle diameters calculated from layering settling rates, i.e. the diameter of a particle which would settle at a rate equal to the layer settling rate. In this calculation it is assumed that the layers are stable, i.e. that particles do not move from one layer to another once a layer forms.

The fact that the maximum measured Thiele diameters are larger than the Stokes diameters suggests that another mechanism is successfully competing with Stokes sedimentation. Comparison of the average Thiele diameters to their respective layer-settling-rate-diameters indicates that the average diameter particles are settling at a rate equivalent to the rate of particles at least twice their size. Particle size distribution plots (not presented here) for the Thiele layers show maxima around 0·08–0·09μ .

The maximum measured microsphere diameters are permissible in terms of the Stokes diameters; however, the values for the respective layer-settling-rate-diameters suggest that these large microspheres are not settling as rapidly as might be expected. Figure 8 is the particle size distribution of the first and second layers and the original sample of a 5·0 g/l microsphere suspension. Since the curves progress asymptotically above the 2·0μ size, this information is not included in the figure. The unusual increase in the number of 0·3–0·7μ particles is not expected as a result of Stokesian sedimentation and suggests that this size range is particularly susceptible to a mechanism responsible for their position in a suspension. It is emphasized that particle size measurements as conducted in this investigation give no information with regard to particle association in suspension.

Table 7. Comparison of various particle diameters

	Thiele No. 1		Thiele No. 4		Microspheres	
	1st Layer	2nd Layer	1st Layer	2nd Layer	1st Layer	2nd Layer
Average diameter	0·10 ± 0·01*	0·10 ± 0·01*	0·11 ± 0·01*	0·11 ± 0·01*	0·59 ± 0·06†	0·59 ± 0·06†
Max. measured Diameter	0·28*	0·28*	0·27*	0·27*	2·00†	2·40†
Stokes diameter	0·20*	0·25*	0·19*	0·22*	2·32†	2·66†
Layer-settling-Rate-diameter	0·22	0·26	0·20	0·30	1·14	1·41

*After 17 days of settling.
†After 5·5 hr of settling.

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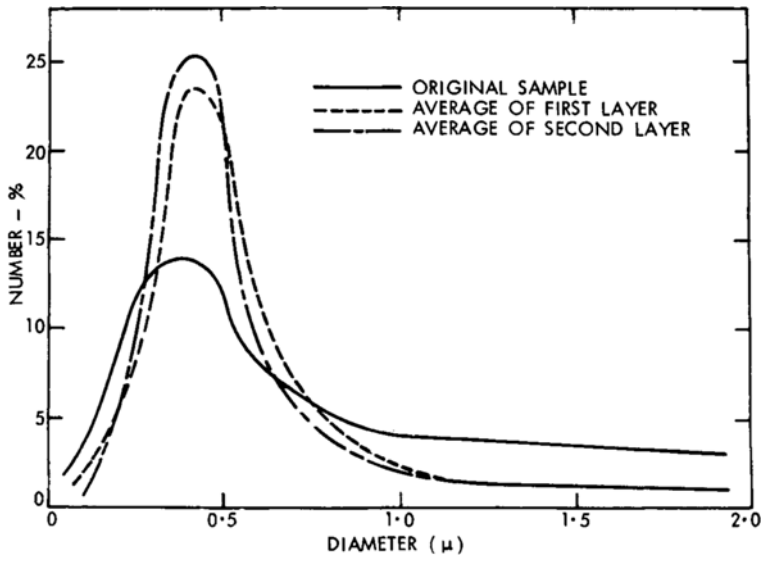


Fig. 8. Particle size distribution in layers of a 5·0 g/l microsphere suspension.

Particle concentration

Since the mean diameter of layer particles in both Thiele No. 1 and No. 4 is constant at 0·10–0·11 μ, a correlation in particle concentration of comparable layers in these two samples could be expected. Thiele No. 4 has 2·5× more particles $<0{\cdot}5\,\mu$ than Thiele No. 1; therefore, at the same g/l concentration comparable layers in Thiele No. 4 should have 2·5× more particles 0·10–0·11 μ in diameter than Thiele No. 1. An approximate 2·5-fold increase in particle concentration in Thiele No. 4 layers is found (Table 5). When particle concentrations of layers in a 1·0 g/l suspension of Thiele No. 1 are compared to comparable layers in 5·0 g/l suspension of Thiele No. 1, a five-fold increase is found. It is noteworthy that this last group of layer samples was taken 40 days apart and that the position of comparable layers in suspension differed by 8·6–10·2 cm.

The above correlations are interpreted as indicating that the factors responsible for layer formation in these suspensions are fairly selective with regard to particle size, specifically particles $<0{\cdot}5\,\mu$ for the Thiele samples and particles between 0·3–0·7 μ for the microspheres.

Layer observations

The maximum number of layers observed in suspensions tends to be a function of the solids concentration, i.e. as the original g/l concentration is increased, the maximum number of observable layers is similarly increased (Table 3). Since the Thiele layers contain only particles $<0{\cdot}5\,\mu$, the expected layering behavior of comparable g/l suspensions is that Thiele No. 4 should have more layers than Thiele No. 1. Although layers in Thiele No. 4 appear denser and were observed later than layers in Thiele No. 1, no definite linear increase in the number of layers was found. It is conceivable that more layers are indeed present toward the bottom of the cylinder in the high g/l suspensions and that these layers are masked by the other particles undergoing sedimentation (Figs. 3 and 4). Support for this interpretation is given by the microsphere suspensions. Since only 4·2 per cent of the microspheres are $<2{\cdot}0\,\mu$, and layers in microsphere suspensions appear within a few hours, this would indicate that particles $\gg 2{\cdot}0\,\mu$ effectively mask layers already present.

In all suspensions, lower layers have higher particle concentrations and settle more rapidly than the upper layers. However, the data also show that the mean particle size between layers of one material is statistically identical. This apparent ambiguity may be resolved by proposing that the layers are behaving as though composed of "particle associations," not individual particles. Another explanation must be sought why comparable layers in one material settle less rapidly as the g/l concentration is increased.

Particle interaction and layer formation

Data presented by Perry (1950) and more recently by Pruppacher and Steinberger (1968)

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strongly indicate that the drag coefficient between spheres and discs is essentially identical at the extremely low Reynolds number calculated for the largest kaolinite plate found in a layer. This, therefore, indicates that settling behavior is not strongly dependent on the geometry of the falling particle and justifies conversion of the measured kaolinite plate sizes to equivalent spherical diameters. Perry (1950) states that: (i) Brownian motion due to gravitational settling. Booth (1954) gravitational settling velocity of a particle; (ii) it becomes appreciable for particles under $3\,\mu$ in diameter; and (iii) for particles $< 0{\cdot}1\,\mu$ in diameter it has a far greater magnitude than any directed motion due to gravitational settling. Booth (1954) also showed that the sedimentation velocity of particles may be reduced because of an interaction between the charge on a particle and the modified double layer field. Elton and Hirschler (1954) stated that settling particles experience an "electroviscous resistance" due to the potential gradient set up by the charge on the falling particle. They found, for example, that "the rate of separation of $2\,\mu$ particles from $1\,\mu$ particles is about 15 per cent less than in the absence of electroviscosity." The effect becomes less significant with larger particles.

Another hypothesis may also be advanced to account for the apparent selectivity of a certain particle size in layers, e.g. particles $< 0{\cdot}28\,\mu$ in the Thiele layers. Large particles subject primarily to Stokes settling generate a potential gradient. This electric potential may be sufficiently large enough to cause particles with an average diameter of $0{\cdot}10\,\mu$ to move upwards in the suspension. The sedimentation potential developed has a finite value which is proportional to the particle concentration, particle velocity and zeta potential. The finite value of this potential would be reflected by a maximum particle size able to be influenced in this manner. It is suggested that the maximum particle size measured in the Thiele layers ($0{\cdot}28\,\mu$) represents the upper limit of such electrophoretic mobility. The absence of particles $> 0{\cdot}28\,\mu$ lends credence to this interpretation. This type of particle movement may be considered as an extension of the "electroviscous resistance" previously mentioned; however, since such particle mobility is preponderantly an electrophoretic phenomena, it would be more accurately termed electrophoretic or electrokinetic mobility. In view of the above considerations the following mechanisms for observed layer formation are proposed.

The electrokinetic effect on Thiele layer particles is indicated by the presence of $0{\cdot}27$–$0{\cdot}28\,\mu$ diameter particles. Brownian motion dominates distribution of particles $< 0{\cdot}28\,\mu$ in diameter (i.e. with an average diameter of $0{\cdot}10\,\mu$). This leads to an increase in local particle concentration, or stated another way, a smaller interparticle distance. The influence of the electric double layer results in interparticle attraction and/or association and stabilizes the particles to form layers. The layers then settle as though composed of particles larger than the average diameter particle. Lower layers would settle more rapidly than upper layers since lower layers would have larger particle associations. The fact that lower layer tops have increasing particle concentrations substantiates this.

The distribution of microsphere particles is similarly influenced. Microspheres $> 2{\cdot}40\,\mu$ are predominantly subjected to gravity sedimentation. The few microspheres $1{\cdot}70$–$2{\cdot}40\,\mu$ diameter are present in layers due to the electrokinetic effect; otherwise gravity would have effectively removed them from suspension. Microspheres $< 1{\cdot}70\,\mu$, and particularly those in the range $0{\cdot}3$–$0{\cdot}7\,\mu$, are susceptible to Brownian motion. The microspheres probably have different electric double layer characteristics than the kaolinite plates; however, due to increased particle collisions as a result of Brownian motion, an interparticle association is set up. This stabilizes the layer, which in turn settles as though composed of particles larger than the average diameter particle.

Comments on the exact nature of the interparticle association in layers would be purely speculative on the basis of available information. It is, however, fairly certain that a definite particle concentration – or interparticle distance – must be obtained before layers form. Two identical suspensions of kaolinite were prepared and after some time, four definite layers were observed. The first suspension was resuspended by the end-over-end method for 1 min. The four layers in the second suspension were separated from the sediment by pipette. The volume was brought up to the original 1 l mark for the pipetted layers and the suspension was subjected to the end-over-end treatment for 1 min. The first suspension showed a repeat performance of four layers. The second suspension of resuspended layers exhibited only two layers. Due to dilution of potential layer-forming particles a critical particle concentration, i.e. a smaller interparticle distance, was not obtained. This dilution may also be considered as a reduction of the probability that Brownian motion might be responsible for increased particle collisions.

All Thiele suspensions exhibit a sharp boundary between what appears to be a clear supernatant liquid and the top of the first layer. Upon closer inspection the supernatant is very slightly milky. Electron microscopic analysis of a sample from the supernatant shows that the particles present have the same average diameter ($0{\cdot}10\,\mu$) and maximum

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size (0·28 μ) as the particles in layers. The amount of such particles present is below the critical particle concentration necessary for layer formation.

Mention has been made of Brownian motion as a means by which particle movements and collisions result in an interaction of electric double layers and eventually an interparticle attraction and/or association. This process is temperature dependent. At 30–35°C the degree of Brownian motion is such that the particle collision energy is slightly less than the interparticle attraction energy. Particles approach one another or collide, electric double layers interact, and an interparticle association forms. At 50°C and above, the increased Brownian motion keeps the majority of potential-layer-forming particles in random distribution. Suspensions aged at 50°C are uniformly milky and exhibit no layering. The observed decrease in the maximum number of layers and the time required to observe such layers at 35 and 40°C (Table 4) represents a compromise between increased Brownian motion and decreased viscosity of the liquid. Since the particle settling velocity is inversely proportional to the viscosity of the liquid, it appears that at these temperatures the larger particles which normally mask layers settle at a faster rate. Hence layers are observable sooner.

Available evidence gives no information regarding the characteristics of the electric double layer. Values for the sedimentation potential, however, do indicate that the configuration around a Thiele particle is different than that around a microsphere. Thiele No. 4 has more particles between 0·28–0·50 μ and a higher sedimentation potential than Thiele No. 1 (Fig. 7). The relatively slow settling rate of Thiele No. 4 layers, therefore, appears due to the large amount of particles $< 0{\cdot}5\,\mu$. The decrease in settling rate as the g/l concentration is increased is a reflection of a larger electrokinetic effect due to the increase in sedimentation potential. The microsphere suspension had an even higher sedimentation potential than did Thiele No. 4. This is interpreted as suggesting different electric double layer characteristics. The larger particle size in the microsphere suspension increases the potential without decreasing the settling rate as was the case in the Thiele suspensions. This is evidence that the relatively large microsphere particles are predominantly subjected to gravity settling.

Since the layers are initially masked by other particles, it is difficult to determine with absolute certainty the position where layers form. This explains why the settling rate curves for layers first begin after some finite time. However, some information may be gained by extrapolating the settling rate curves in Fig. 5 to zero time. The extrapolated origin thus obtained can be correlated with the per cent particles $< 0{\cdot}5\,\mu$ as follows: with an increase in the per cent particles $< 0{\cdot}5\,\mu$ the extrapolated origin is found further below the water surface, i.e. deeper in the suspension. The significance of this correlation is as yet undetermined. Additional questions may also be posed; for example: Do all layers eventually observed in a suspension form simultaneously or do they form successively? Is the assumption that particles do not move from layer to layer with settling time valid?

CONCLUSIONS

Colloidal suspensions exhibit the layering phenomenon under appropriate conditions of particle size, electric double layer characteristics, temperature and time. The following are proposed as possible sequential mechanisms involved in layer formation. The settling rate of particles larger than a certain critical size is primarily determined by gravity or electrokinetic resistance depending on particle size and characteristics of the electric double layer. Such particles are responsible for masking layers which may already be present. Particles below the critical size are competitively influenced by the electrokinetic effect, Brownian motion and gravity. Particles particularly susceptible to Brownian motion may approach one another sufficiently close (or collide) so that their respective electric double layers interact and an interparticle attraction or association results. This is observable as a layer. The particles in this layer then no longer settle as individual particles, but at a rate corresponding to twice the size of the average particle size.

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Résumé – Des suspensions vieillissantes de microsphères et deux kaolins présentent plusieurs couches horizontales. La concentration des particules est plus grande en haut d'une couche; le haut des couches inférieures ont des concentrations de particules croissantes. Les couches inférieures décantent plus rapidement que les couches supérieures; toutefois, une hausse de la concentration d'origine des suspensions entraîne une élévation proportionnelle de la concentration des particules des couches comparables qui se mettent alors au repos plus lentement. Le diamètre moyen équivalent des particules à l'intérieur et entre les couches de kaolin est identique. Les diamètres maximaux mesurés sont aussi identiques. Une dernière décantation des couches en suspension ne donne pas pour résultat des couches observables dans les sédiments. Les données sont interprétées comme indiquant le fait que dans une suspension colloïdale les particules agissent entre elles pour donner des couches horizontales définies observables. On propose un mécanisme cyclique pour la formation des couches.

Kurzreferat – Gealterte Suspensionen von Mikrosphären und zwei Kaoliniten weisen mehrere horizontale Schichten auf. Die Teilchenkonzentration ist oben in der Schicht größer. Je tiefer die Schicht umso größer is die Teilchenkonzentration oben in der Schicht. Die unteren Schichten setzen sich auch schneller ab als die oberen Schichten. Eine Erhöhung der ursprünglichen Suspensionskonzentration führt jedoch zu einer proportionalen Erhöhung der Teilchenkonzentration vergleichbarer Schichten und hat zufolge, daß sich solche langsamer absetzen. Der durchschnittliche äquivalente Durchmesser von Teilchen innerhalb und zwischen Kaolinitschichten ist identisch. Die maximalen gemessenen Durchmesser sind ebenfalls identisch. Mikrosphärenschichten zeigen eine ähnliche Gleichmäßigkeit, was die durchschnittlichen und Maximaldurchmesser anbelangt. Die endgültige Absetzung der Schichten in Suspensionen führt nicht zu erkennbaren Schichten in dem Sediment. Die Daten weisen darauf hin, daß Teilchen in einer kolloidalen Suspension so zusammen wirken, daß sie als definitive horizontale Schichten kenntlich werden. Eine Folge von Mechanismen für die Schichtenbildung wird vorgeschlagen.

Резюме—Подвергшиеся старению суспензии каолинитовых микросфер и частиц двух хорошо окристаллизованных каолинитов состоят из нескольких горизонтальных слоев. Концентрация частиц выше в верхней части каждого слоя; верхние части нижнего слоя отличаются возраста ющей концентрацией частиц. Нижние слои образуются более медленно, чем верхние; увеличе ние начальной концентрации в суспензии имеет следствием пропорцианальное увеличение концентрации частиц в сопоставимых слоях и более медленное их формирование. Средний эквивалентный диаметр частиц в каолинитовых слоях и между ними одинаков. Максимальные измеренные величины диаметра частиц также одинаковы. Слои микросфер обнаруживают аналогичное единообразие средних и максимальных диаметров. Окончательное формирование слоев в суспензии не приводит к образованию осадка, состоящего из различных слоев. Полученные данные рассматриваются как указание на то, что в коллоидной суспензии частицы взаимодействуют с образованием различимых горизонтальных слоев. Предложено объяснение последовательного механизма образования слоев.

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