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INFLUENCE OF PORE FLUID COMPOSITION ON VOLUME OF SEDIMENTS IN KAOLINITE SUSPENSIONS

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Abstract—Reported in this paper is a study of the influence of pore fluid composition on sediment volume of kaolinite suspensions. Laboratory tests have been conducted with kaolinite in water with NaCl, CaCl₂ and AlCl₃ of different concentrations and in 10 types of organic liquids of varying values of static dielectric constant. The types of tests performed include regular suspension tests and leaching and cyclic leaching tests on kaolinite sediments. In the leaching tests, sediments formed during the regular suspension tests in water of low salt concentration were subsequently leached with water of high salt concentration. In the cyclic leaching tests, the salt concentration was increased and then decreased. The purpose of the leaching and cyclic leaching tests was to study the change in existing equilibrium fabric caused by subsequent changes in the concentration of salt in pore fluid. Results of the suspension tests indicate that sediment volume of a water suspension decreases with increase in ion concentration and increase in valence of cation. Leaching and cyclic leaching tests indicate that substantial change in salt concentration is required to change the existing fabric. The effect of dielectric constant of pore fluid on sediment volume is somewhat complex. As the dielectric constant increases from 1.9 for heptane to 110 for formamide, sediment volume first decreases, assuming a minimum at 24 for ethanol, increases with a maximum at 80 for water, and decreases again until 110 for formamide. An approximate physico-chemical analysis model is used to interpret some of the data in a quantitative manner. In the analysis model, recently developed theories of double-layer repulsive and van der Waals attractive forces are combined to simulate the behavior of suspensions.

Key Words—Dielectric Constant, Ion Concentration, Kaolinite, Leached, Mixed, Sediment, Suspension, Valence of Cation, Volume.

INTRODUCTION

Understanding at the level of suspensions is important in explaining many aspects of the behavior of clays. Properties and microstructure of a soil are a direct consequence of how the soil is originally formed. For instance, marine clays, which are formed in a salty water environment, are found to have high porosity, with edge-to-edge or edge-to-face card-house type of microstructure (Pusch 1966; Quigley and Thompson 1966). Such a microstructure is considered to be responsible for marine clays' sensitivity to stiffness and shear strength (that is, loss of stiffness and shear strength upon external disturbance such as an earthquake loading or a static loading that produces sufficient strain, causing disruption of soil fabric). Recent practices in waste disposal in landfills with clay liners demand better understanding of the interaction between clay particles and various chemical pollutants. Experimental studies conducted in the past 2 decades indicate that stress-strain behavior, permeability, shear strength and fabric of soils will change when pore fluid composition is changed as a consequence of chemical pollution (Mesri and Olson 1971; Anandarajah and Zhao 1996).

The relationship between pore fluid composition and soil properties is important in many other areas as well. A soil scientist is interested in conditioning clay-

containing soils to achieve good porosity and permeability characteristics in order to promote root growth and easy workability (Grim 1968). An environmental engineer strives to find an effective way to remove contaminant, which is frequently soil, from waste water through chemical additives by means of sedimentation (Peavy et al. 1985). A practitioner in the oil drilling industry is interested in chemical conditioning of drilling muds to build a thin, impermeable filter cake on the face of a drilling hole (Van Olphen 1977).

The objective of this study is to investigate the influence of pore fluid composition on the behavior of kaolinite suspensions. The compositional variables considered are the valence of cations, the ionic concentration and the fluid's static dielectric constant. A systematic series of suspension tests was conducted on kaolinite in NaCl, CaCl₂ and AlCl₃ water solutions of different concentration. To capture the effect of the pore fluid's dielectric constant, organic liquids of different dielectric constants were used in another series of suspension tests.

After presentation and discussion of the results of experiments, some of the results were analysed using a recently developed, approximate suspension analysis model (Anandarajah 1997). While the model is not yet a predictive model, it has been found to be an excellent tool for interpreting experimental data from a physico-chemical viewpoint.

EXPERIMENTAL PROCEDURE

Georgia kaolinite was used in the experimental study. This type of kaolinite is among the most studied clay minerals in the literature. According to Grim (1968), the clay has a specific surface (S) of about 20 m²/g and a cation exchange capacity (CEC) of about 4.0 meq/100 g. Hydrometer analysis performed on the kaolinite indicates that the particle size falls in the range $10\text{ }\mu\text{m} < d < 0.1\text{ }\mu\text{m}$, where d is the diameter, with a d_{50} (that is, 50% of the volume has particle size less than d_{50}) of about 1.6 μm .

The fluids used in the tests were deionized water with varying amounts of NaCl, CaCl₂ and AlCl₃, and organic fluids of varying values of static dielectric constant. The organic fluids considered include heptane, benzene, triethylamine, acetic acid, ethyl acetate, ethanol, methanol, formamide and ethanol/water mixture.

Three types of tests were performed in the study: suspension tests, leaching tests and cyclic leaching tests. The test procedures are described in the subsequent sections. Also described below are a "washing technique" used to determine the amount of salt present in the source kaolinite mineral used in the study, and the method of estimating an equivalent salt concentration from conductivity measurements.

Suspension Tests

In the suspension tests, 50 g of dry kaolinite were mixed with 125 mL liquid of desired composition in an electric mixer for a duration of 30 min. The kaolinite-fluid solution was then transferred to a cylinder of 1 L volume and more fluid was added to bring the total volume of the mix to 1 L. The cylinder had a cross sectional area of 16.6 cm². The solution was further stirred with a thin, clean metal rod before commencement of recording the sediment thickness with time. The height of sediment was measured once a day until identical results were obtained for 2 consecutive days. The sediment height was measured with an accuracy of within ± 1.0 mm, and an average height calculated. From the height, the sediment's void ratio was calculated. Void ratio is defined as the ratio between the volume of void to volume of solids. In the tests designed to examine the influence of salt types and concentrations, the fluid was prepared by adding the salt to a deionized water. In the series involving organic fluids, the fluid of interest was directly mixed with dry kaolinite.

Once the kaolinite solution was transferred to the test cylinder, kaolinite particles began to settle, eventually leaving a clear supernatant liquid at the top, with a clearly observable interface between sediment and liquid. Typically a period of approximately 2 weeks was needed for the sediment to reach an equilibrium;

that is, for the volume of sediment to remain constant with time.

Leaching Tests

The objective of this series of tests was to investigate the change in the existing equilibrium fabric, and the consequent change in sediment volume, caused by further changes in salt concentration. The tests were performed on equilibrium sediments obtained from kaolinite suspensions prepared with deionized water, as described in the preceding section. Once equilibrium had been reached, ion concentration in pore fluid was changed by simply adding more salt (concentrated salt solution of known concentration) to the supernatant fluid and the change in sediment thickness was monitored with time. Care was taken not to disturb the existing fabric at the time of adding salt. The salt concentration was changed in increments and, for each increment, the sediment was allowed to reach a new equilibrium state. Once equilibrium was reached for a given incremental change, the next incremental change was made and the process repeated until the concentration of salt in the fluid was raised to 1.0 M . Tests were conducted with NaCl, CaCl₂ and AlCl₃.

Cyclic Leaching Tests

The purpose of this series of tests was to study the nature of volume change due to "loading" (increase in salt concentration), followed by "unloading" (decrease in salt concentration). The tests were conducted on kaolinite sediments equilibrated initially with deionized water. Only aluminum chloride was considered in this series. The procedure followed in the "loading" phase was identical to that used in the leaching tests, described in the preceding section. Aluminum chloride in the form of concentrated water solution was added incrementally (in a small amount at a time) to the supernatant fluid and the sediment was allowed to reach a new equilibrium state after each incremental loading. When the total ionic concentration of the suspension reached 1.0 M , the concentration was reduced incrementally by removing a certain amount of supernatant fluid and adding deionized water. The ion concentration in pore fluid was reduced by about half each time this was done. The sediment was allowed to reach a new equilibrium state, the thickness was recorded and further incremental unloading continued. The test was continued until the concentration of AlCl₃ was decreased to about 1.0×10^{-4} M .

Electric Conductivity Measurements

There exists a unique relationship between electric conductivity of an aqueous solution and ion concentration in the solution. A relationship was established by measuring electric conductivity of NaCl-water solution at a number of NaCl concentrations in the range

Figure 1. Variation of sediment's void ratio with settling time for kaolinite-water suspensions.

between $1.0 \times 10^{-4} M$ and $1.0 M$. This relationship is slightly nonlinear and is somewhat dependent on the salt used; for example, the electric conductivity at $1.0 M$ NaCl is 60.0 mS and at $1.0 M$ CaCl_2 is 56.0 mS. In the present study, the conductivity versus concentration relation established for the NaCl-water solution is used. While the method cannot be used to determine the type of salt present in the electrolyte solution, it can be used to find an "equivalent salt concentration" (that is, concentration of NaCl at which the value of electric conductivity of the water-NaCl solution is equal to that measured for the solution at hand).

Washing Technique

The technique of "washing" was used to estimate the amount of salt (in terms of an equivalent concentration) attached to the source kaolinite clay mineral used in the study. The procedure described earlier was followed to prepare a 1-L suspension consisting of 50 g of dry kaolinite and deionized water. The clay particles were allowed to settle and, at equilibrium, electric conductivity of the supernatant (liquid on the top of kaolinite sediment), as well as the suspension thickness were measured. The supernatant liquid was then removed and the sediment poured into the electric mixer to be mixed with fresh deionized water. The procedure was repeated until the measured electric conductivity of supernatant fluid became the same for 2 consecutive suspension tests. The difference between original and final electric conductivity of kaolinite suspension is thus due to salts attached to kaolinite particles and was used to compute an equivalent NaCl concentration.

RESULTS OF SUSPENSION TESTS WITH WATER

Settling Rate

Results showing the variation of sediment's void ratio with time for kaolinite suspension in NaCl-water solution are presented in Figure 1 for different concentrations of NaCl. The behavior is somewhat com-

Figure 2. Variation of sediment's void ratio with concentration of NaCl for kaolinite-water suspensions for low to high concentrations of NaCl.

plex. Particles in a solution of high concentration (for example, $1.0 M$ NaCl) settle more slowly at the start than those in a solution of low concentration (for example, $0.01 M$ NaCl). After a certain period of time, however, the settling rate of particles in a solution of high concentration seems to increase, and exceeds that of particles in a solution of low concentration; for example, the slope of the curve for $1.0 M$ NaCl after a period of 100 min is steeper than the slope of the curve for $0.01 M$ NaCl after 10 min. A detailed study is needed to investigate the cause of this observed behavior. Eventually, higher salt concentrations lead to lower sediment's void ratio.

Effect of Ion Concentration

By conducting suspension tests in salt (NaCl) water of different concentrations, the effect of ionic concentration on sediment volume has been investigated; the results are presented in Figure 2 in terms of the equilibrium sediment's void ratio as a function of salt concentration.

The results indicate that, for the kaolinite used in the study, the sediment's void ratio decreases with increase in ion concentration. The void ratio decreases from 12 to about 9 as the ion concentration increases from 10^{-3} to $1 M$. Increasing salt concentration decreases the diffuse double-layer thickness (Verwey and Overbeek 1948), leading to smaller sediment's void ratio.

There are studies (such as Van Olphen 1977) indicating that, as the electrolyte concentration increases, the sediment's void ratio first decreases and then increases. The increase is attributed to the formation of fractal flocs of large void ratio (Weitz et al. 1991). This was not observed in the present study.

It is of interest to know whether this trend holds true for concentrations beyond the range considered, especially at extremely low concentrations. In studying the behavior at low concentrations, one practical dif-

Table 1. Results of repeated washing of kaolinite suspension with deionized water.

Number of washings (1)	Sediment thickness (cm) (2)	Void ratio e (3)	Electric conductivity (μS) (4)	Equivalent NaCl concn. (M) (5)	Time (day) (6)
0	8.71	12.5	101.5	1.5×10^{-3}	3
1	8.38	12.0	43.7	5.0×10^{-4}	4
2	8.18	11.7	33.3	3.4×10^{-4}	6
3	7.87	11.2	29.6	2.8×10^{-4}	5
4	7.75	11.0	23.2	2.5×10^{-4}	5
5	4.57	6.1	18.2	1.7×10^{-4}	32
6	2.79	3.3	16.4	1.5×10^{-4}	40

ficulty arises from the fact that there is always a certain amount of salt attached to dry kaolinite particles in their natural state. Effort was then devoted to measure the amount of this salt. The "washing" technique was used for this purpose. It may be noted that the "washing technique" is commonly used in environmental engineering and colloidal science (Van Olphen 1977).

Upon mixing of dry kaolinite with deionized water, salt attached to clay particles dissolves into the solution, with the electric conductivity of the supernatant liquid assuming a certain value. Three factors contribute to the electric conductivity of the supernatant fluid: dissolved salt originally attached to kaolinite particles, ions in the deionized water and contributions from clay particles themselves. The "washing technique" provides a means of estimating the salt attached to clay particles.

Test results are summarized in Table 1. Note that the first row of data in Table 1 corresponds to the original sediment. The electric conductivity of the deionized water used in the study was 2.6 μS .

As expected electric conductivity of kaolinite suspension decreased as the sediment was repeatedly washed with deionized water. According to this test, there was 1.35 meq of salt attached to 50 g of kaolinite.

Two striking phenomena were observed during the tests. 1) Suspension volume suddenly decreased drastically after the 5th washing. This occurred at concentrations smaller than $1.7 \times 10^{-4} M$. In accordance with the diffuse double-layer theory (Verwey and Overbeek 1948), the double-layer thickness should increase as the electrolyte concentration decreases; further study is needed in explaining this aspect of the observed behavior. 2) The length of time needed for the cloud in supernatant fluid to clear up increased suddenly from several days before the 5th washing to more than 1 mo for the 5th and 6th washings.

The relationship shown in Figure 3 was obtained by combining the results in Figure 2 and those of the washing tests presented in Table 1. It is seen that, as the concentration of NaCl increases from a very low

Figure 3. Variation of sediment's void ratio with concentration of NaCl for kaolinite-water suspensions for very low to high concentration of NaCl.

value, the sediment's equilibrium void ratio first increases, reaches a maximum around $1.5 \times 10^{-3} M$ and decreases with further increase in ion concentration.

Influence of Valence of Cation

To investigate the effect of salt type on the suspension behavior, 3 types of salts including NaCl, $CaCl_2$ and $AlCl_3$ were used. To avoid difficulty of interpreting the results due to possible influence of anions, salts of the same anion types (Cl^-) were used. Test results are presented in Figure 4.

Equilibrium void ratio decreases with increase in the valence of cation at the same concentrations. However, at low concentrations, the differences among the 3 salts are very small. In fact, at a concentration of $1 \times 10^{-3} M$, the differences in sediment's void ratio in different salts are within experimental errors. As the concentration increases, salts of higher valence become more effective in reducing sediment volume, and the difference in sediment volume of suspensions of different salt types increases.

Figure 4. Variation of sediment's void ratio with concentration of electrolyte for kaolinite-water suspensions.

Figure 5. Changes in sediment's void ratio due to leaching with electrolyte of varying concentrations for kaolinite-water suspensions.

Figure 6. Effect of cyclic leaching on sediment's void ratio for kaolinite-water suspensions.

RESULTS OF LEACHING TESTS

The suspension tests described in the preceding sections were all carried out on separate suspensions, each prepared independently in different solutions. The final equilibrium fabric (arrangement of particles) would in general be different in different specimens, compatible with the system variables and the resulting physico-chemical interparticle forces. This is possible because the particles, when they settle under gravity, are free to rotate, slide on each other and translate, as dictated by the interparticle forces. Once such a fabric is formed, particles lose most of the freedom for further change, due to constraints imposed by the surrounding particles. For example, when the pore fluid composition of an equilibrium sediment is changed, physico-chemical interparticle forces will change, but the fabric cannot change that easily.

This process is akin to the "leaching" that takes place in the field on a soil whose fabric was formed at an earlier time in a different environment (such as marine). To examine this process, a series of leaching tests were conducted by the procedure described earlier. Tests were conducted with NaCl, CaCl₂ and AlCl₃, and the results are presented in Figure 5.

For all 3 salts, sediment volume remained fairly constant up to a concentration of about 0.03 M. Following this, a significant decrease in sediment volume was observed. As more salt was added, salt of high valence was found to be more effective in compressing the sediment, with the degree of volume reduction increasing in the order of AlCl₃, CaCl₂ and NaCl. In comparison to its counterpart in Figure 4, where the results of fresh sedimentation are presented the same trend was observed during leaching for the influence of ion concentration and the valence of cation, except that in the leaching tests volume change occurred only at sufficiently high concentrations, indicating the need for higher energy to change an existing fabric. When the fabric did change, it appeared that it suddenly col-

lapsed, eventually leading to even smaller volumes at corresponding concentrations (Figure 5) than the virgin suspensions (Figure 4).

RESULTS OF CYCLIC LEACHING TESTS

These tests were conducted on the equilibrium sediment of kaolinite-water-AlCl₃ system after the leaching tests had been completed; that is, after the concentration had been increased incrementally to 1.0 M. Tests were then continued to investigate the degree of swelling of sediments due to removal of salts in the fluid. Test results are presented in Figure 6. It is seen that upon decreasing the salt concentration of the sediment, the sediment's void ratio decreased slightly first and then remained fairly constant. This trend continued up to a concentration as low as at 1.0×10^{-4} M. Thus, for the system considered here, the original fabric did not appear to be altered by the reduction in ion concentration in the fluid.

RESULTS OF SUSPENSION TESTS WITH ORGANIC FLUIDS

The influence of pore fluid type has been investigated by conducting suspension tests in different organic fluids. Ten types of liquids including heptane, benzene, triethylamine, acetic acid, ethyl acetoacetate, ethanol, methanol, water, formamide and a mixture of ethanol and water were employed. These chemicals were primarily selected according to their static dielectric constants. Test results are summarized in Table 2, along with the physical properties of the fluids.

Test results are plotted in Figure 7. The sediment's void ratio decreases first with increase in static dielectric constant with a minimum for ethanol, increases up to a maximum for water and then decreases again for formamide. The point $\epsilon_0 = 52$ was obtained by mixing ethanol ($\epsilon = 24$) with water ($\epsilon = 80$) in equal portion. As can be seen from Figure 7, this point falls in between water and ethanol.

Table 2. Test results of kaolinite in organic fluids.

Chemicals (1)	Dielectric constant (2)	Specific gravity (3)	Sediment's void ratio (5)	Time (day) to reach equi- librium (6)
Heptane	1.91	0.68	20.4	4
Benzene	2.28	0.88	19.1	5
Triethylamine	2.45	0.73	16.6	4
Acetic acid	6.15	1.05	9.8	5
Ethyl acetoacetate	15.7	1.01	5.8	22
Ethanol	24.3	0.79	2.6	42
Methanol	33.6	0.80	3.3	36
Water + ethanol	52.4	0.90	10.4	7
Water	80.4	1.00	12.3	5
Formamide	110.0	1.13	7.79	17

The diffuse double-layer theory suggests that the double-layer thickness decreases as the static dielectric constant of the fluid decreases (Verwey and Overbeek 1948), and this leads to a decrease in the double-layer repulsive force. The decrease of the double-layer force with dielectric constant is monotonic.

The van der Waals attractive force, on the other hand, is a function of the difference in dielectric properties of the clay mineral and fluid. It varies in a non-linear manner with the dielectric properties of the fluid, and the variation is approximately similar to that shown in Figure 7 (Chen 1996; Anandarajah and Chen 1997). Quantitatively, however, the net physico-chemical force (that is, the difference between the double-layer repulsive and the van der Waals attractive forces) should control the behavior (that is, the shape of the variation of sediment's void ratio with static dielectric constant).

Also note the difference in the length of time needed for the cloud in supernatant fluid to clear up and the sediments to reach equilibrium void ratio. While in all other chemicals suspension reached equilibrium within 2 weeks, in ethanol and methanol, a period of 1.5 month was needed for the supernatant to clear up before the interface could be clearly seen.

APPROXIMATE ANALYSIS OF THE SUSPENSIONS

The final equilibrium fabric and void ratio are a direct function of the composition of system variables (clay mineral, pore fluid and salt types), and other factors such as environmental (temperature), loading (gravity), and boundary (1-dimensional) conditions. Interparticle forces are predominantly physico-chemical (the double-layer repulsive and the van der Waals attractive forces), although mechanical interactions do exist. (The mechanical interactions are mechanical reactions that develop between 2 particles when they touch each other.)

Motivated largely by the need to provide a more quantitative interpretation of experimental data, a sys-

Figure 7. Effect of pore fluid's static dielectric constant on sediment's void ratio for kaolinite-water suspensions.

tematic study was initiated several years ago. To date, theories have been developed for computing the double-layer repulsive force between 2 nonparallel clay particles (Anandarajah and Lu 1992; Anandarajah and Chen 1994), and for computing the van der Waals attractive force between 2 nonparallel clay particles (Anandarajah and Chen 1997).

Bolt (1956) presented a theory of compressibility for clays, assuming that the clay particles were parallel to each other, and that the externally applied vertical force was completely counterbalanced by the double-layer repulsive force. In an attempt to improve the theory with regard to both of these assumptions, Anandarajah (1997) has recently extended Bolt's model by assuming the particles to be arranged in a nonparallel but regular manner as shown in Figure 8. and by considering both the double-layer repulsive and van der Waals attractive forces. The mechanical interactions are still ignored in the model. The gravity force is considered, along with the externally applied vertical

Figure 8. Nonparallel particle model representing soil in 1-dimensional consolidation-suspension cylinder.

Table 3. Analytical results for kaolinite–water–NaCl suspensions.

n_0	e_{exp} (M)	e_{theory}				
		$\theta = 0$ $F_{att} = 0$ Bolt's	$\theta = 0$ $F_{att} \neq 0$	$\theta = 45^\circ$ $F_{att} \neq 0$	$\theta \neq 0$ $F_{att} \neq 0$	
					e	θ°
0.001	12.1	2.08	2.08	12.2	12.2	45
0.010	11.6	0.834	0.810	11.7	11.6	44
0.100	10.5	0.316	0.232	11.4	10.4	40
1.000	9.30	0.113	0.001	11.4	9.20	36

force. Thus, each particle in this model is assumed to be in equilibrium under the double-layer repulsive force, the van der Waals attractive force and its weight. In addition to these, the topmost particle is subjected to the surface force. The spacing between a particle and its neighbors (above and below) must be consistent with the mechanical (gravity and surface) and physico-chemical (repulsive and attractive) forces. The physico-chemical forces are computed using the theories mentioned earlier.

The model is used here to analyze some of the suspensions reported in the preceding sections. Table 3 presents the results for kaolinite–water–NaCl suspensions for different concentrations of NaCl. The following properties were used in computing the repulsive force: salt concentration (as listed), cation's valence = 1, water's static dielectric constant = 80, cation exchange capacity (CEC) of kaolinite = 4 meq/100 g, specific surface of kaolinite = 20 m²/g and temperature = 293 °K. The properties needed to compute the attractive force are lumped together into a constant known as the Hamaker constant, which is 10.0×10^{-20} J for a kaolinite–water system (Chen 1996). The van der Waals attractive force does not vary with the salt type or the salt concentration.

Column 2 of Table 3 lists the experimental value of equilibrium void ratio. The Bolt's (1956) theory is first used to compute the equilibrium void ratio. Denoting the angle between 2 particles by θ , recall that in the Bolt's theory, $\theta = 0^\circ$ and the attractive force is ignored. It may be seen by comparing Columns 2 and 3, these assumptions do not represent the suspensions; computed void ratios are much smaller than the measured ones. Next, analyses are repeated with consideration to the attractive force, but still assuming $\theta = 0^\circ$, and the results are listed in Column 4. As expected, the computed void ratios are even smaller; the attractive force decreases the net repulsion.

Next, analyses are performed with $\theta = 45^\circ$, with the intention of simulating a random particle orientation, and the results are listed in Column 5. In a random fabric, θ will be uniformly distributed between 0 and 90°, and an average value for a deterministic analysis such as the present one is 45°. A value now has to be assumed for the length of the particles. A length was

computed by matching the theoretical and experimental void ratios at $n_0 = 0.001 M$, with particles assumed random at this concentration ($\theta = 45^\circ$). The computed length was 2.35 μ , which is slightly bigger than d_{50} (= 1.6 μ). The length is used in all of the subsequent analyses.

Now, it is seen that the computed void ratios are very close to the measured ones. For the first 2 lower concentrations (that is, for 0.001 M and 0.01 M), the net force was still repulsive and the analysis was able to find a non-zero spacing between particles at their closest edges at which equilibrium is fulfilled. The computed void ratio decreased from 12.2 to 11.7 as the concentration increased from 0.001 to 0.01 M . However, for concentrations of 0.1 M and higher, even when the separation distance at the closest edges is zero, the net repulsive force is not large enough to carry the weight of the particles. This is due to decrease in the double-layer repulsive force as a result of increase in salt concentration. The particles at these concentrations can only be in equilibrium under mechanical interaction between them; the analysis does not have the capability to account for this and it simply computes the void ratio by assuming that the particles are touching one another, and that the spacing between them at the closest edges is zero.

The angle that will bring the experimental and theoretical void ratios closer to each other lies between 0° and 45° , as indicated by the results presented in Columns 6 and 7. The theory does not have the means of "predicting" this angle at this point; they had to be assumed. The angles are changed until a good match is obtained between theoretical and experimental void ratios. The computed angles are 44°, for 0.01 M , 40° for 0.1 M and 36° for 1.0 M concentrations.

The analysis results suggest that increase in concentration of salt decreases the double-layer repulsive force, which leads to, in this specific example, flatter particle arrangements. But, more importantly, the results suggest that particles are far from being parallel. A direct and a more accurate method of analysis is what is known as the discrete element method, and interested reader may find an application of this to clays in Anandarajah (1994).

SUMMARY AND CONCLUSIONS

The influence of pore fluid composition of the equilibrium sediment volume of kaolinite suspensions was studied. The compositional variables considered were the valence of cation, the ionic concentration and the fluid's static dielectric constant. Regular suspension tests, as well as leaching and cyclic leaching tests, were conducted. The results of the suspension tests conducted in water indicate that sediment volume decreases with increase in ion concentration and increase in valence of cation. It is observed from the leaching tests that as the salt concentration in the pore fluid of

an existing equilibrium sediment increases, the volume decrease occurs only when the increase in salt concentration is substantial. The cyclic leaching tests reveal that, for the system studied, removal of salt from the pore fluid of an existing equilibrium sediment does not lead to noticeable swelling.

The effect of dielectric constant of pore fluid on sediment volume is somewhat complex. As dielectric constant increases from 1.9 in heptane to 110 in formamide, sediment's void ratio first decreases, reaches a minimum of 24 in ethanol, increases to a maximum of 80 in water and then decreases again in formamide. While the observed trend is complex, it is consistent with the variation of the van der Waals attractive force with dielectric properties of organic fluids.

The suspension tests conducted on kaolinite–water–NaCl systems have been analyzed using an approximate, physico-chemical model. The results sheds some light on the possible internal fabric of the suspensions, and the nature of interparticle forces. It is found that particle arrangement is closer to random than parallel.

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