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Sedimentation Behavior of Clays in Response to Pore-Fluid Chemistry: Effect of Ionic Concentration and pH on Its Trends

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ABSTRACT

This study investigates the effect of pore fluid chemistry on the sedimentation trends and liquid and plastic limits within the new fines classification framework for four clayey soils with different specific surface and mineralogy. The sedimentation tests and fall cone tests are performed with seven different ionic concentrations ($c = 1 \times 10^{-5} \sim 1.8$ M) and the four target pH values (pH = 3, 5, 7, and 9) for each of the ionic concentrations. Three different sedimentation trends such as flocculated, dispersed, and mixed (at c = 0.0015-to-0.003 M) modes are observed at different ion concentrations and pH conditions of the pore fluids. Three sedimentation parameters named A_1, A_2 and A_3 are defined from the sedimentation curve. The relationship between them implies the salient features of the sedimentation trend for tested clayey soils. These parameters confirm the observed sedimentation modes and the critical ionic concentration; $c^* \sim 3 \times 10^{-3}$ M for AMK and EPK (high specific surface) and $c^* \sim 1.5 \times 10^{-3}$ M for LKW and MI (low specific surface) where notable fabric change occurs. The higher specific surface clays are classified as intermediate electrical sensitive clays whereas the lower specific surface clays are categorized into low electrical sensitivity fines in the new classification chart. A complementary data analysis for the sedimentation parameters and the new fines classification chart reveals that the robust link between distinct sedimentation trends and salient features of clay particles captured in the new fines classification chart can be useful to predict the sedimentation modes of clays with different pore fluid chemistry.

1. Introduction

The most unique behavior of clay particles is their ability to readily form flocs when they are in contact with a fluid. A floc can be defined as an agglomeration of many primary clay particles clumping by attractive electrochemical forces or biochemical bonding (Mehta, 2014). When forming of a floc, clay particles settle down and deposit in the process of sedimentation under a gravity. Previous investigations have identified three typical sedimentation trends at different ion concentrations and pH conditions of the pore fluids such as flocculated, dispersed, and mixed modes (Imai, 1980; Pierre and Ma, 1999; Sridharan and Prakash, 2001; Palomino and Santamarina, 2005; Kaya et al., 2006).

In the flocculated sedimentation mode (Fig. 1(a)), the suspension height (h) decreases over time with a clear distinction between the suspension and clear supernatant (Vitale et al., 2016). For the flocculation mode, the induction period is relatively short while the sedimentation rate is relatively faster. No demarcation between the sediment and the suspensions is generally observed and the sedimentation height decreases with the time. On the other hand, the particles in the dispersed mode are very stable and there is no clear interface between the turbid suspension and the supernatant (Fig. 1(b)). Consequently, relatively long induction period prevails and the dispersed soil particles settle under gravity, and form compact sediment at the bottom. Lastly, the mixed sedimentation mode exhibits that the more massive colloidal particles settle faster without undergoing particle-particle interaction whereas the finer particles remain in suspension long enough to interact and initiate a substantial flocculation attribute. In the light of presented facts, it is clear that sedimentation characterizations require time-consuming laboratory efforts.

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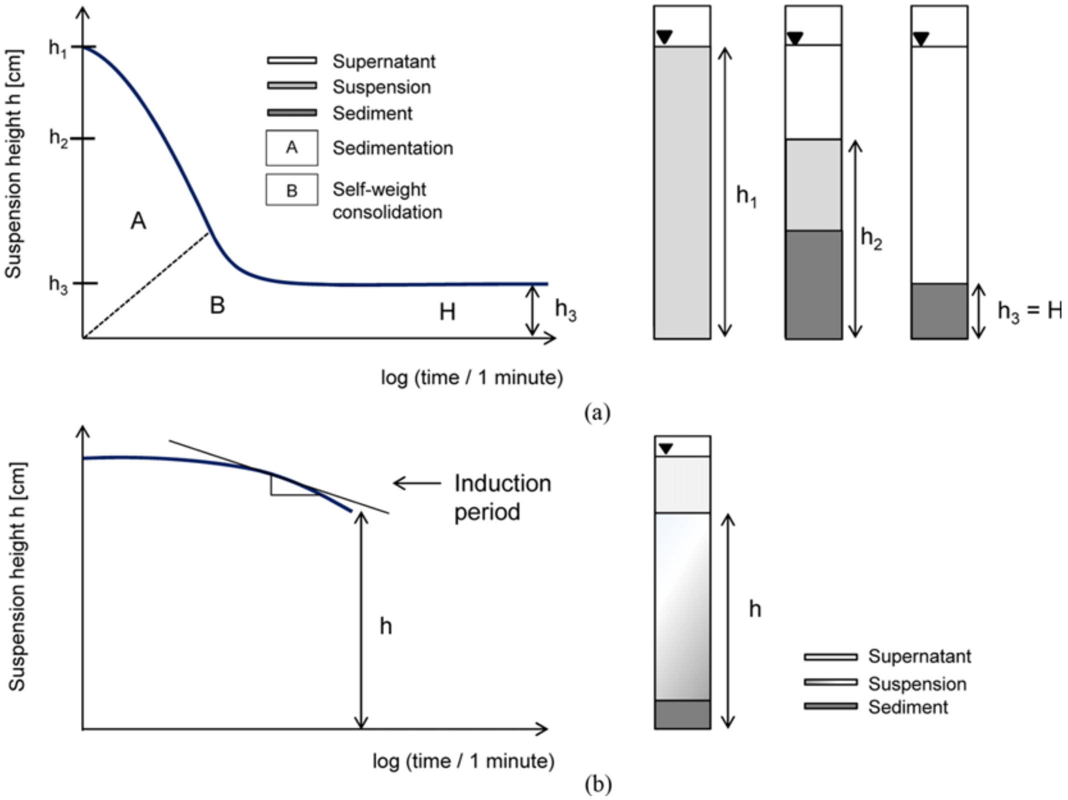


Fig. 1. Schematic Drawing of Different Sedimentation Patterns: (a) Flocculated System, (b) Dispersed System (modified after Vitale et al., 2016)

Having taken into consideration statements showed above, engineers have widely adopted the soil consistency (i.e., Atterberg limits) as useful indicator of clay behavior (Jefferson and Rogers, 1998; Santamarina et al., 2001; Mitchell and Soga, 2005). Furthermore, new fines classification system in terms of electrical sensitivity and plasticity helps them understand the fine behavior in response to pore fluid chemistry (Jang and Santamarina, 2016; Jang and Santamarina, 2017; Park and Santamarina, 2017; Park et al., 2018). This system is built on the soil index properties readily available from the laboratory tests such as three liquid limits measured with deionized (DI) water, 2M brine, and kerosene. However, the robust link between sedimentation trends and fines behavior in response to different pore fluid chemistry remains overlooked although they seem to be complementary with each other to enhance the predicting of clay sedimentation trends.

This study investigates the sedimentation trends for clays with different specific surface and mineralogy when subjected to a broad range of ionic concentrations and pH. Then, three critical sedimentation parameters are defined to seek strong correlations for each other. Next, the tested clays are characterized based on their liquid and plastic limits within the new fines classification framework. The sedimentation parameters and new fines classification chart are analyzed in the context of different ionic concentrations and pH. Data analyses suggest that the robust link between distinct sedimentation trends and salient features of clay particles captured in new fines classification chart can be used to predict the sedimentation modes of clays in a broad range of plasticity.

2. Previous Studies: Sedimentation Modes

Sedimentation behavior of clay suspension in various pore fluids is similar to the electrochemical interactions acting at particle level (Pierre and Ma, 1999; Palomino and Santamarina, 2005; Kaya et al., 2006). A variational assessment of the sedimentation behavior of clay suspensions under different pore water chemistry was conducted x-raying the chemo-physical mechanisms influencing particle arrangement and the soil fabric formation. For several decades, sedimentation phenomenon has been the subjects of research, yet limitations in the knowledge of the particle–particle interactions and the dynamics of diffuse double thickness abounds. The flocculation behavior of kaolinite dispersions under different pore fluid conditions has been investigated by some researchers (Taylor et al., 2002; Żbik and Horn, 2003; Itami and Fujitani, 2005; Palomino and Santamarina, 2005; McFarlane et al., 2006; Nasser and James, 2006), while others were able to distinguish between different sedimentation modes that are observed in kaolinite clay (Patton, 1979; Imai, 1980; Pierre and Ma, 1999; Ravisangar, 2001; Palomino and Santamarina, 2005). With the aid of the Scanning Electron Microscope (SEM), Pierre et al. (1995) confirmed the structures of kaolinite sediments formed from suspension exhibiting flocculation and dispersed settling behavior. However, most of these studies are limited to kaolinite and the effects of specific surface areas within and outside a given mineralogy were rarely considered. In this context, the range of ionic concentration and pH selected in this study benefits from the previous investigations and it is compatible with pore fluid chemistry adopted in previous studies (Palomino and Santamarina, 2005; Palomino et al., 2008).

3. Experimental Study

This study emphasizes on the sedimentation trends of four clayey soils with different mineralogy and specific surface when subjected to different pore fluid chemistry such as pH and ionic concentration. A brief description of tested materials, specimen preparation, and test procedure can be found below.

3.1 Materials

This study uses four clayey soils with different mineralogy and specific surface (S_s). The clays include three kaolinite-dominant clays named AMK, EPK, and LWK and one illite-dominant clay named MI. Table 1 summarizes basic index properties of tested materials with measurement devices or methods. Four clayey soils were selected to investigate the effect of mineralogy and specific surface on sedimentation behavior with different pore fluid chemistry: same mineralogy but different specific surfaces (i.e., EPK/AMK and LWK) and samples of different mineralogy but similar specific surfaces and CEC (i.e., LWK and MI). The AMK and the EPK soils have similar specific surface values of approximately $S_s \approx 60$ m^2/g with the same mineralogy while two other soils, such as LWK and MI, have the similar specific surface values of approximately $S_s \approx 10$ m^2/g but with different mineralogy. In general, the trend of median particle size (D_{50}) for the four clays measured in this study is in accordance with the inverse relationship between specific surface and median particle size.

3.2 Specimen Preparation

The suspension preparation for sedimentation tests starts with a pretreatment process to eliminate the excess and inherent salts and any residual organic components in the clays (Van Olphen, 1963). All soils are vigorously mixed with a 2 mol/L NaCl solution at about 4 mL of solution per gram of each clay by using a mechanical stirrer. Then, the suspension is kept for 48 hours to settle. Thereafter, the supernatant is decanted and replaced with 1 mol/L NaCl solution. The suspension is mixed by using a mechanical stirrer and left for 24 hours to equilibrate. The supernatant is replaced with fresh 1 mol/L NaCl solution and the suspension is mixed again and left another 24 hours to equilibrate. Finally, all soils are washed with a deionized (DI) water several times until the electrical conductivity of the supernatant is less than 1×10^{-3} S/m in order to eliminate the excess and inherent salts and any residual organic components on the soil (Accumet XL500 Dual pH/ISE and Conductivity Benchtop Meters). After the pretreatment process, all specimens of soils are dried in an oven for 24 hours at 100 ± 5ºC. The oven-dried samples of soils are ground and sieved by using a Sieve No. 200 (i.e., opening size = 75 μm).

3.3 Test Procedure

Pore fluids used for sedimentation tests involve NaCl solutions with seven different ionic concentrations c (i.e., $c = 1 \times 10^{-5}, 4 \times 10^{-4}$, 1.5×10^{-3}, 3×10^{-3}, 5×10^{-2}, 0.1, and 1.8 M) and four target pH values (i.e., pH = 3, 5, 7 and 9) for each of the ionic concentrations. These combinations result in 28 solutions in total to cover a

Table 1. Index Properties of Various Clays Used in This Study (All soil samples are passed through the sieve No. 200 (particle size < 75 μm))

Index Properties	Clay Samples				Device/Technique
	AMK	EPK	LWK	MI	
Major Mineralogy	Kaolinite			Illite	Philips, X'Pert MPD X-ray Diffractometry
Mineralogical composition [%] by weight	$SiO_2 = 48.4$ $Al_2O_3 = 33.5$ $CaO = 5.83$ $Fe_2O_3 = 1.19$ $K_2O = 0.36$	$SiO_2 = 46.6$ $Al_2O_3 = 38.3$ $CaO = 0.011$ $Fe_2O_3 = 0.541$ $K_2O = 0.286$	$SiO_2 = 47.7$ $Al_2O_3 = 34.0$ $CaO = 5.51$ $Fe_2O_3 = 1.32$ $K_2O = 0.481$	$SiO_2 = 72.6$ $Al_2O_3 = 14.4$ $CaO = 0.03$ $Fe_2O_3 = 4.59$ $K_2O = 4.10$	Zetium, PANalytical X-ray fluorescence (XRF)
Specific Gravity G_s	2.62	2.60	2.53	2.77	Pycnometer (ASTM D845)
Median Particle Size D_{50} [μm]	0.6	1.4	23.0	20.0	Hydrometer (ASTM D7928)
Specific Surface S_a [m^2/g]	68.5	59.4	9.79	10.7	Methylene Blue (Santamarina et al., 2002)
Liquid Limit LL under DI Water [%]	82.3	76.2	43.8	49.3	Fall Cone BS 1377 (1990)
Plastic Limit PL under DI Water [%]	51.0	43.9	21.5	25.3	Fall Cone Wood and Wroth (1978)
Cation Exchange Capacity CEC [meq/100 g]	20.2	18.1	12.9	9.1	Methylene Blue (Wang et al., 1996)
Manufacturer	Active Minerals	Edgar minerals INC	Lakwoo	Medex	-

broad range of pore fluids. Note that the range of pH values from 3-to-9 is designed because physico-chemical mechanisms appear to be dominant within selected pH ranges as well as significant changes in the mineral structure occur including the dissolution of Al^{3+} in a very acidic environment, i.e., < pH 3 or the formation of new minerals such as a zeolite at very high pH, i.e., > pH 9 (Sivapullaiah and Manju, 2006).

The solid volume fraction (ϕ) is the ratio between total volume of solid and total suspension volume. The suspensions are prepared for a solid volume fraction $\phi = 0.02$ in all cases. The cylinder is filled with 25 mL of the selected pore solution and 5 g of oven dried and sieved sample is gently mixed with the pore-fluid in the cylinder. Then, more pore fluid is added to rinse any adhering particles on the sides of the cylinder until it reaches a total height of 19 cm corresponding to 100 mL (note, the cylinder diameter = 2.8 cm) After placing a stopper, the cylinder is slowly and gently turned upside down and back to mix the suspension. When a uniform appearance is observed, the suspension is left for 24 hours to ensure a full hydration of clay. After a stabilization, the cylinder is vacuumed to remove trapped air bubbles and

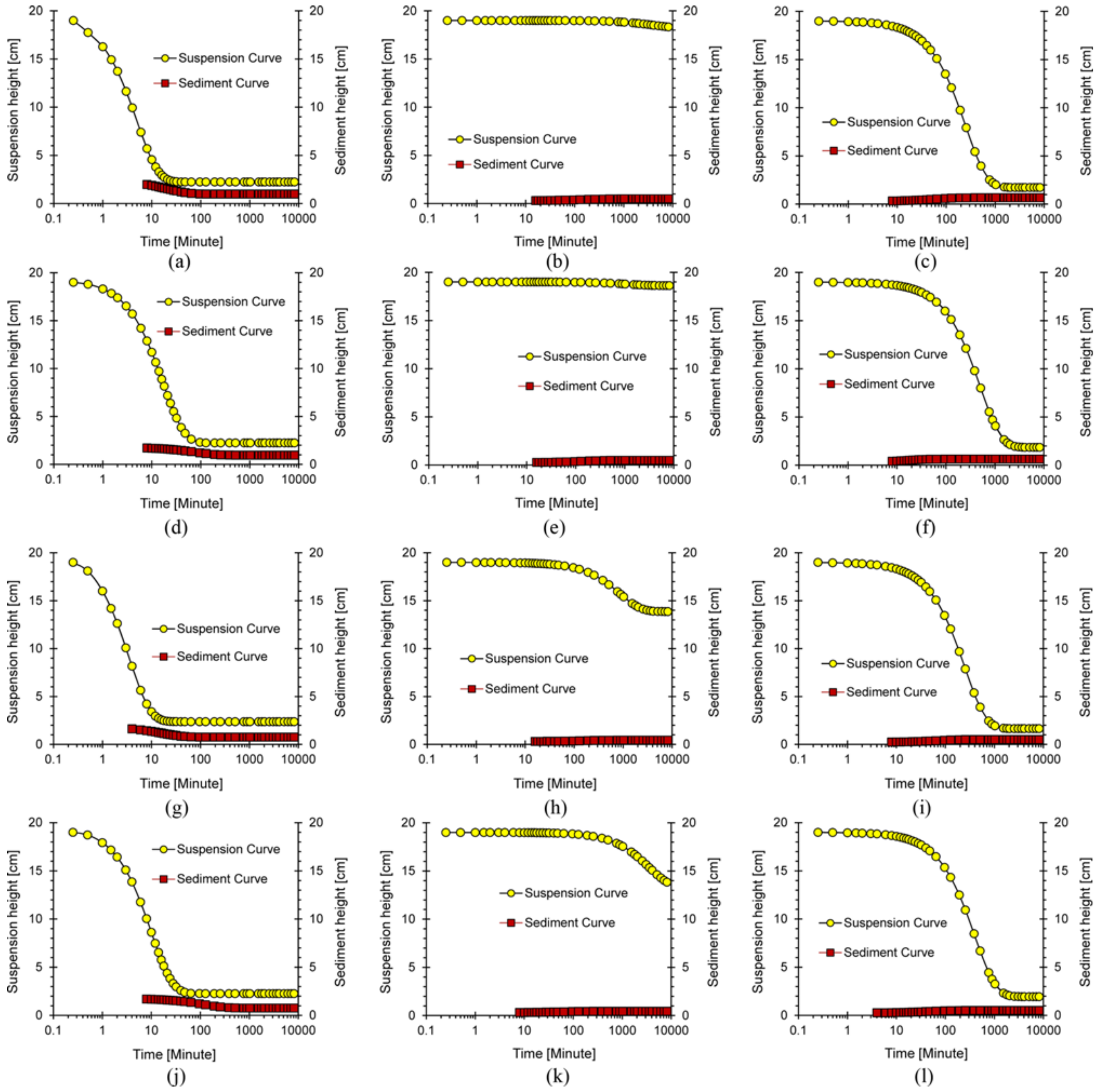


Fig. 2. Three Typical Sedimentation Trends for All Tested Samples. Note that (a-c) Obtained from AMK, (d-f) Obtained from EPK, (g-i) Obtained from LWK, and (j-k) Obtained from MI: (a) Flocculation at c = 0.1 M, (b) Disperse at c = 10^{-5} M, (c) Mixed at c = 0.003 M, (d) Flocculation at c = 0.1 M, (e) Disperse at c = 10^{-5} M, (f) Mixed at c = 0.003M, (g) Flocculation at c = 0.1 M, (h) Disperse at c = 10^{-5} M, (i) Mixed at c= 0.0015 M, (j) Flocculation at c = 0.1 M, (k) Disperse at c = 10^{-5} M, (l) Mixed at c = 0.0015M (Note: pH = 7 in all cases)

dissolved gas in the suspension. The cylinder is re-mixed for a minute and placed on an undisturbed smooth level surface for the settlement initiation (i.e., time zero t_o) (see a similar suspension preparation method in Palomino et al., 2008). Time-laps images are taken to monitor the change in the suspension and sediment heights by using a digital camera (Canon PowerShot G9).

As a part of this study, fall cone tests are also conducted to measure the liquid limit (LL) and plastic limit (PL) of the four clays with the seven different ionic concentrations *c* and the four target pH values for each of the ionic concentrations. Procedure for the fall cone test starts with about 50 mL to 150 mL of each pore solution that is mixed with 150 g – 350 g of the clay sample. The soil paste is left to hydrate for 12 hours before taking the first measurement point. The paste is thoroughly re-mixed, and carefully placed in a fall cone cup to avoid voids. The excess soil is scraped, leaving a flat surface. The cone is released from the device, once sufficient penetration depth is achieved; about 15 g of the soil mixture is taken for water content determination. The remaining soil mixture is mixed with more pore fluid for the next measurement. Electrically contrasting pore solution such as deionized water, 1.8 M NaCl brine solution, and kerosene are used to define the "electrical sensitivity" of the soil, while same procedure as the fall cone test above was applied. In addition, both LL and PL of the four clays are measured with 2M brine and kerosene (BS 1377, 1990). Results are interpreted in the context of electrical sensitivity and plasticity (Jang and Santamarina, 2016).

The two different laboratory tests such as sedimentation test and fall cone test were performed in this study. For sedimentation tests, the 7 different ionic concentrations of NaCl solutions and the 4 different pH values were applied to 4 different clay samples. Therefore, the number of sedimentation tests is 112 in total. Similarly, for fall cone tests, the 7 different ionic concentrations of NaCl and the 4 different pH values were applied to 4 different clay samples; the number of pore fluids described above is 112. Additionally, kerosene is used for 4 clay samples. Therefore, the total number fall cone tests is 116.

4. Experimental Results

Different sedimentation modes play a critical role in the determination of the engineering properties of clayey sediments such as friction angle, compression index, small strain stiffness, and hydraulic conductivity. Therefore, it is important to understand the soil behaviour before its formation.

Figure 2 shows the typical sedimentation trends for clays tested at pH = 7. In general, the sedimentation trend varies depending on the ionic concentration (*c*) at neutral pH. The flocculation predominates at a high ionic concentration (i.e., $c \geq 0.1$ M) while disperse mode becomes pronounced at a low ionic concentration (i.e., $c \leq 1 \times 10^{-5}$ M). In particular, there is a distinct transitional sedimentation behavior from dispersed to flocculated patterns in the range of ionic concentration 1.5×10^{-3} M $\leq c \leq 3 \times 10^{-3}$ M (defined as "mixed" mode in this study). The ionic concentration that initiates the mixed mode tends to be smaller as the specific surface of clays decreases (Figs. 2(b), 2(e), 2(h), and 2(k)).

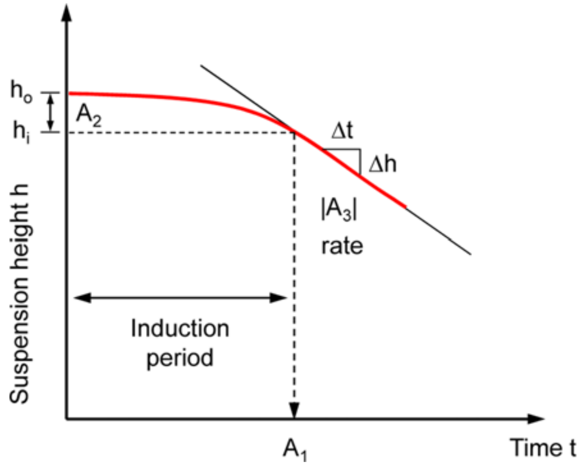


Fig. 3. Definition of Parameters Associated with Sedimentation Analyses

Figure 3 presents the schematic drawing of the sedimentation curve to define the three sedimentation parameters. The parameter A_3 captures the time-dependent linear sedimentation process and corresponds to the slope in the suspension height versus time where $A_3 = \Delta h/\Delta t$ (note: this study adopts the absolute value of A_3 for convenience). After induction period, the linear slope is determined by a line that provides minimum error between data and the line. Next, parameter A_1 captures the induction period which is the initial segment of the sedimentation curve in the suspension height versus time. The induction period A_1 corresponds to the intersection between the sedimentation curve and the linear line for $|A_3|$. Lastly, the parameter A_2 is the change in suspension height during the induction period, so that $A_2 = h_o - h_i$ where h_o is the initial suspension height and h_i is the suspension height at the end of the induction period. Detailed analyses associated with sedimentation parameters are presented in the next section.

5. Analyses and Discussion

5.1 Sedimentation Parameters

Figure 4(a) presents the sedimentation parameters A_3 versus A_1 for all clay suspensions when subjected to ionic concentration $c = 1 \times 10^{-5}$ to 1.8 M and pH = 3-to-9. Clearly, the sedimentation rate $|A_3|$ after the induction period tends to decrease with a higher induction period captured by parameter A_1 in all cases. The bilinear trend in A_3 versus A_1 space highlights the three distinct sedimentation trends as a function of ionic concentration (*c*): flocculated, mixed, and dispersed modes. The effect of pH on this trend seems to be minute although the low pH values such as pH = 3 and 5 results in flocculated mode even at the low ionic concentrations).

On the other hand, there is an inverse relationship between the sedimentation rate $|A_3|$ and the change in the suspension height A_2 during the induction period in all cases (Fig. 4(b)). Fig. 4(b)

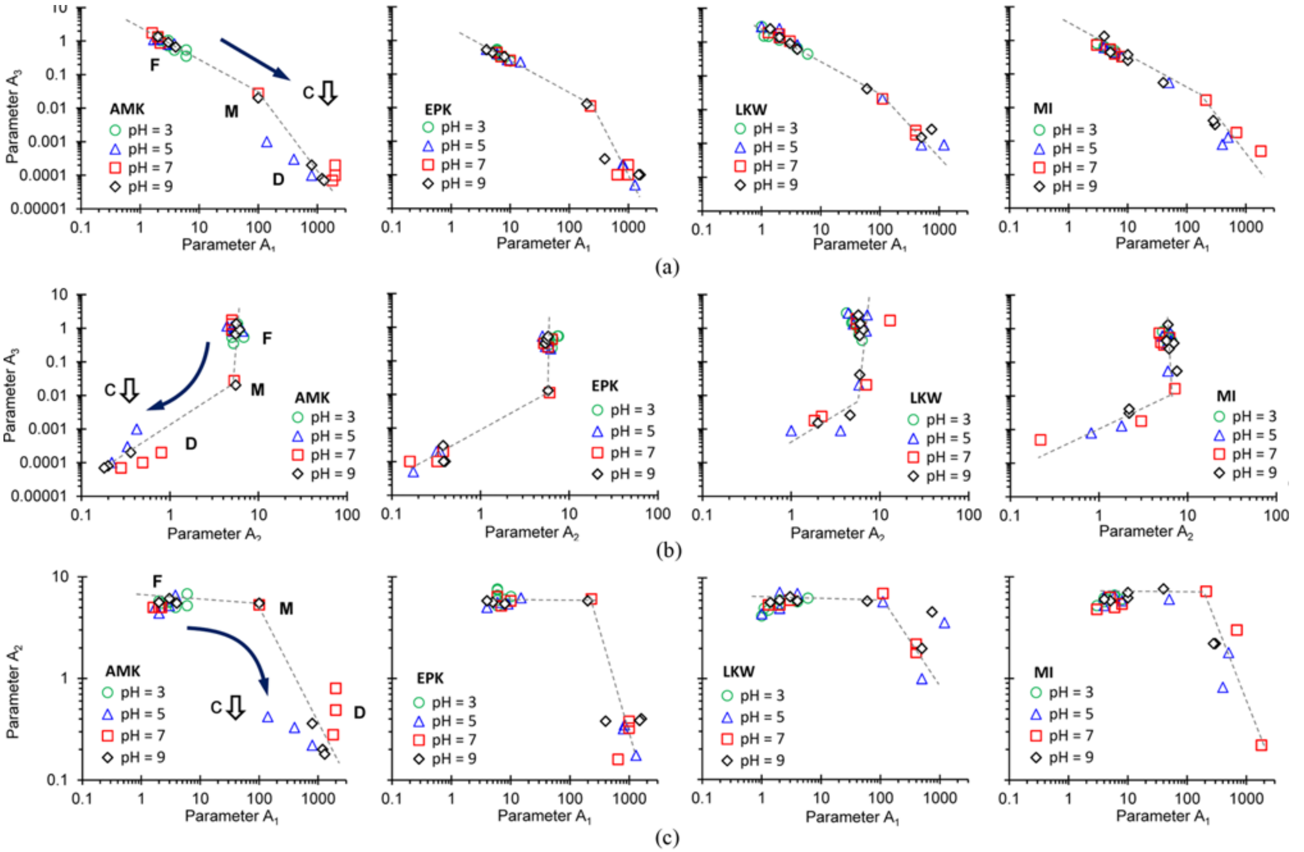


Fig. 4. Sedimentation Parameters – Correlation: (a) A3 vs A1, (b) A3 vs A2, (c) A2 vs A1 (The capital letter indicates F for flocculated, M for mixed, and D for dispersed sedimentation modes.)

shows that parameter $|A_3|$ increases with increasing parameter A_2. Obviously, the transition from flocculated to dispersed sedimentation occurs at distinctive ionic concentration $c^* \sim 3 \times 10^{-3}$ M for AMK and EPK (i.e., high S_s and smaller D_{50}) and $c^* \sim 1.5 \times 10^{-3}$ M for LKW and MI (i.e., low S_s and greater D_{50}) (refer to Table 1).

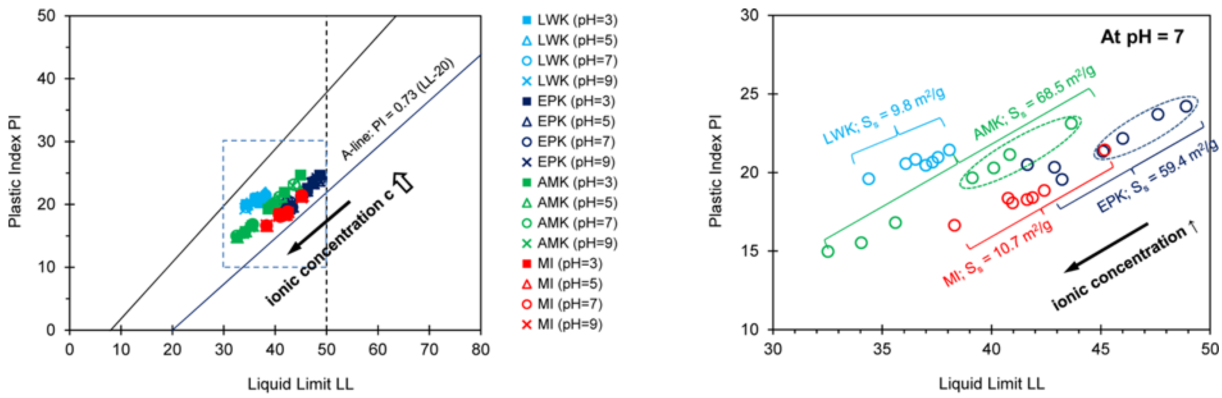
Figure 4(c). shows the relationship between A_2 and A_1. The change in the suspension height A_2 during the induction period also shows the inverse relationship of induction period A_1 (Fig. 4(c)). As the ionic concentration decreases, the parameter A_2 decreases as well. The characteristic ionic concentration that corresponds to the mixed mode appears at $c^* \sim 3 \times 10^{-3}$ M for AMK and EPK (i.e., high S_s and smaller D_{50}) and at $c^* \sim 1.5 \times 10^{-3}$ M for LKW and MI (i.e., low S_s and greater D_{50}) (refer to Table 1). In fact, all sedimentation parameters proposed herein adequately reflect the salient features of clayey soils. Specific surface rather than clay mineralogy seems to be critical in the determination of sedimentation behavior.

The variations of the sedimentation parameters A_1, A_2, and A_3 in this study confirm the observed sedimentation modes in the previous studies (Patton, 1979; Imai, 1980; Pierre and Ma, 1999; Ravisangar, 2001; Palomino and Santamarina, 2005) and the critical ionic concentration; $\sim 3 \times 10^{-3}$ M for AMK and EPK (high specific surface) and $c^* \sim 1.5 \times 10^{-3}$ M for LKW and MI (low specific surface). Associated fabric change due to the pore fluid chemistry can be inferred from there critical ionic concentrations.

5.2 Plasticity Charts

Although the soil consistency (i.e., Atterberg limits) has been proven many times to be useful indicators of clay behavior (Jefferson and Rogers, 1998; Santamarina et al., 2001; Mitchell and Soga, 2005), there has not been a general agreement regarding the dependence of soil consistency on pore fluid chemistry (Arasan, 2010; Jang and Santamarina, 2016): 1) for low-plasticity clays, both of liquid limit and plastic limit are slightly decreased when the salt concentration in the pore fluid increases because the salinity in the pore fluid might attribute to the reduction of double layer thickness (Rao and Mathew, 1995; Sridharan and Sivapullaiah, 2005; Arasan and Yetimoglu, 2008). Addition of $CaCl_2$ in the pore fluid somewhat increases liquid limit while decreasing the plasticity of low-plasticity clays because the structure of clay is altered into a more flocculated structure with adding Ca cation (Park et al., 2006); 2) for high-plasticity clays, both the liquid limit and plasticity are decreased with increasing NaCl or $CaCl_2$ concentrations in pore fluid, which is consistent with double-layer theory (Sridharan et al., 1986; Gleason et al., 1997; Petrov et al., 1997; Lin and Benson, 2000; Schmitz et al., 2004; Lee et al., 2005).

Furthermore, in acid environment (i.e., low pH), liquid limit



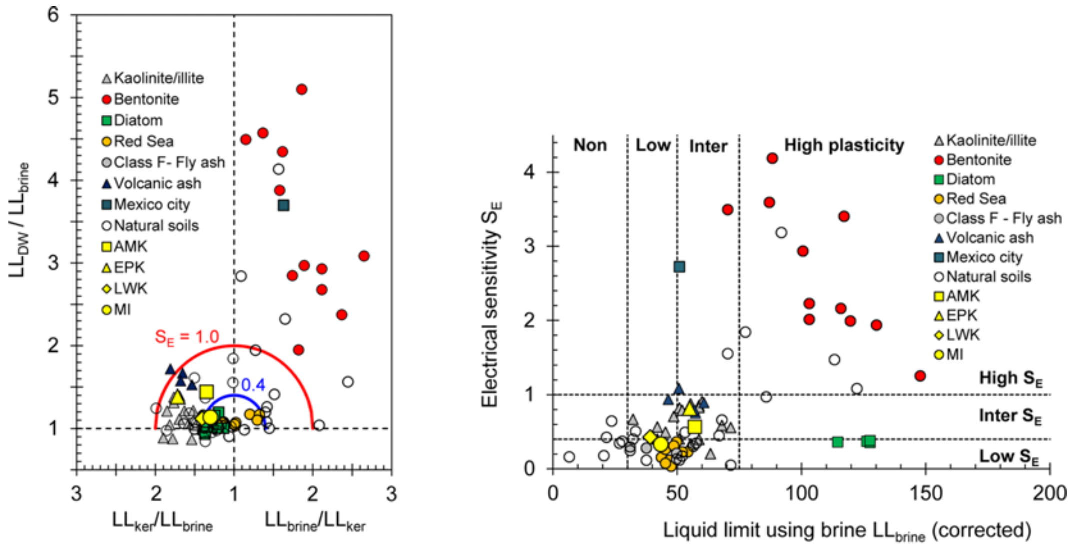
(a) (b)

Fig. 5. Plastic Index Versus Liquid Limit as a Function of pH and Ionic Concentration (This study uses seven different ionic concentrations that involves $c = 1 \times 10^{-5}$, 4×10^{-4}, 1.5×10^{-4}, 3×10^{-3}, 5×10^{-2}, 0.1, and 1.8 mol/L): (a) Variation of PI and LL, (b) Zoomed-In Plot of the Fig. 5(a)

and plasticity for low-plasticity clay are increased due to either the formation of flocculation with the dominant face-to-edge aggregation (Bowders and Daniel, 1987) or the dissolution of calcium carbonates (Gratchev and Towhata, 2016). On the other hand, low pH reduces the thickness of the diffuse double layer, leading to a lower liquid limit value for high-plasticity clays (Gajo and Maines, 2007).

In this context, Fig. 5(a) shows the plastic index (PI) versus liquid limit (LL) for all clays as a function of ionic concentration and pH. Once more, seven different ionic concentrations $c = 1 \times 10^{-5}$, 4×10^{-4}, 1.5×10^{-3}, 3×10^{-3}, 5×10^{-2}, 0.1, and 1.8 mol/L and four different pH = 3, 5, 7, and 9 were used in this study; therefore, the total number of cases is 28 for each clay sample. Results show that the PI decreases as the ionic concentration increases although all tested clays are classified into the CL according to the USCS. From the mineralogy point of view, the overlap in liquid limit for EPK, and MI clearly suggests the unstable and complex nature of illite (MI) (Long et al., 2006; Gratchev and Sassa, 2009) in comparison to other kaolinites despite having lower specific surface area, possibly because of the stable nature of kaolinite (Santamarina et al., 2001). Indeed, the role of pore fluid chemistry should be considered in soil classification systems for engineering purpose. The effect of pH on the liquid and plastic limits seems to be negligible.

For clarity, Fig. 5(b) shows the change in PI as a function of LL for pH = 7. Similar to the sedimentation parameter analyses, the characteristic ionic concentration $c^* \sim 3 \times 10^{-3}$ M for high specific surface clays, such as AMK and EPK, appears to divide clay plasticity behavior into two groups. This observation shows that the notable fabric change for the high specific surface clays is likely to arise near ionic concentration $c \approx 3 \times 10^{-3}$ mol/L. On the other hand, the effect of ionic concentration on the liquid and



(a) (b)

Fig. 6. Fines Classification in Terms of Pore-Fluid Chemistry: (a) Soils Response to Changes in Fluid Conductivity and Permittivity. The Liquid Limit Ratios are Greater than 1.0 in All Quadrants; The Inset Defines the Electrical Sensitivity SE where the Red Line Corresponds to SE = 1.0 and Blue to SE = 0.4 (Jang and Santamarina, 2016), (b) New Fines Classification Chart in Terms of Electrical Sensitivity SE and Liquid Limit LL. Result from the Current Study is Superimposed on Data and Other Published Studies

plastic limits for LWK and MI is not obvious due to the smaller specific surface (i.e., typical kaolinite $S_s = 10 \sim 20$ m^2/g). This observation indicates that the sedimentation tests appear to be more efficient to capture the low specific surface clay behavior in response to the change in pore fluid chemistry. Furthermore, the low specific surface clay hardly follows the double layer theory. They are prone to form the structures (e.g., edge-to-face and edge-to-edge) when subjected to different ionic concentrations whereas the change in double layer thickness could be minute.

5.3 Fine Classification Charts in Terms of Pore Fluid Chemistry

Figure 6(a) shows the electrical sensitivity of four tested clays (Jang and Santamarina, 2016). This chart uses two liquid limit ratios LL_{DW}/LL_{brine} and LL_{ker}/LL_{brine} to capture soil response to changes in fluid conductivity and permittivity. The distance between measured value and absolutely non-sensitive soil response at (1,1) indicates the electrical sensitivity S_E. Across the mineralogy and specific surfaces, liquid Limit with deionized water (LL_{DW}) and kerosene (LL_{ker}) were greater than that of brine (LL_{brine}). This is because the clay particle surface interacts with deionized water and develops thicker double layer, which increased interparticle repulsion, and develops higher porosity fabric unlike in the soil-brine mixture. Whereas the localized surface charge which are made more pronounced in low permittivity fluids (i.e., kerosene) than ionic concentration, generate clustered fabric, hence the higher void ratio obtained in the kerosene pore fluid than in the case involving ionic concentrations.

As shown in Fig. 6(a), the lower specific surface clays, such as LWK and MI, exhibit low electrical sensitivity. Comparison between LKW and MI indicates that index properties, such as median particle size, specific surface, and liquid limit rather than mineralogy, appear to be a good indicator to capture the electrical sensitivity of clayey soils (Table 1). By contrast, the higher specific surface clays, such as AMK and EPK, are classified as intermediate electrical sensitive clays. Therefore, the two high specific surface clays (i.e., AMK and EPK) fall into the II group, where the first letter corresponds to the “intermediate plasticity” and the second letter to “intermediate electrical sensitivity” fines. On the other hand, the two low specific surface clays, such as LWK and MI, tend to be “low plasticity” and “low electrical sensitivity” fines.

Figure 6(b) shows the new fines classification chart in terms of electrical sensitivity S_E and liquid limit with brine LL_{brine} (Jang and Santamarina, 2016). The samples are classified into non-, low-, intermediate-, or high-plasticity fines and low, intermediate, or high electrical sensitivity fines. Therefore, there are 12 soil groups in the new system. The comparison between data obtained in this study and data compiled from the literature indicates that volcanic ash may follow similar sedimentation trends as AMK and EPL while the Red Sea sediment or Class F-fly ash may attain a similar sedimentation parameter as LWK and MI. Data analyses for the sedimentation parameters and new fines classification chart suggest that the robust link between distinct sedimentation trends and salient features of clay particles captured in the new fines classification chart can be used to predict the sedimentation modes of clays in a broad range of plasticity.

5.4 Engineering Implications

The use of three parameters A_1, A_2, and A_3 defined in this study is a first attempt to capture distinct sedimentation curves with various pore fluid chemistry as shown in Fig. 3. Then, these three parameters are used to further examine the three distinct sedimentation trends such as flocculated, mixed, and dispersed sedimentation modes suggested in previous studies as shown in Fig. 4. In particular, the newly-proposed correlations between A_1, A_2, and A_3 vary with sedimentation modes. These correlations help geotechnical engineers anticipate the result of long-term and time-consuming sedimentation tests given these three measurable parameters in short-term period.

Accurate prediction of sedimentations for fine-grained soils gain relevance over many engineering implications. Associated examples include dispersion in dams, rainfall driven hydro-chemo coupled erosion of slopes/scouring, landfills, and dredging. In particular, different sedimentation modes determine the engineering properties of clayey sediments. From this aspect, one of the main contributions of this study is to link the new fines classification chart and sedimentation modes. Therefore, the relationship between the three sedimentation parameters (i.e., A_1, A_2, and A_3) and new fines classification chart proposed in this study enables geotechnical engineer adequately anticipate sedimentation trends with simple laboratory tests without time-consuming sedimentation tests.

6. Conclusions

This experimental study explores the variation of the sedimentation trends and liquid and plastic limits within the new fines classification framework for four clayey soils with different ionic concentrations and pH of the pore fluid. The relationship between the three sedimentation parameters (i.e., A_1, A_2, and A_3) and new fines classification chart enables geotechnical engineer adequately anticipate sedimentation trends with simple laboratory tests without time-consuming sedimentation tests. Notable observations and remarks from this study are as follows:

1. The sedimentation trends are strongly related to the ionic concentrations (c): flocculation is observed at high ionic concentrations, and dispersion is observed at low ionic concentrations. A transitional sedimentation behavior from dispersed to flocculated patterns is found at 1.5×10^{-3} M $\leq c \leq 3 \times 10^{-3}$ M, however, the ionic concentration that initiates the mixed mode tends to become smaller as the specific surface of clays decreases.
2. Three sedimentation parameters named A_1, A_2, and A_3, were defined from the sedimentation curve. The bilinear trend in $|A_3|$ versus A_1 space highlights the three distinct sedimentation trends as a function of ionic concentration (c). On the other hand, an inverse relationship between $|A_3|$

and A_2 was observed during the induction period in all cases. The effect of pH on this trend seemed to be minute.

3. The critical ionic concentration (c*) observed in the sedimentation test successfully captures the transition from flocculated to dispersed modes: the c* for high specific surface occurs at $c^* \sim 3 \times 10^{-3}$ M while c* for low specific surface c* occurs at $\sim 1.5 \times 10^{-3}$ M.
4. The variation of PI as a function of LL decreases as the ionic concentration increases. Similar to the sedimentation parameter analyses, the characteristic ionic concentration $c^* \sim 3 \times 10^{-3}$ M for high specific surface clays properly divide clay plasticity behavior into two groups. On the other hand, the effect of ionic concentration on the liquid and plastic limits for low specific surface clays diminishes. This observation indicates that the sedimentation tests appear to be more efficient to capture the low specific surface clay behavior in response to the change in pore fluid chemistry.
5. The new fines classification chart in terms of pore fluid chemistry classifies the higher specific surface clays (AMK and EPK) as intermediate electrical sensitive clays whereas the lower specific surface clays (LWK and MI) are categorized into low electrical sensitivity fines.
6. A complementary data analysis for the sedimentation parameters and the new fines classification chart reveals that the robust link between distinct sedimentation trends and salient features of clay particles can be useful to predict the sedimentation modes of clays with different pore fluid chemistry.

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