

# Settling of Kaolinite in Different Aqueous Environment

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*Settling characteristics of soils carry great importance for geotechnical engineers since sediments properties are formed during the settling of soil particles in an aqueous environment. In this study, settling characteristics of kaolinite are investigated. Different ionic strengths of NaCl, CaCl<sub>2</sub> and AlCl<sub>3</sub> were considered as a function of pH in aqueous environment of varying solid concentrations. Factors affecting the settling characteristics and fabric of kaolinitic sediments have been identified. The results of the study reveal that kaolinite settles in either flocculated or dispersed forms depending on pH and ion concentration. Flocculated settling occurs in acidic pH due to formation of flocs in edge-to-face structure with increasing positive charges at the particle edges. Dispersed settling occurs in alkaline pHs when ionic strength is low. When ionic strength is increased in alkaline pHs, kaolinite particles settle in flocculated form. Furthermore, the results show that pH has a significant role on the final sediment thickness or void ratio of kaolinite. Densely packed structures in alkaline and loosely packed structures in acidic aqueous environments are formed depending on pH level. Results also show that as the solid concentration increases, the settling rate decreases due to buoyancy effect. Finally, the zeta potential of kaolinite is correlated with the final sediment thickness or void ratio of kaolinite as a function of pH. This correlation proves that there is a good agreement between zeta potential and the final sediment thickness or void ratio, especially when the soil is settled in a dispersed form.*

**Keywords** dispersed, edge-to-face, flocculated, kaolinite, pH, sediment thickness, settling, solid concentration, void ratio, zeta potential

## Introduction

In general, clay mineral type, ionic strength, pH and solid to water ratio control the settling process of soils in aqueous environment. Although intermediate settling characteristics can be observed, flocculated and dispersed settlings are the two extreme characteristics that soil particles undergo depending on the above mentioned factors. The structure and fabric of the settled soils are the functions of a complex interaction between soil particles and the aqueous environment because surface charges of particles are influenced by the ionic strength of the medium.

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The surface charge of the particles decreases (becomes less negative and sometimes attains positive values) with increase in ionic strength. When electrical charges on the soil particles become less negative or attain positive values, the soil particles tend to flocculate and form flocs. When ionic strength is low in the medium, the electrical charges on the soil particles become negative and particles tend to repel each other and settle independently according to the diffuse electrical double layer theory. Flocculation or dispersion of the clayey soil particles varies depending on the electrical surface potential on their surfaces. In the past, researchers have attempted to determine the role of electrical charges on settling characteristics of soils; however, these studies are very few and have limited scope (Ohtsubo and Ibaraki 1991).

The fabric and structure of the settled sediment show variations depending on the soil particles settling in a dispersed or flocculated form. When soil particles settle in the dispersed free settling form, the coarsest particles are on the bottom grading to the finest particles at the top. When the particles form flocs, there occurs a uniform soil particle distribution throughout the sediment bed. The two distinctly formed sediments produce different engineering characteristics, and these are the functions of their settling characteristics.

For a given soil, settling may change from the flocculated to dispersed settling or vice versa depending on the environment. Thus, it is important to understand the factors that affect the settling characteristics of clayey soils in different environments and the effects of sedimentation characteristics on the factors mentioned above. Imai (1980) investigated the settling behavior of clay suspensions as a function of initial water content and ionic concentration, and determined four types of settling: (i) dispersed settling in which soil particles disperse and settle without interacting with each other; (ii) flocculated free settling in which soil particles flocculate and form flocs of different sizes; (iii) zone settling in which flocs are formed and settle with strong interaction with each other; and (iv) consolidation settling in which visible flocs cannot be formed and the mixture settles mainly due to consolidation. Based on the observed settling characteristics, Imai (1980) concluded that degree of flocculation and the degree of mutual interaction among soil particles controlled the settling type. He also indicated that total soil weight was another factor that controlled settling characteristics such as the larger the total solid weight, the higher the settling rate and the lower the average water content at the end of settling.

Sridharan and Prakash (2001) studied the effects of clay mineralogy on the settling characteristics of clayey soils by investigating settling characteristics of kaolinitic and montmorillonitic clays. They concluded that the diffuse double layer controlled the settling characteristics of montmorillonitic clays, whereas fabric controlled that of kaolinitic clays. In addition, they found that limiting water content (water content at which soil particles cannot settle freely as discrete particles) increased with the increase in the plasticity of clays. On the other hand, limiting water content of kaolinitic clays decreased with an increase in the plasticity.

Although Sridharan and Prakash (2001) attributed the settling behavior of kaolinitic soils to fabric, we believe that the fabric of clayey soils is an end product dependent on the environment where the soil particles settled (e.g., type of clay minerals, type and concentration of ions). In other words, for a given soil, for instance kaolinite, a different fabric can be obtained depending on the settling environment. Thus, fabric is a general term and cannot adequately explain the observed settling behaviors of kaolinitic soils.

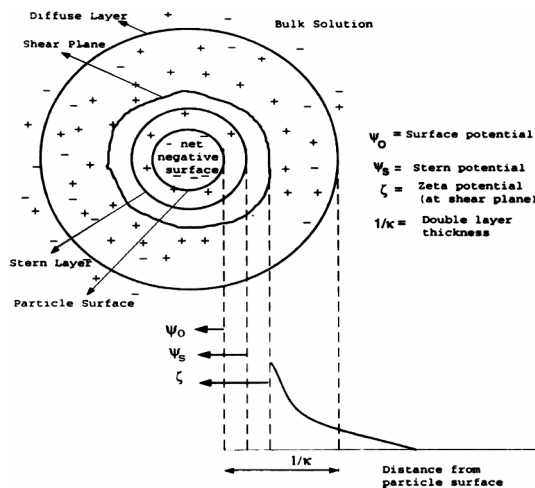
The objective of this study is to determine the factors such as solid concentration (initial water content), ion type, and concentration on the settling characteristics of kaolinite. We also investigated the surface charge variation of kaolinite by means of determining the zeta potential of kaolinite with different ion types and concentrations. A good correlation between zeta potential and final average void ratio of kaolinite in the presence of different ion types and concentrations is determined.

Since the zeta potential of clayey soils is not a commonly used parameter by the geotechnical engineering community, a brief description of this potential is presented below.

### Background: Zeta Potential of Clay Minerals

The electrical surface potential of particles cannot be measured directly. Instead, the zeta potential, which is smaller than the surface potential, can be measured. The zeta potential is the electrical potential developed at the solid-liquid interface in response to relative movement of soil particles and water (Fang, 1997; Sparks, 1986). Admittedly, the position of the zeta potential is imaginary; however, it is a good indicator of the surface potential of particles: the higher the zeta potential, the higher the electrical surface potential. The location of the zeta potential on a charged particle is illustrated in Figure 1.

The zeta potential of most soils is negative because soil surfaces usually carry negative charge. Increases in acidity cause the zeta potential to become less negative and even attain positive values at low pH (Williams and Williams 1978). The zeta potential of particles can vary with the pH of the pore fluid since this fluid has a significant role on the charge distribution on the particles. One can adjust the pH of particles to produce a zero value of electrical potential. The pH value that creates a zero electrical potential is called point of zero charge, *pzc*. Yukselen and Kaya (2003) have compiled the reported pHs that give *pzc* for kaolinite along with its maximum zeta potential values which are presented in Table 1. The table shows that the pH values that produce *pzc*s for kaolinite show very large variations: from no *pzc*



**Figure 1.** Schematically illustrates the position of zeta potential on charged clay (Kaya and Fang 2000).

**Table 1.** Comparison of the reported *pzc* and maximum and minimum zeta potential of kaolinite

pH that creates <i>pzc</i>	Maximum		Minimum		References
	pH	Zeta potential (mV)	pH	Zeta potential (mV)	
<3 <sup>c</sup>	12	−32	3	Small values	West and Stewart 1995
2 < pH < 3 <sup>b</sup>	10	−54 <sup>a</sup>	2	0.7 <sup>a</sup>	Vane and Zang 1997
2.2 <sup>d,e</sup>	10	−40	0	2.2	Smith and Narimatsu 1993
	11	−30	3.5	5.5	Williams and Williams 1978
4	11	−40	3.5	~7	Lorenz 1969
4.5	11	−85	3	~8	Hotta et al. 1999 <sup>a,b</sup>
	9.5	−65	3	~−3	Hotta et al. 1999
6	12	−40	2	10	Dzenitis 1997
	7 and 11	−25	3	−8	Stephan and Chase 2001 <sup>f,a</sup>
	11	−43	3	−25	Stephan and Chase 2001 <sup>g,b</sup>

<sup>a</sup>With 0.01 MKCL, <sup>b</sup>Georgia Kaolinite, <sup>c</sup>Steswhite kaolinite, <sup>d</sup>Lewiston, Montana, <sup>e</sup>Na kaolinite, <sup>f</sup>Low salt concentration, <sup>g</sup>0.14 M NaCl.

to pH 6, indicating that *pzc* of kaolinite is affected by composition and measurement techniques.

The zeta potential of a charged particle is obtained under an externally applied electrical field using the Helmholtz-Smoluchowski theory which is expressed as:

$$\zeta = \frac{u\eta}{\varepsilon_0\varepsilon E} \quad (1)$$

where  $\zeta$  is the zeta potential,  $\eta$  is the viscosity,  $\varepsilon_0$  is the permittivity,  $\varepsilon$  is the relative permittivity of free space,  $u$  is the particle velocity, and  $E$  is the field electrical strength.

## Materials and Methods

Commercially available Georgia kaolinite was used during the experiments. The physicochemical properties of the test soil are given in Table 2. Before commencing the tests, kaolinite was washed with 1 N ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>) solutions. This procedure was repeated several times until negligible change was observed in the electrical conductivity of supernatant liquid. Then treated kaolinite was washed with distilled water in order to remove free ions in the diffuse layer. Washing was terminated when electrical conductivity of the supernatant reached below 100  $\mu$ mohs.

In the sedimentation tests, 2.5 g, 5 g, and 10 g of purified kaolinite with solid contents of 2.6, 5.2, and 10.6 % were used respectively. The tests were conducted at room temperature in DDI (distilled deionized) water and in DDI water containing  $1 \times 10^{-4}$  and  $1 \times 10^{-2}$  M sodium (NaCl), calcium (CaCl<sub>2</sub>·2H<sub>2</sub>O), and aluminum (AlCl<sub>3</sub>). HCl and NaOH were used for the pH adjustment. When the water contained a NaCl solution, KOH was used.

Once the pH of the solution was adjusted, kaolinite was transferred into 100 mL graduated cylinders with an inside diameter of 2.75 cm. We chose to use 100 mL

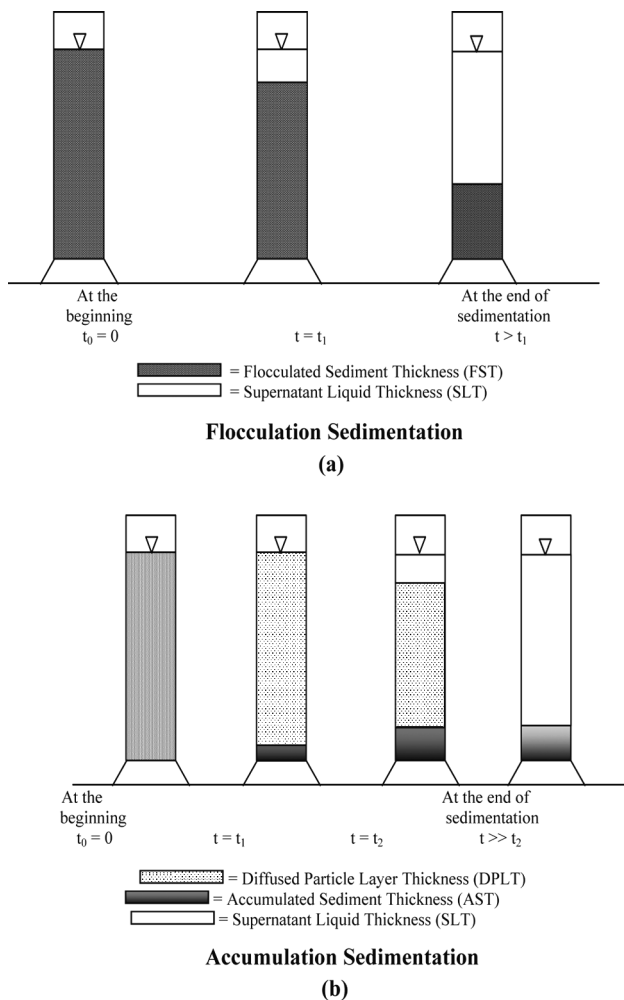
**Table 2.** Physicochemical properties of the kaolinite used

Physical properties	
Surface area, BET ( $\text{m}^2 \text{g}^{-1}$ )	$18 \pm 2$
Particle size, %finer than 2 microns	$80 \pm 5$
pH (10% solids)	$6.25 \pm 1.25$
Specific gravity	2.55
Chemical Properties	
$\text{Al}_2\text{O}_3$	39%
$\text{SiO}_2$	45%
$\text{TiO}_2$	1.7%
$\text{Fe}_2\text{O}_3$	1.0%
CaO	< 0.25%
MgO	< 0.1%

graduated cylinders since previous studies established that the size of the sedimentation tube had no effect on the settling characteristics of soils (Michaels and Bolger 1962). The top of the cylinder was covered with a piece of parafilm and kept for 24 hours to ensure that the kaolinite suspension reached equilibrium. Then, the graduated cylinders were shaken by hand for few minutes to make sure that the soil particles were thoroughly mixed in the solution. The soil was allowed to settle until there were no changes in the sediment thickness.

As shown in Figure 2, sediment thicknesses of the suspensions were determined by the two types of sedimentation behavior monitored during the experiments: flocculation sedimentation and accumulation sedimentation. For the first type of sedimentation, a sharp interface was observed between flocculated sediments and supernatant liquid (Figure 2a). At the beginning, particles formed a network between each other and consolidated rapidly on account of porous structure of network. This is because water can be easily driven out during settling. Sediment thickness readings were recorded by observing the downfall behavior of soil-liquid interface with time. Second type of sedimentation occurs when accumulated particles settled at the bottom of the cylinder in a packed form and followed by the layer of diffused particles (Figure 2b). In this type sedimentation, accumulated particles settled faster than those of flocculation sedimentation whereas diffused particles had enough time to make free settling. In this type of settling, the upward movement of the sharp interface between the accumulated and diffused particles was recorded as the sediment thickness during the tests.

The zeta potential of the soil particles was measured using an automated electrophoresis instrument (Zeta Meter 3.0+, Zeta Meter Inc., NY) equipped with a microprocessor unit. This unit enabled all statistical calculations to be made on the sample. For zeta potential measurements, a 50 mg sample was transferred into an aqueous solution and a magnetic stirrer was added to mix the soil particles homogenously. To determine the right amount of solid concentration, the zeta potential of kaolinite with different solid concentrations was established. The results showed the fact that the zeta potential of kaolinite changes slightly up to a concentration of 100 mg/L and then remains constant. Therefore, all the measurements were conducted at 100 mg/L concentrations. The time vs. zeta potential results indicated that the pH of the solution stabilized after 10 minutes. The zeta potential was measured before and after



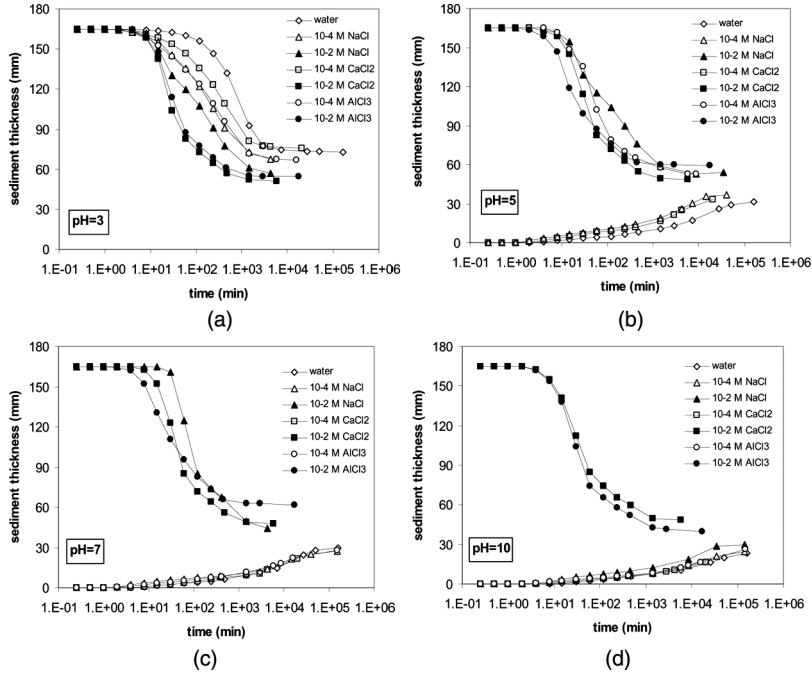
**Figure 2.** Settlement characteristics of kaolinite (a) flocculation sedimentation, (b) accumulation sedimentation.

each measurement. When changes occurred in the pH, the last pH values used for the values of the solution. Zeta potential measurements had standard deviation readings of less than 2 mV. Room temperature was  $22.5 \pm 2.5^\circ\text{C}$ . Further details of zeta potential measurements are described by Yukselen and Kaya (2003).

## Results

### *pH Effects on Sediment Thickness*

Figures 3a through 3d present the sedimentation characteristics of kaolinite as a function of pH at different ionic concentrations for  $w = 1000\%$ . The figures show that the sediment thickness of kaolinite either increases or decreases with time depending on pH and ionic type and concentration. When the particles are flocculated, due to high ion concentration, they all settle together and consolidate at their



**Figure 3.** Settling characteristics of kaolinite with time at different ionic type and concentration, (a) pH 3, (b) pH 5, (c) pH 7 and (d) pH 10.

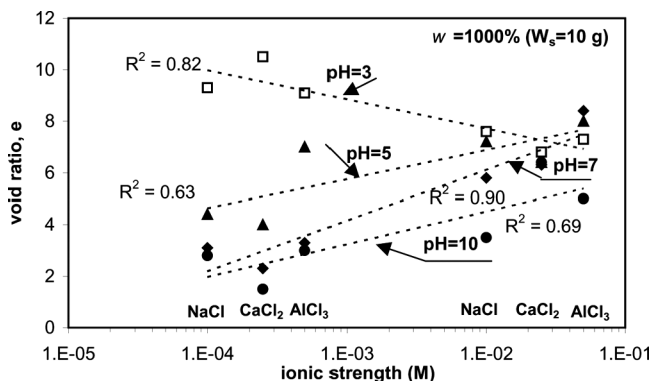
own weight. Thus, the thickness of the sediment decreases in time until it reaches equilibrium (Figures 2a and 3a). On the other hand, when the ionic concentration is low, the particles are in dispersed form and settle according to Stokes' sedimentation law which states that large particles settle first and small particles settle last by creating size gradation with depth (Figure 2b).

Note that kaolinite particles have settled both in flocculated and dispersed forms depending on pH of the solution for a given ionic concentration. Figures 3a through 3d compare the settling characteristics of kaolinite for pH 3, 5, 7 and 10. Note that kaolinite has settled in flocculated form in all tested solutions when the pH of the solution is 3 whereas it has only settled in flocculated form in solutions  $1 \times 10^{-2}$  M  $\text{CaCl}_2$  and  $1 \times 10^{-2}$  M  $\text{AlCl}_3$  concentration at pH 10. Kaolinite particles settle in flocculated form in the presence of  $1 \times 10^{-4}$   $\text{AlCl}_3$  at pH 5 and  $1 \times 10^{-2}$  M  $\text{NaCl}$  at pH 7 indicating the role of ionic strength

$$I = \frac{1}{2} \sum v_i^2 c_i \quad (2)$$

where  $v_i$  is the valence, and  $c_i$  is the concentration of ion.

Figure 4 shows the role of ionic strength on the final average void ratio of the tested kaolinite. It appears that there is a linear relationship between the final void ratio of kaolinite and the ionic strength of the solution in which the particles have settled. The trend of the correlation is positive when the pH of the solution is 5, 7 and 10 with varying slope. However, the trend of the correlation is negative when the pH of the solution is 3. Positive correlation should be expected at neutral or near



**Figure 4.** Linear correlation of void ratio of kaolinite with ionic strength of solution at different pHs.

neutral pHs since increase in ionic strength leads to development of edge-to-face type structures with wide spaces between the particles.

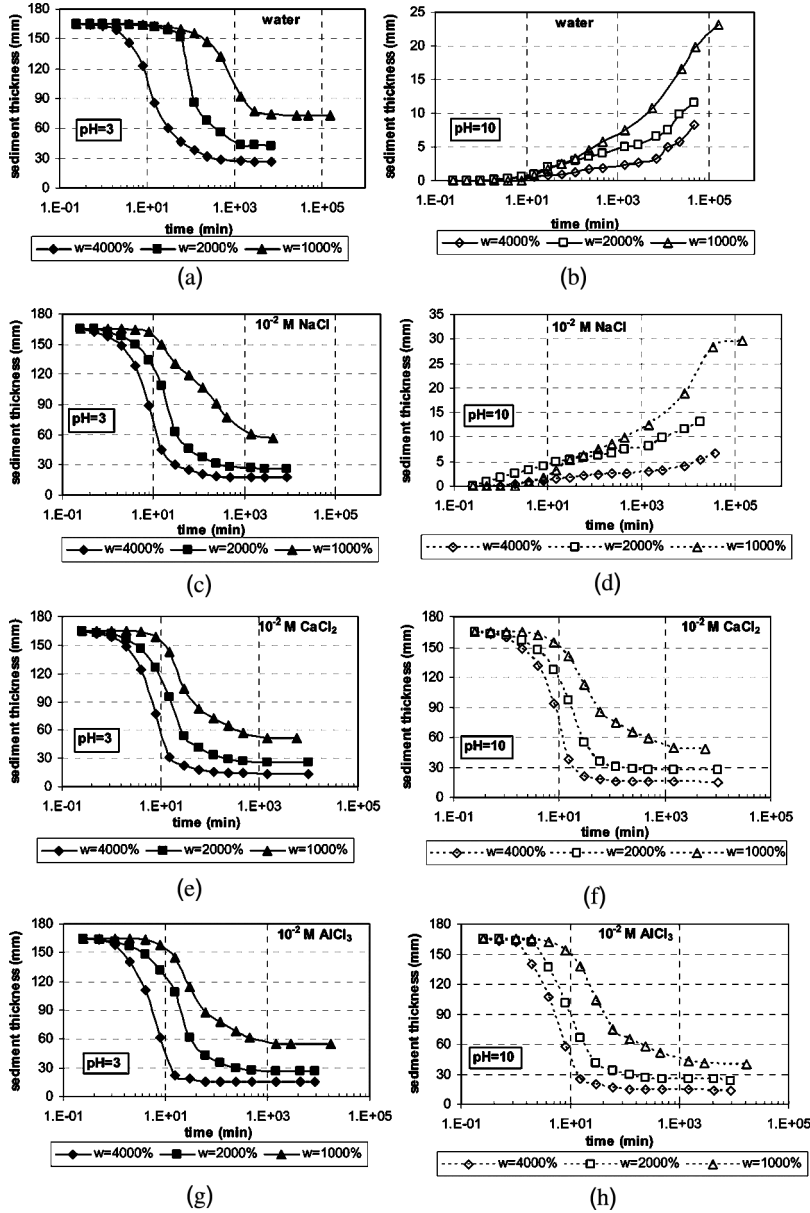
Figure 4 also shows that settled kaolinite has the highest void ratio when the pH of the solution is 3 and ionic strength is the lowest. At low pHs, i.e. pH 3, edges of particles tend to be charged with positive ions. However, face of the particles is still negatively charged. The orientation of particles in flocs can be either edge-to-face or face-to-face. Positively charged edges of particles attract negatively charged ions in the solution and other particles to form edge-to-face structure (Yong and Warkentin 1966; Miyagara et al. 1998). However, particles may form face-to-face structure by the help of the counter ions in the solutions. As a result of SEM analysis, Ma and Pierre (1997) conclude that accumulated sediments has lower sediment thicknesses than that of flocculated sediments due to the face-to-face formation of kaolinite particles in the presence of  $\text{FeCl}_3$  at low pH values.

It appears from the Figure 4 that the space between the particles in edge-to-face structures decrease as the ionic strength increases. The reason for the decrement in the void ratio may be attributed to the reduced thickness of double layer surrounding the clay particle. Yet, increasing the salt concentration leads to shrink the double layer and particles approach each other closely; therefore, lower sediment thicknesses are achieved as a result of higher ionic strengths.

### **Solid Concentration**

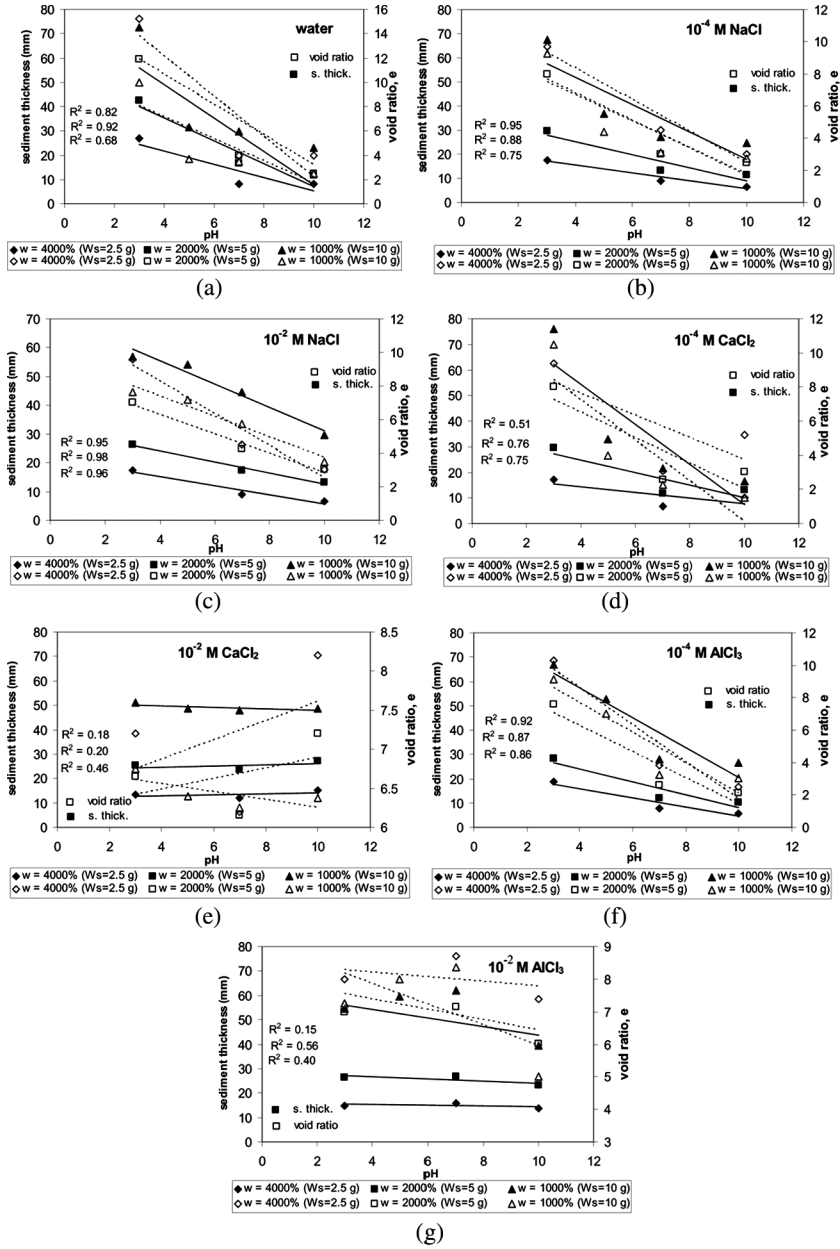
The settling characteristics of kaolinite were determined with 2.5 g, 5 g and 10 g kaolinite to determine the role of the solid concentration in 100 mL graduated cylinders. These soil weights correspond approximately 4000%, 2000% and 1000% water content, respectively. The typical effects of solid concentration of settling characteristics of kaolinite with time are shown on Figures 5a through 5h. For comparative reasons, the settling characteristics are presented at pH 3 and pH 10. The figures show that an increase in solid concentration also increases the settling time. Our data on settling characteristics of kaolinite are in agreement with Imai (1980) and Sridharan and Prakash (2001). The results indicate that the settling time increases as the solid concentration increases whether or not the kaolinite particles settle in either dispersed form or flocculated form.





**Figure 5.** Typical examples of solid concentrations effects on settling characteristics of kaolinite, (a) water at pH 3, (b) water at pH 10, (c)  $1 \times 10^{-2}$  M NaCl at pH 3, (d)  $1 \times 10^{-2}$  M NaCl at pH 10, (e)  $1 \times 10^{-2}$  M  $\text{CaCl}_2$  at pH 3, (f)  $1 \times 10^{-2}$  M  $\text{CaCl}_2$  at pH 10, (g)  $1 \times 10^{-2}$  M  $\text{AlCl}_3$  at pH 3 and (h)  $1 \times 10^{-2}$  M  $\text{AlCl}_3$  at pH 10.

As solid concentration increases, sediment thickness also increases and final sediment thickness is a function of the pH of the solution. Figures 6a through 6g present these correlations. Open symbols with dashed lines and close symbols with solid lines represent the void ratios and sediment thickness, respectively. Figure 6 shows that linear change in sediment thickness (void ratio) diminishes with the pH



**Figure 6.** Variation of sediment thickness with pH at different ion type and concentration, (a) water, (b)  $1 \times 10^{-4}$  M NaCl, (c)  $1 \times 10^{-2}$  M NaCl, (d)  $1 \times 10^{-4}$  M CaCl<sub>2</sub>, (e)  $1 \times 10^{-2}$  M CaCl<sub>2</sub>, (f)  $1 \times 10^{-4}$  M AlCl<sub>3</sub>, and  $1 \times 10^{-2}$  M AlCl<sub>3</sub>.

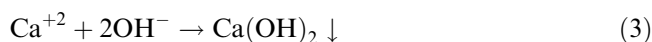
in the presence of  $1 \times 10^{-2}$  M CaCl<sub>2</sub> and  $1 \times 10^{-2}$  M AlCl<sub>3</sub>. This is because  $1 \times 10^{-2}$  M concentration level for CaCl<sub>2</sub> and AlCl<sub>3</sub> solutions are so high; therefore, kaolinite particles tend to make flocculated sedimentation independent of pH. It is known that sodium has lower anhydrated ionic radius; yet, higher hydrated ionic radius than that of calcium and aluminum: the higher the hydrated ionic radius,

the lower the Coulombic forces. Since electrical forces are inversely proportional to the distance between two charged surfaces, higher hydrated ionic radius of an element is attracted to a charged surface which is weaker than that of lower ones (Bohn et al. 1985). Hence, two charged surfaces could approach each other limited while treated with sodium. However, calcium and aluminum treated surfaces approach nearly each other to form network with porous structure and results flocculation sedimentation. Otherwise, both accumulated and flocculated sedimentation are seen for lower concentration levels and ion type with respect to pH.

### ***Zeta Potential of Kaolinite***

Figures 7a through 7c shows the variation of the zeta potential of kaolinite as a function of pH at  $1 \times 10^{-2}$  and  $1 \times 10^{-4}$  M concentrations of NaCl, CaCl<sub>2</sub>, and AlCl<sub>3</sub>, respectively. The zeta potential of kaolinite in water is also plotted for comparative reasons in Figures 7a, b, and c. Contrary to the results reported in Table 1, the tested kaolinite in this study did not produce any *pzc*, indicating that the reported *pzc*s for soils may show large variations. However, our test data is in good agreement with those of West and Stewart (1995) and Vane and Zang (1997) who reported that the *pzc* of Georgia kaolinite is produced when the solution pH < 3.

The zeta potential of kaolinite becomes more negative with an increase in alkalinity in the presence of NaCl (Figure 7a). On the other hand, the zeta potential of kaolinite in the presence of CaCl<sub>2</sub> becomes less negative with increase in pH. It reaches a plateau, and then attains more negative values. Such variation in the zeta potential of kaolinite in the presence of CaCl<sub>2</sub> can be explained by precipitation of Ca<sup>+2</sup> as salt hydroxide in high alkaline environments (Yukselen and Kaya 2003)



The ↓ sign indicates precipitation of Ca(OH)<sub>2</sub>. Thus, the measured zeta potential of kaolinite in a high alkalinity environment may not represent the true zeta potential of kaolinite, instead, it may be that of precipitated calcium hydroxide as it is demonstrated in Equation 3.

Contrary to CaCl<sub>2</sub> and NaCl solutions, both  $1 \times 10^{-4}$  M and  $1 \times 10^{-2}$  M AlCl<sub>3</sub> produce positive zeta potential at near neutral pHs and become negative again with an increase in alkalinity.

### ***Correlation between Sediment Thickness and Zeta Potential***

Figures 8a through 8c correlates sediment thickness (average final void ratio) of 10 g of kaolinite with zeta potentials. The dashed lines represent zeta potentials, and the solid lines void ratio. Figure 8(a) shows a good correlation between the final sediment thickness, and its zeta potential in the presence of NaCl solutions. As the zeta potential of kaolinite particles becomes more negative, the final sediment thickness decreases. This can be explained by the structural model of flocs and their networks. As the zeta potential of kaolinite becomes less negative in acidic environments, flocculation among particles develops and edge-to-face type structure occurs. With an increase in flocculation among the particles and formation of flocs, larger spaces are created among them that lead greater final sedimentation thickness. However, flocculated structures may develop in alkaline pHs when ionic concentration is relatively high and may trigger limited flocculation according to the diffuse double layer theory.

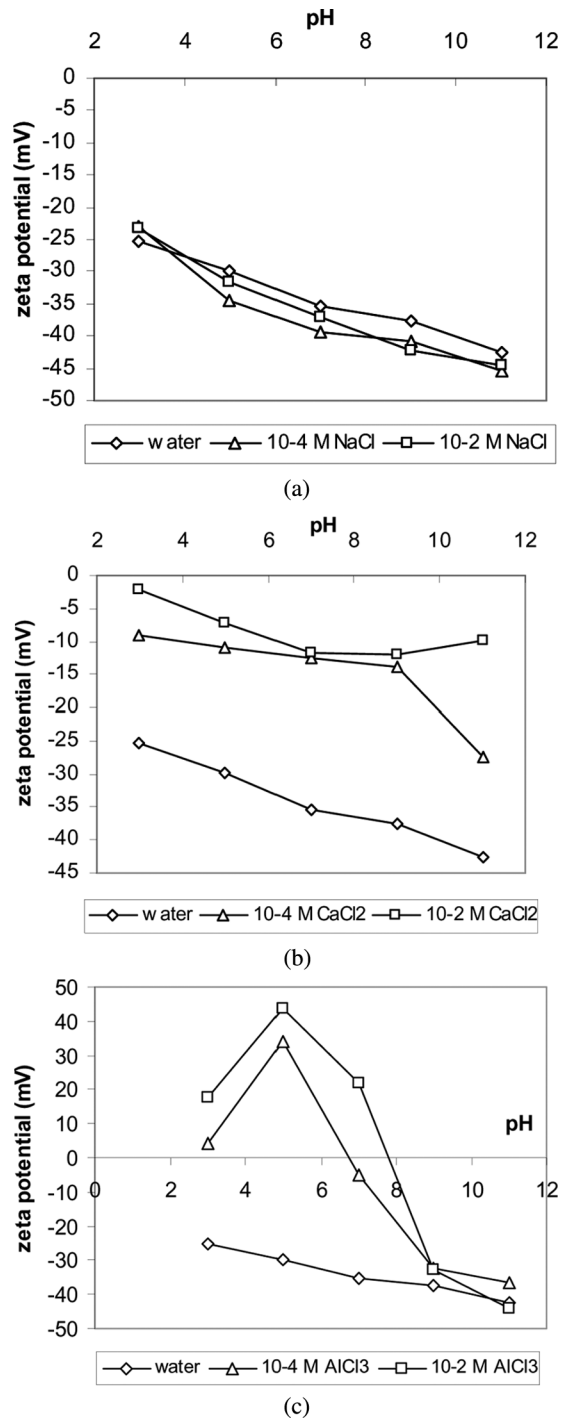
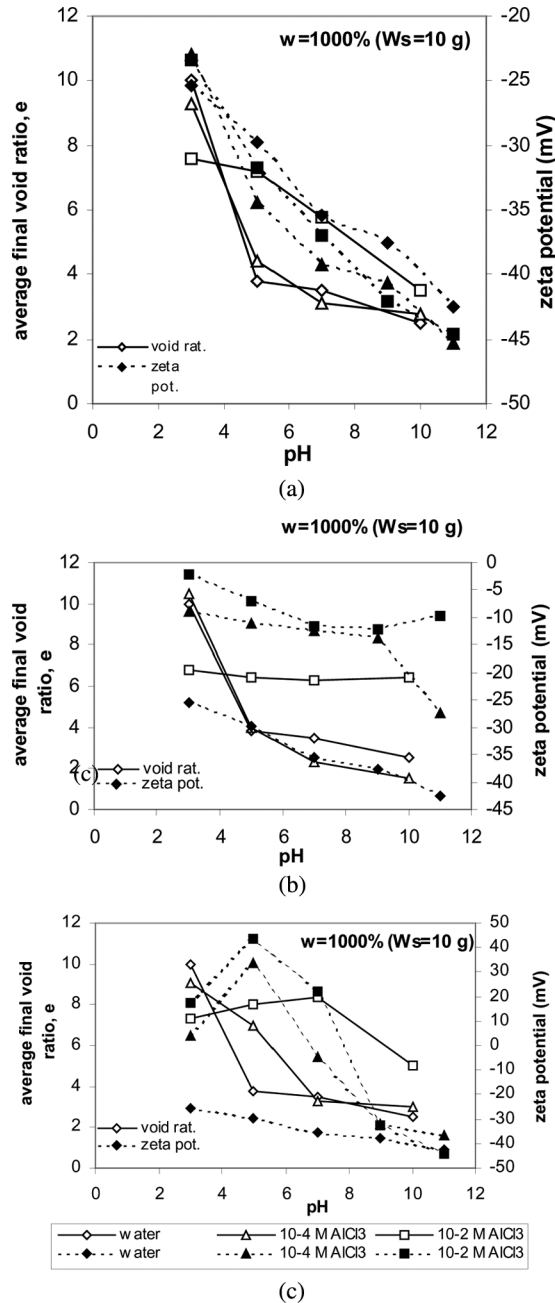


Figure 7. Zeta potential of kaolinite with (a) NaCl, (b) CaCl<sub>2</sub>, and (c) AlCl<sub>3</sub>.



**Figure 8.** Correlation of zeta potential of kaolinite with sediment thickness as function of pH, (a) NaCl, (b)  $\text{CaCl}_2$ , and (c)  $\text{AlCl}_3$ .

Although the general trend is still there in the presence of  $\text{CaCl}_2$  and  $\text{AlCl}_3$ , a good correlation between zeta potential and the final sediment thickness of kaolinite diminishes probably due to precipitation of  $\text{CaCl}_2$  and  $\text{AlCl}_3$  as calcium hydroxide and aluminum hydroxide. This is because the calcium

hydroxide and aluminum hydroxide precipitate alter the zeta potential of kaolinite in alkaline pHs.

## Discussion

The results indicate that the settling characteristics of kaolinite vary with pH of the medium such that kaolinite settles as a flocculated form in acidic environments and as in a dispersed form in alkaline environments. Kaolinite is a hydrous aluminum silicate with chemical composition of  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . Under an acidic environment ( $\text{pH} < 6$ ), aluminum exposed at the edges binds with hydrogen ions to attain positive charges. Such electrostatic environment causes an edge-to-face attraction that creates a card-house structure. As the pH becomes more acidic and the ionic strength increases in the aqueous environment, the size of the card-houses increases (Figure 3a). Under an alkaline environment of low ionic concentration, the edges become neutral or negatively charged and particles deflocculate and settle independently. However, when ionic concentration is relatively high, positive charges develop at the edges causing flocculated settling (Figure 3d). Kaolinite settles in flocculated form at  $1 \times 10^{-2}$  M NaCl,  $\text{CaCl}_2$  and  $\text{AlCl}_3$  at pH 7; however, it settles in a flocculated form only at  $1 \times 10^{-2}$  M of  $\text{CaCl}_2$  and  $\text{AlCl}_3$  at pH 10 (Figures 3c and 3d, respectively). Such settling characteristics of kaolinite show that it can be altered with ionic strength in aqueous environment.

As it is stated above, totally flocculated and totally dispersed settling of soil particles are two extreme characteristics of soil settling. However, depending on the pH and ionic concentration, soil particles may settle between these two types. In other words, soils may present both flocculated and dispersed form of settling in a given aqueous environment depending on the positive charges at the edges of particles and on the number of the particles that develop a card-house type structure.

As the aqueous medium becomes more alkaline, the final sediment thickness decreases (Figures 6a–6g). As the pH increases, the bonding forces between edge-to-face particles decrease due to the decrease in positive charges at the edge of the particles. Such an arrangement between the particles would create small spaces between the particles forming a denser soil structure. On the other hand, in an acidic aqueous environment, the strength between bonding and the forces between edge-to-face structures is high due to high positive charge at the edges of the particles. Strong edge-to-face structure would create large spaces between the particles forming a less dense particle arrangement in the final sediment thickness. In very acidic environments, aggregation is unavoidable because of the collision of flocs during settling.

In the aqueous environment, kaolinite surfaces are negatively charged and are uniformly distributed over basal surfaces due to substitution of aluminum for silicon in the crystal lattice. The zeta potential of the kaolinite also reflects the changes in the electrical charge that occur on the basal surface of kaolinite with changes occurred with ionic strength and pH of the aqueous medium (Kaya and Fang 2000). Thus, it should be expected that the final sediment thickness should be correlated with the zeta potential, and indeed there is a good correlation between final sediment thickness and zeta potential of kaolinite, especially when the particles settle in dispersed form.

There is a poor correlation between the zeta potential and average sediment thickness in  $\text{CaCl}_2$  solutions; however, this poor correlation is due to problems of measuring the zeta potential of kaolinite with  $\text{CaCl}_2$  in alkaline solutions.  $\text{CaCl}_2$

precipitates as  $\text{Ca(OH)}_2$  in alkaline pHs. The results also agree well with those of Ohtsubo and Ibaraki (1991) who have found a good correlation between zeta potential and the  $D_{50}$  diameter of flocs formed under pH 4 and pH 7. Furthermore, Pierre and Ma (1999) have found acceptable correlations between the final sediment thicknesses of kaolinite treated with  $\text{AlCl}_3$ .

Sridharan and Prakash (2001) concluded that the settling characteristics of kaolinite are due to their fabric. However, the test results of this study on kaolinite show that the fabric is formed during the settling of the kaolinite particles.

In the experiments, we chose to shake kaolinite to mix it thoroughly with the aqueous medium. Such a mixing procedure might potentially affect settling characteristics. However, the results indicate that the mixing procedure did not alter the settling characteristics since the settling characteristics were clearly different in alkaline and acidic aqueous environments. The mixing procedure might affect the floc sizes, but this did not change the overall observed settling characteristics of kaolinite.

In this study, we have shown that increase in the solid concentration causes increase in the settling rate of kaolinite. This can be explained by the buoyancy force discussed extensively in the studies by Chu et al. (2002), Cho et al. (1993), and Bhargava and Rajagopal (1993).

## Conclusions

Based on the results of this study, the following conclusions have been derived:

1. Settling characteristics of kaolinite is a function of solid concentration, ionic strength and pH of the aqueous environment. Kaolinite settles in flocculated form due to formation of edge-to-face structures in acidic environments and settles in dispersed form in alkaline pH, providing that the ionic strength is low. Kaolinite particles form edge-to-face structures due to increased positive charges at the edge of the particles.
2. As the pH of the medium becomes more alkaline, the final sediment thickness decreases. The final sediment thickness increases in acidic pH due to large spaces formed between the flocs in the edge-to-face structures. It appears that there is an inverse correlation between sediment thickness and pH of the aqueous environment.
3. As the solid concentration increases, the settling rate decreases because of the buoyancy effect.
4. The fabric of the sediment soils is a function of the clay mineral as well as the chemistry of the aqueous environment. The fabric of the sediments is formed during their initial sedimentation process. Thus, the sediments with different fabrics would have different engineering properties.
5. In general, the sediment thickness and zeta potential shows a fairly good correlation. More negative zeta potential leads to the thinner sediment thickness. This correlation is strong especially when kaolinite particles settle in dispersed form.

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