

DEPOSITION OF MONTMORILLONITE FROM SUSPENSION DURING FLOW THROUGH POROUS MEDIA*

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ABSTRACT

SODIUM-SATURATED montmorillonite was used to prepare aqueous suspensions of varying concentration between 0.06% and 3.0%. Compacted columns of glass beads and carborundum constituted the porous media. The system was maintained under saturated flow conditions at hydraulic gradients of 2 and 4. In order to study the relationship of clay properties to those of the porous media, the zeta potential of both suspension and media was determined. A mathematical model of the system was developed that would predict the deposition of clay at various depths in the columns, given concentration and flow rate of the suspensions. In order to test this model, a procedure was developed for tagging the clay with ^{46}Sc , sampling the columns, and determining the amount of deposition using a single-channel gamma-ray spectrometer. Using an activity level of 0.15 microcurie per liter of a 1% suspension it was possible to detect reliably 10 mg of clay in a 40 g sample of the porous media. The results indicate two mechanisms operating in the process of removal of the clay from suspension. One of these, interstitial straining, operates at the surface of the porous media column; while the second, a combination of diffusion and gravitational settling, operates below the surface.

The results of this research have potential applications in the solution of engineering problems relating to water resources conservation such as reservoir seepage control, infiltration of sediment-laden water into the soil, and ground water recharge. Also, the results may be important for answering questions concerning pollutant movement into the water supply through porous strata. All the above are examples in which a colloidal suspension is moving into or through porous media; therefore, an improved understanding of the principles of flow of colloidal suspensions in porous media can contribute to the solution of these engineering problems.

INTRODUCTION

THE efficient conservation and utilization of water is an important problem in agriculture, industry, and domestic life today. Conservation requires, for

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example, the reduction of seepage from reservoirs and conveyance systems. Efficient utilization demands improvements in filtration and other pollution removal systems. The phenomena of the movement of water, laden with colloidal-size particles into and through porous media such as soils, gravel beds or filter sands, is involved in many aspects of the conservation and utilization of water. This study was initiated to investigate the principles involved in the flow of colloidal suspensions in porous media. In order to understand the factors affecting this movement, it is necessary to isolate the system and study it under controlled conditions. An attempt was made to isolate the physical and chemical properties of the system by using inert materials for the media. The suspensions were prepared using Wyoming bentonite in order to limit the suspended material used to a widely studied clay colloid.

Specific objectives of this study included determination of the relevant physical and chemical properties of both the media and the suspension, and the development of a model of the flow system that would relate the properties of the system to the quantity and location of deposition of the clay in the porous media during flow. The model would also be used to give some degree of understanding to the mechanism operating in the removal process.

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MATERIALS

As was stated previously, inert materials were chosen for the porous media. Carborundum (silicon carbide granules) and glass beads were used. Both are relatively inert. The carborundum has a rough angular particle shape with a density of 3.2 g/cm^3 , while the glass beads are spherical with a density of 2.5 g/cm^3 . The selection of these two materials also provided a variation in particle shape as shown in Plates 1 and 2.

The suspensions were prepared from Wyoming bentonite (Vol-Clay), which is a Na-montmorillonite, and de-aired, deionized water. The suspension of the clay was accomplished by vigorous mixing after a period of wetting. The suspensions were prepared at a slightly higher concentration than the desired concentration by weight of dry clay and then let stand for 24 hr to remove all coarse material. The suspension to be used was then decanted from the original and restirred. This produced stable suspensions with particle sizes less than 2 microns.

The properties of the porous media determined were particle size distribution, porosity of the compacted column, and zeta potential of the media in the column. The zeta potential was calculated from measurements of the streaming potential made on a column of the porous media using the Helmholtz-Smoluchowski equation. The carborundum or glass beads were placed in a Teflon cylinder (4.3 cm in diameter and 15.0 cm long). Platinum screen

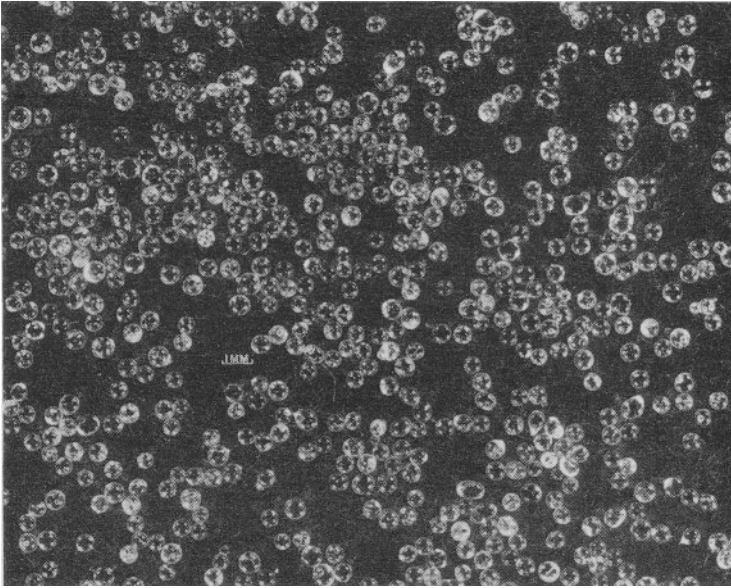


PLATE 1. Photomicrograph of glass beads.

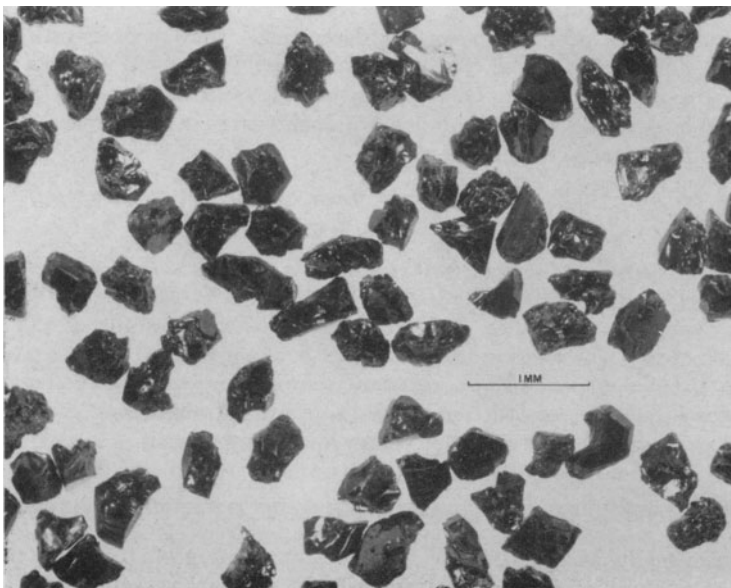


PLATE 2. Photomicrograph of carborundum.

electrodes were placed in both ends of the column. The columns were filled under water and compacted to as uniform a porosity as possible. The columns were maintained under a positive constant head and washed with deionized de-aired water until the conductivity of the outflow was approximately equal to the inflow conductivity. Temperature was controlled in the laboratory at $23^{\circ}\text{C} \pm 1$. After washing, the streaming potential was measured during flow with an electrometer-amplifier and recorded. The column and flow control tank were located inside an electrostatically shielded enclosure to increase the stability of the measurements. The zeta potential was calculated using the Helmholtz-Smoluchowski equation

$$\zeta = \frac{4\pi\eta\lambda_s\Delta E}{PD} \quad (1)$$

where ΔE is the streaming potential (millivolts), P is the pressure causing flow (centimeters), D is the dielectric constant of the liquid (dimensionless), η is the viscosity of the liquid (poise), and λ_s is the electrical conductivity of the liquid (mhos per centimeter). It was necessary to modify the electrical conductivity term in the equation because it was developed for flow in capillaries. To apply the equation to a porous medium, the term electrical conductivity of the liquid in the pores of the media was introduced. This term, λ_s , was determined by measuring the cell constant of the column with an electrolyte strong enough to suppress the surface conductivity of the medium. This cell constant was then used to calculate the electrical conductivity of the liquid in the pores.

The properties of the suspension determined were concentration, pH, viscosity, and zeta potential. The viscosity of each suspension was determined with a Brookfield Synchro-Lectric rotating viscometer. The zeta potential was calculated using the Helmholtz-Smoluchowski equation rearranged for electrophoretic measurements, *i.e.*

$$\zeta = \frac{4\pi\eta\nu}{HD} \quad (2)$$

where ζ is the zeta potential (millivolts), η is the viscosity (poise), ν is the velocity of the particles (microns per second), H is the applied electrical field (volts per centimeter), and D is the dielectric constant of the liquid (dimensionless). The electrophoretic velocity was measured using a modified Burton U-tube suspended in a constant temperature bath. A voltage of 75 volts was applied across the suspension and rate of movement of the interfaces was measured with a cathetometer and a stop watch.

THEORETICAL DEVELOPMENT OF THE MODEL

The generally accepted theory of filtration presented in the literature, based on research on water filtration systems, was first presented by Iwasaki (1937). The theory stated that the removal of particles from the flow is

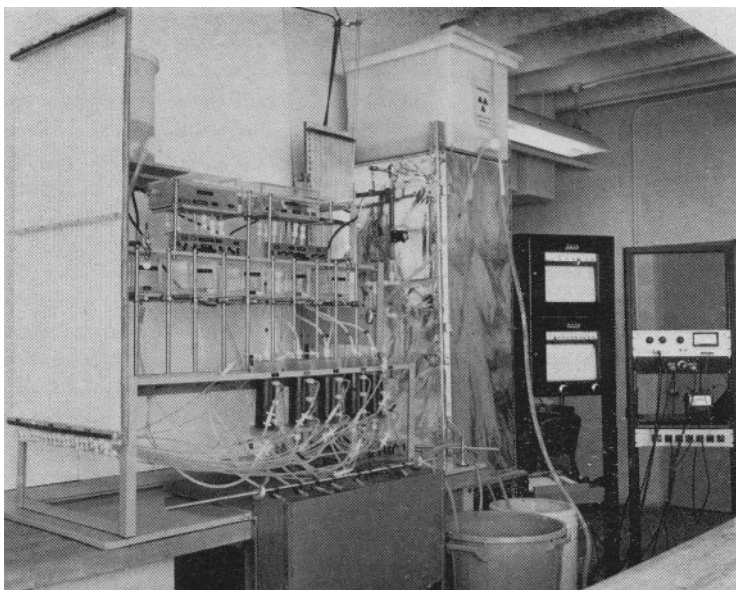


PLATE 3. Side view of equipment in operation, including inflow and outflow tanks, permeameters (filled with carborundum), recorders, electrometer-amplifier, and manometers.

proportional to their concentration in the flow. Stated mathematically, the theory is

$$\frac{\partial C}{\partial Z} = -rC \quad (3)$$

where: C = the concentration of the suspension (g/cm^3),

Z = depth from the surface of the filter,

r = distance rate factor (centimeter^{-1}).

In addition the continuity equation holds, i.e.

$$\frac{\partial W}{\partial t} = -V \frac{\partial C}{\partial Z} \quad (4)$$

where: W = weight of material deposited per unit volume of the filter (g/cm^3),

t = time in minutes,

V = velocity of flow (centimeters per minute).

Several assumptions were made in the development of these equations. First, the suspension is homogeneous applied at a constant rate under laminar-flow conditions to an isotropic homogeneous porous filter medium. Second, the particles of the suspension are significantly affected by gravity.

Third, if particles of the suspension come close enough to particles of the media they will be attracted and held on the surface by Van der Waals-type forces.

If it is further assumed that creep flow is negligible and that the mechanism of removal is the same throughout the filter, equations (1) and (2) can be solved simultaneously and integrated to produce,

$$W = V_r C_0 t e^{-r z} \quad (5)$$

where in addition to the previously described symbols,

C_0 = initial concentration of the suspension (g/cm³).

This theory has been studied and modified by Ives and co-workers (1960, 1965) for application to the design of rapid sand filters. Hall (1957) attempted to relate this theory to depth of penetration in filters. He identified interstitial straining and gravitational sedimentation as two important mechanisms of removal.

In order to study the factors affecting the removal of clay from stable suspensions flowing through porous media, the theory mentioned above was applied to this system. Several of the assumptions made in developing the above theory for the rapid sand filter may not be completely valid for the system reported here. Nevertheless, it was appropriate to use equation (5) to see if it would predict the behavior of the system under study.

EXPERIMENTAL

In order to check the validity of equation (5), a procedure was developed to determine the amount of clay deposited at particular depths in the column of porous media in a given time. Sampling, separation of clay from the porous media, and gravimetric determination of the amount of clay proved to be unsatisfactory because of problems of separation and lack of sensitivity.

Selection of Isotope

The possibility of incorporating a radioactive isotope into the clay complex in order to trace the movement and deposition of the clay was investigated. ⁴⁶Sc was used by McHenry and McDowell (1962) in sediment transport studies by bonding it to the surface of quartz grains. This particular isotope was found to have the desired characteristics for this study. ⁴⁶Sc is a gamma emitter with a moderate energy level, having photopeaks at 0.89 and 1.2 meV, which would be sufficient energy to penetrate the sample in order to be detected. The half-life of the isotope is 84 days, which is long enough so that decay during a test period (approximately 24 hr) would be insignificant, yet short enough to make the disposal of used material as simple as possible. ⁴⁶Sc has an atomic size and weight of the same order of magnitude as calcium, sodium, and magnesium (ions commonly found on the exchange

complex of the clay) and therefore would reduce the probability of preferential attachment or repulsion between particles of clay and media.

The isotope has a valence of +4 and therefore would be strongly bonded to the clay complex reducing the possibility of reaction with the surface of the media. This criterion was necessary in order that a determination of radioactivity be a true measure of clay content.

The detection system used was a single-channel spectrometer with a solid 3×2 in. NaI (Tl) scintillation crystal. Three inches of lead shielding surrounded the crystal. Cross sections of the columns were taken to represent, geometrically, horizons in the column and counted by placing them directly on the top of the crystal. With this system, the background counting rate was typically ten counts per minute. This low background enabled the level of activity of ^{46}Sc in the suspension to be kept low, reducing the radiation health hazard, but still provided adequate sensitivity.

Two preliminary tests were conducted to substantiate the assumption that the isotope was held tightly to the clay. A check was made to determine if the isotope diffused into the liquid from the suspended particles and to determine if there was any exchange of ^{46}Sc between the clay and the porous media. Both cases gave negative results; therefore, ^{46}Sc was a satisfactory isotope for tagging clay in this system. A more detailed description of the instrument selection and design, and the procedure used in this phase of the study are given by Curry (1966).

Procedure

The granular materials were placed in permeameters 18 cm long and 5.1 cm in diameter with manometer taps located along the side. The permeameters were filled under water and compacted to produce a uniform porosity. The columns were maintained under a constant head for both the initial flow of water and suspension. A schematic of the system is shown in Fig. 1. The laboratory temperature was controlled at $23^\circ\text{C} \pm 1$. The columns were washed until the conductivity of the outflow was approximately equal to the conductivity of the inflow water. The suspension was then introduced into all columns and allowed to flow in the first column for approximately $1\frac{1}{2}$ hr after outflow from the column had begun. The flow in the first column was then switched to water and the column was washed until clay particles still in suspension in the media were removed. This procedure assured that the clay measured in the column was removed by the media and not excess suspension in the pores. The same procedure was followed for the remaining columns at $1\frac{1}{2}$ -hr intervals. This variation in time of flow provided a means for determining the relation between rate of removal and time. Immediately after washing, each column was drained and sectioned at intervals along the columns. These samples were placed in plastic cups, the same diameter as the column, and the activity determined with the spectrometer system (counting each sample for 30 min). The activity of a sample of the suspension

used in the particular test was also determined. Calculation could then be made of the amount of clay in each section of the column. The amount of clay retained in the columns could be determined with a sensitivity of 1×10^{-4} g of clay per cubic centimeter of the porous media. A total of twenty-eight tests were made.

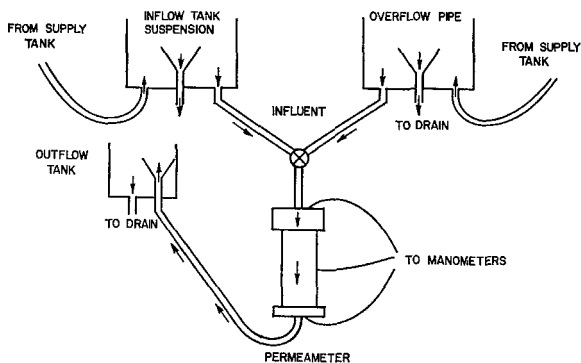


FIG. 1. Flow diagram of the system.

RESULTS

The theory indicates that the relationship between the amount of clay retained in the column at any point and the depth from the surface is exponential and should be linear on a semi-log plot. The rate factor (r) would then be related to the slope of this line. The twenty-eight tests provided 133 individual columns on which the applicability of the theory could be checked. All tests were replicated. The value for the amount of clay in the cross-section samples was corrected for background, radiation decay, differential absorption by varying thicknesses of samples, and weight variance of the samples.

Examples of the results are shown in Figs. 2, 3, and 4. Figure 2 shows the amount of deposition plotted against depth from the surface on semi-log paper. The calculated linear regression line was drawn to show the degree of fit. Figure 3 shows the same information but for a longer column used to determine effect of depth of the column on deposition of the clay. The effect of time on deposition is shown in Fig. 4. Each curve represents a column of the same test in which the suspension had been allowed to flow for different periods of time.

Table I presents a summary of the results. Both hydraulic data and deposition data are given. The particle size is the mean size of the particular group of material. The uniformity coefficient was approximately one for all tests except two series in which combinations of sizes were prepared to produce media with a larger uniformity coefficient. The porosity and intrinsic permeability were calculated from measured data and represent averages of several individual columns in each size class. The suspension concentration was

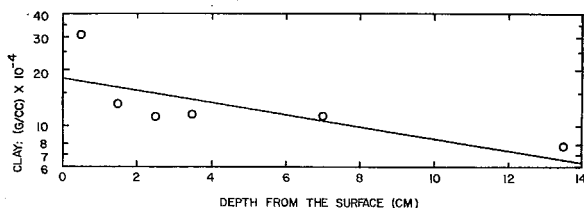


FIG. 2. Clay deposition in glass beads, data from a single column with the regression line drawn.

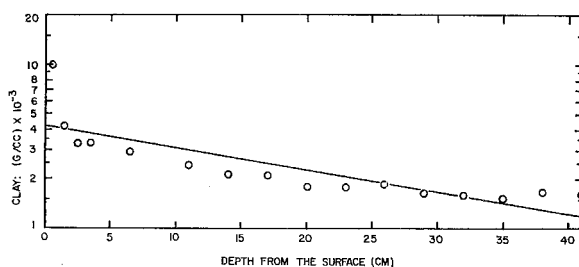


FIG. 3. Clay deposition in a single column of glass beads of extra length to indicate effect of column length. Regression line drawn to show non-exponential nature of data.

determined by weight. In order to arrive at an average total accumulation for each column, the accumulations in each cross sectional sample were weighted with regard to the portion of the column they represented and summed. The data represent the average of several columns in each size class.

The electrokinetic properties of the media and the clay suspension indicated that the zeta potentials of the glass beads and carborundum calculated from streaming potential measurements were 74 and 83, respectively. These values were essentially independent of particle size. The values of zeta potential for the suspensions of montmorillonite calculated from cataphoretic velocity measurement were a function of concentration ranging from 65 mV for a 0.06% concentration to 136 mV for a 1% concentration. Measurements on suspensions above 1% were considered invalid and the value for a 1% suspension may be questioned.

DISCUSSION

Figures 2 and 3, indicate that the data do not fit the theory developed. Nearly all data from the twenty-eight tests exhibited a similar behavior, showing a high accumulation near the surface followed by a rapid decline and then a section in which a uniform change in deposition occurred with depth.

TABLE I.—SUMMARY OF RESULTS

Material	Size (microns)	Uniformity coefficient (approximate)	Hydraulic gradient (approximate)	Porosity (per cent)	Intrinsic permeability (microns ²)	Suspension concentration %	Av. total accumulation g/cm ³ × 10 ⁻³
Glass beads	70	1	2	35.5	3.01	1	0.8029
	120	1	2	30.7	11.2	3	0.0965
	120	1	2	37.1	10.2	0.3	0.0205
	120	1	2	34.5	8.72	0.06	0.0118
	120	1	4	37.4	11.4	0.1	0.0168
	120	1	4	36.3	10.9	1	0.0480
	100	3	2	26.8	2.77	1	2.200
Carborundum	70	1	2	43.8	3.13	1	1.139
	97	1	2	44.0	6.88	1	*
	163	1	2	42.0	15.5	1	0.412
	163	1	2	42.0	17.2	0.1	0.020
	100	3	2	38.8	2.49	1	6.320

* In these tests various length columns were used, therefore the clay accumulation value was not comparable with the other tests.

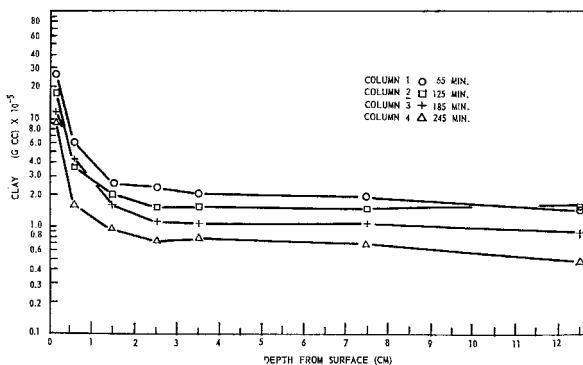


FIG. 4. The curves shown are for four columns operated at the same time but for different lengths of time.

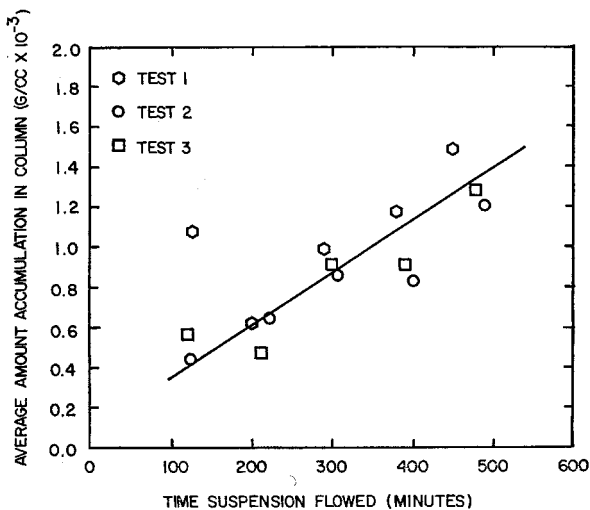


FIG. 5. Relation of clay deposition in a column of porous media to time of suspension flow.

Since the suspensions used were relatively stable montmorillonite suspensions and the time of tests was short compared with the fall velocity of these small particles, surface accumulations due to settling was not a factor. The observation of very little clay on top of the surface confirmed this conclusion. Therefore, it is postulated that two different mechanisms of removal operated in the system. At or near the surface the mechanism of mechanical sieving or interstitial straining operated. Below the surface the removal mechanism more nearly follows the theory presented earlier in the paper and is probably a combination of diffusion and gravitational settling in the pore spaces where

flow is restricted. It is unfortunate that none of the theories of Hall (1957), Ives (1960), or Hunter and Alexander (1963) held for this system. It appears that even though they held for the conditions under which they were tested, they are not the universally-applicable fundamental theory of flow of colloidal suspensions in porous media necessary to predict behavior over a wide range of conditions. The factors that influence flow and deposition can be enumerated. Particle shape, particle size, and suspension concentration are important factors. From Table 1 it can be seen that the rate of removal for the carborundum (a sharp angular material) was greater than for the glass beads (nearly spherical). The effect of size can be seen from Table 1. Size and shape are important factors because they control the geometry of the pores in the column through which the clay must move.

There is not enough difference between the zeta potential of the glass beads and the carborundum to verify the hypothesis that the interrelation of the zeta potential of the clay suspension and the zeta potential of the porous media is an important factor in the behavior of the system. Certainly if it were possible to produce a suspension with a zeta potential of opposite sign to that of the porous media, the rate of removal of clay would be influenced markedly.

The effect of duration of flow seems to be linear as can be seen from an inspection of either Figs. 4 or 5. The rate factor would not therefore be a function of time but of other properties of the system.

SUMMARY

Based on the data presented, the important factors affecting the flow of colloidal suspensions through porous media are particle size and shape, and suspension concentration. Hydraulic gradient appears to be relatively less important. The relation of the zeta potential of the porous media and the suspended particles is also an important factor. The difficulty of measurement of zeta potential and the difficulty of producing material with a desired zeta potential make the verification of this factor difficult.

The data indicate that two mechanisms of removal operated in the system. The mechanism of removal at the surface was mechanical sieving or interstitial straining, while the process of removal below the surface was a combination of diffusion and gravitational settling. If these mechanisms truly control then the existing theory does not hold for this case. The major deviation from the theory is the non-logarithmic distribution of the accumulated material throughout the porous media. This deviation also applies to other theories developed including those of Ives (1960) and Hunter and Alexander (1963). These theories appear to be valid for combinations of large particle size media and suspensions, but do not hold for stable suspensions and relatively fine particle size suspensions. The possibility of developing a model, which would incorporate the mechanism of removal for a wide

range of particle sizes and account for the physical and chemical properties of the system, seems within the realm of attainment. It appears that this model will await the further development of the model Bodziony and Litwinišzyn (1962) proposed, based on random processes, to include clay-shaped particles.

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