Evaluation of the particle sizes of four clay minerals

Xiaoling Tan¹, Fengyin Liu^{1,2}, Liming Hu³, Allen H. Reed⁴, Yoko Furukawa⁴, and Guoping Zhang^{5,*}

¹ *Department of Civil & Environmental Engineering, Louisiana State University, Baton Rouge, LA 70803, USA*

² *School of Civil Engineering and Architecture, Xi'an University of Technology, Xi'an, Shaanxi, 710048, China*

³ *State Key Laboratory of Hydrosience and Engineering, Tsinghua University, Beijing, 100084, China*

⁴ *Naval Research Laboratory, Stennis Space Center, MS 39529, USA*

⁵ *Department of Civil & Environmental Engineering, University of Massachusetts Amherst, Amherst, MA 01003, USA*

ABSTRACT

The particle size distributions (PSD) of four clay minerals from the US Clay Minerals Society, kaolinite, illite, Ca²⁺-montmorillonite, and Na⁺-montmorillonite, were analyzed using different dispersion techniques to evaluate their PSD variability and intrinsic particle sizes. Both dry dispersion in pressurized air and wet dispersion in water and ethyl alcohol with and without an interlayer expanding agent, glycerol, were employed, along with mechanical ultrasound disaggregation and chemical dispersion. Results show that all four clay minerals exhibit multimodal PSD consisting of superimposed subordinate lognormal distributions from submicron and 1-2 μm primary particles, 10-20 μm flocculi (and trace impurities). Microflocs of 50-500 μm occur only in the dry dispersion mode. Owing to the presence of relatively strong flocculi that are not prone to breakdown to smaller primary particles, the intrinsic PSD of these clay minerals cannot be readily obtained by the adopted dispersion methods. The two swelling clay minerals, Na⁺-montmorillonite and Ca²⁺-montmorillonite, are more sensitive than the non-swelling ones, kaolinite and illite, to different dispersion solvents. The variability of these clay minerals' PSD is further discussed in terms of the complex interactions among clay mineral particles, polar or less polar solvent, and dispersant, such as swelling, cation exchange, exfoliation, and electrical double layer repulsion. A significant practical implication is that most existing dispersion methods for PSD analysis tend to overestimate the silt-sized fraction but

* Corresponding author; Phone: +1 (413) 545-3970; Email: zhangg@umass.edu or gzhang@alum.mit.edu.

33 underestimate the clay-sized fraction, which may yield misleading classification for clay
34 mineral-rich soils. For expansive clay minerals, appropriate dispersants should be selected to
35 avoid cation exchange between the sample and dispersants, which can change their intrinsic PSD.

36

37 **Keywords:**

38 Clay mineral; Dispersion; Exfoliation; Floc; Flocculus; Particle size distribution

39

1. Introduction

Clay minerals are the major solid constituents of cohesive soils, most dispersed sediments, and some fine-grained rocks. As a naturally occurring geomaterial, clay minerals are also one of the most important mineral resources used in many industrial and domestic applications. The particle size or size distribution of clay minerals is a key parameter for mineral identification (i.e., usually requiring size separation) and soil's engineering classification, as well as understanding a soil's mechanical, physical, and chemical properties that are in turn of critical importance for many environmental processes and industrial applications, such as water quality monitoring, environmental abatement, sediment transport, oil well drilling, clay-polymer nanocomposites, and nanoclay catalysts (Walling & Moorehead, 1989; Harvey & Murray, 1997; Hill, 1998; Zbik & Smart, 1998; Murray, 1999; Pavlidou & Papaspyrides, 2008; Anderson *et al.*, 2010; Kiliaris & Papaspyrides, 2010). For instance, it is a recommended practice that separation and extraction of clay fractions (i.e., $<2\ \mu\text{m}$ particles) is performed for qualitative and quantitative analysis, at least for clay minerals (Moore & Reynolds, 1997). In addition, particle size affects a soil's hydraulic conductivity and moisture retention capability (Daoud & Robert, 1992) and dye and clay mineral interactions (Neumann *et al.*, 2002).

However, owing to their micrometer to sub-micrometer sizes, determination and evaluation of clay minerals' particle size distributions (PSD) are not routinely performed in most engineering or industrial practices, usually because of constraints of time or device availability. For example, according to the ASTM Standards (ASTM, 2007), PSD are very important parameters for soil classification, yet no further effort is required to characterize PSD for the $<2\ \mu\text{m}$ fraction or to check whether the $>2\ \mu\text{m}$ fraction contains non-clay minerals. As a result, all particles in this fraction are collectively treated as clays without further differentiating their sizes (e.g., submicrometer vs. micrometer). On the other hand, some well-crystallized clay minerals

(e.g., kaolinite) may have relatively large, $>2\ \mu\text{m}$ particles. Although these particles are truly clay minerals having chemically active surfaces, they may be counted toward the silt-sized fraction, which may yield misleading soil classification and lead to inappropriate perception on soils' physico-chemical properties.

The majority of existing techniques for PSD measurements require preparing an ideally or appropriately dispersed clay mineral dispersion, mostly in water. A few issues arise from this sample preparation process. The first one is interactions between clay mineral and water, including the formation of electrical double layer on charged clay mineral surfaces, adsorbed cation hydration, and intercalation of water into expandable clay minerals. Of these interactions, water intercalation in swelling clay minerals can cause an initial increase in particle thickness, which then may result in an increase or decrease in size, depending on the types of interlayer cations or degree of swelling and other environmental conditions, as discussed later; The second one is stability of the dispersion. A non-stable clay mineral dispersion can lead to particle aggregation, resulting in coarser PSD; The third one is the use of chemical dispersants to obtain stable clay mineral dispersions (i.e., no flocculation or aggregation). Owing to clay minerals' cation or anion exchange capability, the cations or anions from dissolved dispersants may change clay minerals' properties and hence alter their PSD. For example, a Ca^{2+} -smectite may be partially or completely converted via cation exchange to a Na^{+} -smectite if a Na^{+} -based dispersant is used. After the conversion, because Na^{+} has a stronger hydration tendency than Ca^{2+} , the Na^{+} -smectite can swell to a higher degree such that its interlayer spacing can theoretically increase to infinity, leading to the formation of exfoliated individual 2:1 layers as separate particles. In contrast, Ca^{2+} -smectite or smectites with other divalent interlayer cations (e.g., Mg^{2+}) have limited swelling due to both the van der Waals and electrostatic attractions between interlayer

cations and negatively charged 2:1 layers (Helmy, 1998; Segad *et al.*, 2010). Therefore, swelling may result in either an increase in particle size via water intercalation or decrease by exfoliation.

For clay minerals with variable PSD, another concern arises with the definition and determination of truly representative primary particles. According to the literature, primary particles usually refer to the physically solid, homogeneous, individual particles without aggregation (Zhang *et al.*, 2005). For swelling clay minerals, primary particles are the physically coherent stacks of parallel, equally spaced aluminosilicate layers (Güven, 1992). Therefore, primary particles are intrinsic or inherent to the material, and their sizes should not be affected by different sample preparation techniques. The PSD obtained from a clay mineral dispersion that consists of only primary particles are the intrinsic PSD. That is, the intrinsic PSD reflects the particle sizes of primary particles only, but no aggregates or flocs.

It is worth noting further the importance of appropriate dispersion of dispersed clay mineral particles for PSD analysis. Due to crystal imperfections and isomorphous substitutions, most clay mineral particles possess net negative charges on face surfaces, which are balanced by adsorbed and/or interlayer cations (e.g., Na^+ , K^+ , Ca^{2+}). The broken bonds on edge surfaces result in pH dependent charges (e.g., positive if pH is below the isoelectric point). As such, electrostatic forces together with other interactions, such as van der Waals attraction and double layer repulsion, between dispersed clay mineral particles usually lead to aggregation. Therefore, a clay mineral dispersion is a very complex system that contains both individual clay mineral particles and most likely clay mineral aggregates. Together with other unique features of clay mineral particles, such as irregular shapes, flexible layers, and heterogeneous layer charges, clay minerals usually exhibit a wide range of particle sizes even in pure water under stable equilibrium condition (Murray, 2000; Wu, 2001; Lagaly & Ziesmer, 2003).

Both mechanical and chemical methods can be used to facilitate dispersion or disaggregation of clay minerals (Zhang *et al.*, 2005). The former usually involves the application of mechanical energy to breakdown and separate aggregated particles, such as ultrasound disruption, flow-induced shearing in a high-speed stirrer, while the latter refers to the use of dispersants to remove or eliminate the physical cementation or chemical bonds holding particles together (Zhang *et al.*, 2004, 2005). Therefore, accurate measurement of intrinsic PSD largely depends on the effectiveness of the employed dispersion methods to separate clay mineral aggregates or flocs and keep them stable at their primary particles in a dispersion (Crowley & Welch, 1954). This may also require a continuous dispersion process to maintain the clay mineral dispersion at a completely dispersed, equilibrated state even during measurement. With the development of some new instruments (e.g., laser diffraction-based particle size analyzers), the size of clay mineral particles and their PSD can be quickly measured (de Boer *et al.*, 1987) when a clay mineral dispersion is continuously circulated. Additionally, different dispersion methods, either chemical or mechanical or both, in different solvents (e.g., air, water, or a less polar liquid) can be employed for PSD measurements.

This paper presents an experimental study to evaluate the PSD of four source clay minerals, kaolinite, illite, Na⁺-montmorillonite (Na⁺-Mt), and Ca²⁺-montmorillonite (Ca²⁺-Mt), which are abundant in natural soils and are representative of four major species of clay minerals with distinctly different behavior. Kaolinite and illite are non-swelling 1:1 and 2:1 minerals, respectively, while the two montmorillonites are swelling 2:1 minerals but with different interlayer cations as well as layer charges. The objectives of this paper are three-fold: (1) to investigate the effect of different dispersion methods on the PSD of different clay minerals, (2) to evaluate the degree of PSD variability of four source clay minerals, and (3) to obtain reference

data on the PSD of these representative clay minerals. The findings are expectedly of interest to primarily soil engineers and secondarily researchers who study or use clay minerals for different industrial applications or environmental processes.

2. Experimental

2.1 Materials

Four relatively pure clay minerals, kaolinite (KGa-1b), illite (IMt-1), Ca^{2+} -Mt (STx-1b), and Na^{+} -Mt (SWy-2), which have been well analyzed and widely used by many studies as reference clay minerals, were purchased from the US Clay Minerals Society Source Clay Repository (Hower & Mowatt, 1966; Pruett & Webb, 1993; Chipera & Bish, 2001; Costanzo, 2001). Their geographic origins and basic properties are summarized in Table 1. Kaolinite and two montmorillonites were supplied as dry powder, which had been pre-processed by wet-sieving through a #325 mesh to remove the $>44\ \mu\text{m}$ fractions before shipping to users (Pruett & Webb, 1993). These three “*as-received*” dry powdery clay minerals were directly used without further treatment. The “*as-received*” illite sample consisted of small rock chips. To obtain powdery illite, the sample was first hand ground by a mortar and pestle and then wet ground with ethyl alcohol using a McCrone micronizing mill (McCrone Accessories & Components, Westmont, IL, USA) for 3 mins, which typically results in a fine powder with $\leq 38\ \mu\text{m}$ particles for most silicate minerals. To identify clay minerals and impurities, the processed powdery illite was side-packed into a sample holder and analyzed by X-ray diffraction (XRD) using a Bruker/Siemens D5000 automated powder diffractometer using a $\text{Cu } K\alpha$ radiation at 40 kV and 30 mA with a scan range of $2\text{--}40^\circ\ 2\theta$, a scan speed of $0.02^\circ\ 2\theta$ per 2 sec, and a step size of 0.02°

2 θ . The XRD pattern validates illite as the only clay mineral phase and trace quartz as an impurity (Figure 1).

2.2 *Preparation of clay mineral dispersions*

PSD measurements require the preparation of clay mineral dispersions either in air or liquid. Table 2 summarizes the different methods employed to prepare clay mineral dispersions. Details for each method are also provided as follows:

- I-A: To obtain the <2 μm fractions and hence their PSD, 0.2 g dry powder was first dispersed in 80 mL deionized (DI) water by using a Sonic Dismembrator Model 300 probe-type ultrasonic disruptor (Fisher Scientific, Pittsburgh, PA, USA) for 15 mins, followed by diluting with DI water to 1000 mL in a beaker. The resulting dispersion was allowed to settle for 3.5 hrs. The upper 5 cm supernatant was extracted as the <2 μm fraction for subsequent PSD measurement.
- I-B: To investigate the necessity of “*overnight soaking*” or “*pre-equilibrating with water*” that is usually required for sample preparation and hence its influence on PSD, 0.2 g dry clay mineral was used directly to prepare a dispersion or pre-soaked overnight (i.e., >16 hrs) before preparing a dispersion.
- I-C: To evaluate the effectiveness of mechanical disaggregation, 0.2 g overnight pre-soaked clay mineral was dispersed in 80 mL DI water by the aforementioned probe-type ultrasonic disruptor for 15 mins.
- I-D: To evaluate the influence of chemical dispersant, Na-hexametaphosphate (NaHMP; Mallinckrodt Baker Inc., Philipsburg, NJ, USA) solution at a concentration of 40 g/L was used to replace DI water for dispersion preparation (ASTM, 2007).

- I-E: To investigate the influence of swelling as a function of the dielectric constant of the dispersing solvents and the adsorbed exchangeable cations on the PSD of two montmorillonites, ethyl alcohol (EA; 190 Proof, Pharmco-AAPER, Brookfield, CT, USA), a glycerol (EMD Chemicals Inc., Darmstadt, Germany) solution in EA with a 2 vol.% concentration (Kinter & Diamond, 1958; Burt, 2004), and a glycerol solution in DI water with a 2 vol.% concentration were used as solvents to prepare clay mineral dispersions.
- II: To evaluate the effectiveness of dry dispersion that may avoid the clay mineral-water interactions, four dry clay mineral powders were also dispersed in and transported by pressurized dry air.

In summary, air, water, EA, NaHMP, and glycerol were used as a dry dispersion medium, polar solvent, less polar solvent, chemical dispersant, and interlayer expanding agent, respectively, to prepare clay mineral dispersions so that the effectiveness of different dispersion methods can be evaluated.

2.3 *Methods*

All PSD measurements were conducted in a Cilas 1190[®] laser particle size analyzer (PSA) (Cilas Particle Size, Madison, WI, USA) under either wet or dry mode (Figure 2). In the wet mode, clay mineral dispersions at a concentration of 0.2 g dry clay mineral powder in 80 mL solvent prepared by the above methods were transferred to the PSA's liquid bath and then diluted to 500 mL, which is the total volume of the PSA's closed-loop liquid circulation system (including the liquid bath and circulation tubes), followed by running a built-in ultrasound disperser beneath the liquid bath for 1.0 min to achieve better dispersion. To prevent unnecessary

flocculation and settling, all clay mineral dispersions were continuously agitated by a pedal-like stirrer located in the middle of the liquid bath at a constant speed of 180 rpm and continuously circulated in the PSA's circulation system by a peristaltic pump at a constant speed of 30 rpm, while the PSD were continuously monitored by three laser beams. The pump resulted in an average flow velocity of 0.15 m/s and a Reynolds number of ~1091, which indicates one-dimensional laminar flow inside the circulation tubes. Sufficient time (usually 15-20 mins) was allowed for the circulating dispersions to reach a steady state (i.e., no further significant change in the measured PSD even for prolonged circulation). After validating an equilibrated state, PSD measurement was then conducted. Selective images of particles were also taken using a 3032 series preconfigured, inverted microscope (Accu-Scope[®] Inc., Commack, NY, USA) that is externally connected to the PSA's liquid circulation system.

In the dry mode, dry powdery samples were placed in a vibrating mass distributor and then transported and dispersed by pressurized dry air. Table 3 summarizes the selected dispersing parameters (determined by trial and error) used for the four clay minerals, including vibration frequency, vibration ratio, and air pressure.

For both modes, the laser diffraction data was analyzed using the Lorenz-Mie theory, which is an exact description of the diffraction field. This theory is more accurate than the Fraunhofer theory (an approximation of Lorenz-Mie theory) for PSD characterization of clay minerals, especially when the sizes are close to the laser wave length of 635-830 nm (de Boer *et al.*, 1987). Particle size obtained by the PSA was defined as the diameter of equivalent spheres calculated based on the volume moment mean value of multiple particles at a given size range. That is:

$$D = \frac{\sum n l^4}{\sum n l^3} \quad (1)$$

where D is the mean diameter of all particles or flocs within a given size range, n the number of particles of a fixed size in the considered size range, and l the diameter of a particle or floc.

3. Results and discussion

3.1 PSD of the <2 μm fractions

The PSD curves of the <2 μm fractions (Figure 3) show that their particle size ranges from 0.04 (the practical particle size limit that this PSA apparatus can detect) to ~4 μm and more than 90-95% (by number) particles are <2 μm . This is consistent with the purpose of ultrasound disaggregation and subsequent settling (or fractionation) used to disperse clay mineral flocs and remove impurities (e.g., quartz), which typically leaves only the <2 μm individual clay mineral particles in the supernatant (Chipera *et al.*, 1993; Moore & Reynolds, 1997; Chipera & Bish, 2001; Furukawa *et al.*, 2009). In fact, this also serves as an indirect and partial calibration of the accuracy of the PSA.

Of the four clay minerals, kaolinite and illite exhibit a trimodal lognormal distribution with the local maxima at 0.075, 0.3, and 1.2 μm (Fig. 3b). The first one at ~0.075 μm is extremely small with only 10-15% particles finer than this value. This range of sizes could be the particle thickness and the laser measurements may only take place on a very small percentage of clay mineral particles. The other two maxima represent the true basal plane dimensions of kaolinite and illite, resulting in two aspect ratios of 16 and 4 for both clay minerals. Other studies reported that this kaolinite has an aspect ratio of ~10 (Zbik & Smart, 2002) with an average of 5.3 (Zbik & Frost, 2009). In addition, some studies (e.g., (Mackinnon *et al.*, 1993)) found that a

similar kaolinite has two different sizes, ~ 0.3 and ~ 1.2 μm , in its <2 μm fraction. The aspect ratio of this illite has not been reported in the literature, but it can be reasonably assumed to have similar values.

For the two montmorillonites, Ca^{2+} -Mt exhibits a superimposed bimodal lognormal distribution with two maxima at 0.6 and ~ 1.5 μm , while Na^+ -M has a monomodal distribution with a maximum at ~ 1.5 μm . Such different PSD stem from their different chemical compositions and distinct swelling behavior. According to their chemical formulas (Table 1), both clay minerals can be regarded as a mixed $\text{Ca}^{2+}/\text{Na}^+$ -Mt, but with different mole ratios of $\text{Ca}^{2+}/\text{Na}^+$ (i.e., 27/4 and 3/8 for the Ca^{2+} -Mt and Na^+ -Mt, respectively). As reported by (Laird, 2006), during swelling in water, cation demixing in montmorillonite occurs so that Na^+ and Ca^{2+} are separated and relocated into different interlayers. The basal spacing, $d(001)$, of Na^+ -dominated interlayers can swell to >9 nm (Posner & Quirk, 1964; Olejnik *et al.*, 1974), while that of Ca^{2+} -dominated interlayers only swells to <1.9 nm (Theng, 1982). When mechanically dispersed by a probe-type ultrasound disruptor, the swollen montmorillonite particles readily break apart or exfoliate at the interlayers dominated by Na^+ , leading to the formation of two types of particles (Figure 4): (1) ~ 1.0 nm thick, Na^+ -based individual 2:1 layers as single particles, and (2) particles with Ca^{2+} as the dominant interlayer cations. The latter are stacks of parallel 2:1 layers (Quirk & Aylmore, 1971; Kleijn & Oster, 1982), which are relatively stable under shaking, stirring, sonication, and even certain pressure (Kjellander *et al.*, 1988; Yariv & Lapidés, 2003; Laird, 2006). For both Ca^{2+} -Mt and Na^+ -Mt, the process of 3.5 hr sedimentation can eliminate those relatively large Ca^{2+} -Mt swollen particles (i.e., they readily settle down faster), resulting in a supernatant containing the relatively smaller swollen particles and exfoliated 2:1 layers. As the major particles in the Na^+ -Mt supernatant, the very thin, flexible,

and soft (Bihannic *et al.*, 2001) Na⁺-based individual 2:1 layers can easily curl and form irregularly shaped particles in the PSA's circulation system, which yields a monomodal distribution for the Na⁺-Mt. However, for the Ca²⁺-Mt, the extracted supernatant may contain both relatively smaller Ca²⁺-Mt swollen particles and Na⁺-based individual 2:1 layers (Lagaly, 2006), resulting in a bimodal distribution.

3.2 *Effect of overnight soaking in water*

Figure 5 compares the PSD of the DI water-soaked vs. unsoaked samples for the four clay minerals. All curves show a maximum size of 30-60 µm. The two non-swelling clay minerals, kaolinite and illite, exhibit a trimodal distribution with three maxima at 0.3, 1.5-2.5, and 13-20 µm, while the two swelling clay minerals, Ca²⁺-Mt and Na⁺-Mt, have a bimodal distribution with local maxima at 2.1-2.5 and 13-16 µm. The PSD value of the soaked kaolinite is in agreement with that of another similar kaolinite (KGa-1) reported by (Franco *et al.*, 2004). For all samples, the two maxima at smaller sizes (e.g., <10 µm) of water-soaked sample (Figure 5) are almost at the same locations as those from the <2 µm fractions (Figure 3), indicating that they are caused by dispersed, primary clay mineral particles. The third maximum located between 10-20 µm is not observed in the <2 µm fractions. As reported in the literature (Lee *et al.*, 2012), flocculi, the smallest clay mineral-based aggregates of 10-20 µm in size, are relatively strong and hence hardly break down to the primary clay mineral particles (Vandeven & Hunter, 1977). In addition, impurities (e.g., quartz) may also contribute to this peak (Pruett & Webb, 1993). Figures 6a to 6d show some representative optical microscope images of soaked clay mineral samples. The particle sizes observed from these images are consistent with the above

analysis. For instance, Ca^{2+} -Mt has larger flocculi than other samples, while illite has the smallest flocculi.

Except kaolinite, the PSD of the soaked and un-soaked samples of the other three clay minerals are identical, indicating that the PSD of these three clay minerals with relatively higher layer charges are not sensitive to overnight soaking. For kaolinite, overnight soaking shifts the cumulative PSD curve toward the left, or makes the PSD finer, as indicated by the change in the D_{50} from 16 to 4 μm for the unsoaked and soaked samples, respectively. This well-crystallized kaolinite has low defects (Pruett & Webb, 1993), with very low but opposite electrical charges of -0.17 and +0.11 in the tetrahedral and octahedral sheets per $\text{O}_{10}(\text{OH})_8$, respectively (Table 1). The kaolinite dispersion has a measured pH 5.97 (Table 1). Under such a slightly acidic condition, the outmost octahedral sheet (as one face surface) is positively charged, while the outmost tetrahedral sheet (as the other face surface) is negatively charged (Gupta *et al.*, 2011). As such, the electrical field generated by charges on face surfaces is very weak and there is also a weak electrostatic attraction between the octahedral face surface of one particle and the tetrahedral face of the other particle. Therefore, it may take a relatively long time for kaolinite particles to reach a fully hydrated and dispersed state. In contrast, illite, Ca^{2+} -Mt, and Na^+ -Mt have relatively higher electrical charges of same polarity on face surfaces (Table 1), resulting in a stronger electrical field generated by the face surface as well as a stronger electrostatic repulsion between the face surfaces of individual particles. As such, they can hydrate quickly and a fully hydrated clay mineral particle facilitates subsequent dispersion. In addition, compared with the kaolinite dispersion of the same concentration (e.g., 0.4 g/L), the much higher specific surface area (SSA) of the other three clay minerals renders them a larger surface density (i.e., total surface area per unit volume of dispersion) for particle-particle interactions, which may

facilitate a quicker hydration and dispersion (Quirk & Aylmore, 1971; Rengasamy *et al.*, 1976; Kleijn & Oster, 1982; Laird, 2006).

In summary, although overnight soaking is recommended as a routine step to prepare clay mineral dispersions for particle size analysis, its necessity or influence has rarely been reported. Based on the above analysis, prolonged soaking is necessary for clay minerals with small layer charges, such as kaolinite. Although this step may not be very important for highly charged clay minerals, it is still a good practice to perform this step for most PSD measurements.

3.3 *Effect of dispersion methods*

Figure 7 shows the PSD of the four clay minerals treated by different dispersion methods, including overnight soaking, NaHMP dispersion, ultrasound (US) dispersion, and dry dispersion in air (Dry). The most striking feature is that, compared with dispersion methods in the liquid mode, the PSD curves obtained in the dry mode lie on the rightmost for all four clay minerals, indicating that much coarser particles or aggregates exist in the air-dispersed samples or, in other words, the samples are not well dispersed. The frequency distribution curves show four major peaks, with the largest one at 40-320 μm . In this mode, pressurized dry air is used as both a solvent for transporting and floating clay mineral particles and a mechanical disaggregation tool, which is hoped to eliminate the influence of complex clay mineral-water interactions on PSD measurements. However, it is known that air-dried clay minerals still contain some water adsorbed from the moisture in air, and hence clay mineral particles can still interact with each other to form aggregates via clay mineral-water interactions (e.g., van der Waals attraction, hydration, capillary, and Coulomb force). In addition, the air-dispersed clay mineral in dry mode is not circulated in a closed-loop system in the PSA, but is quickly transported through the laser

measurement window. Therefore, an equilibrium state may not be reached during the measurement. In conclusion, dry dispersion cannot be employed to characterize the PSD of source clay minerals.

For other dispersion methods in liquid mode, all four clay minerals show a trimodal, lognormal distribution with a size range of 0.04-50 μm . The three maxima are at 0.3-0.6, ~ 2 , and ~ 13 μm . Again, the former two represent primary clay mineral particles, while the last is caused by clay mineral flocculi. The effect of chemical dispersion and ultrasound disaggregation on each clay mineral's PSD is further discussed separately below.

3.3.1 Kaolinite

Compared with the water-soaked sample, both chemical and mechanical dispersions generate finer PSD, although the latter even results in a higher population of <1 μm particles. This result is consistent with others in the literature (Crowley & Welch, 1954; Genrich & Bremner, 1972b, a). As mentioned above, the two face surfaces (i.e., one is the outmost tetrahedral sheet, and the other is the outmost octahedral sheet) with opposite, low charges can generate electrostatic attraction between the basal planes of two different particles, leading to the formation of flocs. Another reason for floc formation is that kaolinite's edge charge is positive at $\text{pH} < 7$ (i.e., a pH 5.97 was measured) and the interaction of positively charged edge to negatively charged tetrahedral face can also contribute to flocculation (Du *et al.*, 2010). However, kaolinite has very low layer charges, which means that the electrostatic attraction is not very strong, and hence kaolinite flocs can be dispersed by ultrasonic dispersion. Chemical dispersion by NaHMP is achieved by the edge charge reversal through adsorption of PO_3^- .

3.3.2 Illite

The cumulative PSD curve obtained by the ultrasound disaggregation lies in the leftmost, while that by chemical dispersant just overlays with the one of soaked sample (Figure 7b). This suggests that NaHMP dispersion is not effective for illite. Two reasons may possibly contribute to this: (1) illite possesses a very high layer charge (e.g., -1.68 for this sample, Table 1) and (2) the amount of used dispersant may not be enough to reverse the edge charges, indicating that the NaHMP concentration may be too low for illite. Therefore, for the highly charged, non-swelling illite, chemical dispersion by NaHMP is not as effective as ultrasound dispersion.

3.3.3 Ca^{2+} -Mt

According to the relative locations of the cumulative PSD curves (Figure 7c), chemical dispersion is more effective than ultrasound dispersion, although both methods yield finer particles than soaking. Moreover, ultrasound dispersion generates more $<1\ \mu\text{m}$ particles, while chemical dispersion yields more $>1\ \mu\text{m}$ particles. The chemical dispersant, NaHMP, may alter the particle sizes in two ways: (1) it can partly reverse the clay mineral's positive edge charges by $(\text{PO}_3^-)_6$ and hence reduce the tendency of aggregation via edge-face interactions (Levy *et al.*, 1991) and (2) the added Na^+ can exchange with the interlayer Ca^{2+} , resulting in a change of Ca^{2+} -Mt to Na^+ -Mt that can swell further and then exfoliate into smaller particles (as discussed previously). Therefore, adding the dispersant, NaHMP, to Ca^{2+} -Mt may generate misleading PSD results because of the partial conversion of Ca^{2+} -Mt to Na^+ -Mt.

3.3.3 Na^+ -Mt

It appears that either ultrasound dispersion or overnight soaking can yield the finest PSD for Na^+ -Mt, although the former can generate more $<1\ \mu\text{m}$ particles. Chemical dispersion causes the presence of more $>1\ \mu\text{m}$ particles. Therefore, NaHMP is not effective for dispersing this Na^+ -

Mt. Similar observations have been reported in the literature. For instance, (Frenkel *et al.*, 1992) stated that NaHMP is less effective in dispersing Na⁺-Mt than kaolinite.

Finally, it is noteworthy to further discuss the effectiveness of ultrasonic dispersion. For all four clay minerals, the population of the smallest primary particles (i.e., <1-2 µm) obtained by ultrasound dispersion is the highest of all dispersion methods, indicating that this mechanical disaggregation method helps breakdown clay mineral flocs. Ultrasound dispersion, by creating and fracturing microbubbles in an aqueous medium, results in a sudden energy release, which generates locally high temperature, high pressure, and strong shock waves to help disperse, expand, or split clay mineral particles (Lapides & Yariv, 2004; Zhang *et al.*, 2010). Thus, the microprobe-type ultrasonication indeed facilitates the swelling and exfoliation of the two montmorillonites. As reported by Franco *et al.* (2004), ultrasound can cause both exfoliation and size reduction in other particle dimensions. As such, for the non-swelling kaolinite and illite, and limited swelling Ca²⁺-Mt, the ultrasound processed samples show a size reduction in all size ranges when compared with their corresponding soaked samples. This reduction can be attributed to either particle delamination (e.g., as for Ca²⁺-Mt) or breakdown of clay mineral particles into smaller sizes (as measured along the basal plane dimension) or both. While the former can occur only in the two montmorillonites, the latter may happen in all four clay minerals.

3.4 Effect of different solvents for swelling clay minerals

Figure 8 shows the PSD of the two montmorillonites dispersed in DI water, EA, a glycerol in DI water solution (Gly-DI), and a glycerol in EA solution (Gly-EA). The PSD obtained from the water-soaked samples are used as a reference for comparison. For all four solvents, both Ca²⁺-Mt and Na⁺-Mt exhibit a bimodal lognormal distribution with a size range of

0.1 to 70 μm and two maxima at $\sim 2.2\text{--}2.5$ and $\sim 13\text{--}15$ μm for primary particles and flocculi, respectively. Moreover, the PSD change in $\text{Ca}^{2+}\text{-Mt}$ caused by different solvents is not as significant as that in $\text{Na}^+\text{-Mt}$.

For $\text{Ca}^{2+}\text{-Mt}$, although the PSD dependence on the type of solvent is not so significant, some changes in PSD are still discernable. Of the four solvents, the Gly-EA yields the coarsest PSD, while water generates the finest PSD. Also, the Gly-DI yields a coarser PSD than the DI water, and the PSD obtained from the EA is finer than that from Gly-EA, but coarser than that from DI water. The dielectric constant of water, EA, and glycerol at 20-25 $^{\circ}\text{C}$ is 80.3, 24.3, and 42.5, respectively (Table 4). If the interlayer of $\text{Ca}^{2+}\text{-Mt}$ is filled with EA (to replace water), the Coulomb attraction between the interlayer exchangeable cations (i.e., Ca^{2+}) and negatively charged 2:1 layers will be much stronger, thus preventing the $\text{Ca}^{2+}\text{-Mt}$ from swelling. In fact, neither $\text{Ca}^{2+}\text{-Mt}$ nor $\text{Na}^+\text{-Mt}$ swells in pure alcohol (Brindley *et al.*, 1969). For $\text{Ca}^{2+}\text{-Mt}$, the difference between the PSD in water and in EA is not significant, even though the clay mineral swells in water but not in pure EA. This can be reasoned by the fact that the increase in particle size caused by swelling in water is counterbalanced by the decrease in particle size caused by exfoliation, which in turn is promoted by the existence of Na^+ in some interlayers (as discussed previously) and flow-induced shearing (causing exfoliation).

It is also interesting to discuss the influence of glycerol as an expanding agent on PSD (Figure 8). Glycerol is completely soluble in water and alcohol. According to (Kinter & Diamond, 1958), glycerol molecules can enter the interlayer space of montmorillonite and easily form a stable glycerol complex without heating. The basal spacing $d(001)$ for montmorillonite with two layers of glycerol, monolayer of glycerol, and absence of glycerol as its interlayer is 1.84, 1.42, and 0.99 nm, respectively. The partial replacement of water molecules by larger

glycerol molecules in the interlayer may further increase repulsive interlayer force (Brindley *et al.*, 1969), which results in an increase in swollen particle's basal spacing and hence the particle size. As shown in Figure 8, the Gly-DI slightly increases the size of particles within the size range of ~1-10 μm , but without the change in the mean particle size (D_{50}), when compared with the PSD from DI water. The Gly-EA can further increase the particle sizes, with a change in D_{50} from 12 to 17 μm . In the Gly-EA solvent, montmorillonite's basal spacing increases by intercalating glycerol molecules into its interlayer space, which causes the size increases (i.e., when compared with the DI water as a solvent). Again, due to the smaller dielectric constants of both glycerol and EA, the interlayer attraction force is stronger in the Gly-EA solvent than in water, and hence the swollen montmorillonite particles cannot be easily exfoliated by hydraulic shearing force. Therefore, there are two reasons why the PSD in the Gly-EA is much coarser than in the DI water: (1) particle swelling due to the intercalation of glycerol and (2) less hydraulic shear-induced particle exfoliation.

For $\text{Na}^+\text{-Mt}$, the PSD dependence on different solvents is more significant (Figure 8b). The four PSD curves can be separated into two groups: DI water and Gly-DI as the first group, and EA and Gly-EA as the second group. The difference in PSD within each of the two groups is very small. As mentioned above, $\text{Na}^+\text{-Mt}$ can swell to infinity in water, and hence an individual 2:1 layer is a particle. Moreover, glycerol can be intercalated into $\text{Na}^+\text{-Mt}$'s interlayers. For Na^+ -dominated interlayers, glycerol intercalation causes exfoliation, resulting in a decrease in size, while for Ca^{2+} or K^+ -dominated interlayers, glycerol intercalation further expands basal spacing but will not cause exfoliation, resulting in an increase in size. Therefore, the Gly-DI yields a slightly coarser PSD than DI water.

For the second group where EA and Gly-EA are used as solvents, Na^+ -Mt does not readily swell in EA. As such, Na^+ -Mt in EA exhibits much coarser PSD than in DI water. In fact, its D_{50} increases from $\sim 2.2 \mu\text{m}$ in water to $\sim 13 \mu\text{m}$ in EA. Because Na^+ -Mt swells in the Gly-EA by intercalating glycerol (but probably not EA), some of which can be exfoliated into smaller particles by hydraulic shearing, resulting in finer PSD in the Gly-EA than in EA. However, due to the smaller dielectric constants of glycerol and EA (Table 4), which results in stronger interlayer Coulomb attraction force (between interlayer cations and 2:1 layers), the exfoliation can be very limited, and hence the change in the PSD is very small.

The PSD dependence on different levels of clay mineral swelling in different solvents is also demonstrated by the images shown in Figure 6. Both the Ca^{2+} -Mt and Na^+ -Mt in EA (Figure 6e and 6f) exhibit larger particles than in DI water, because they can swell in water and subsequently exfoliate into smaller particles (Figure 6c and 6d).

3.5 *Intrinsic PSD of the four clay minerals*

As pointed out earlier, intrinsic PSD should be obtained from the sample dispersions consisting of only primary particles, and should truly represent the sizes of original, physically individual particles that are not affected by sample preparation, such as chemical dispersants, excessive physical disruption or disaggregation, or solvent-clay mineral interactions, nor affected by aggregation or flocculation in the prepared clay mineral dispersions. Strictly speaking, because of the presence of flocculi, a kind of clay mineral aggregates, it is difficult to obtain the intrinsic PSD of the four source clay minerals. However, if the 10-20 μm flocculi are treated as inherent to the clay minerals, the above analyses can be used to find their intrinsic PSD, as discussed below.

For the non-swelling kaolinite and illite, although ultrasound dispersion yields the finest PSD (Figure 7), it may also cause particle disruption or breakage along the basal plane dimension or delamination along the c -axis. Thus the obtained PSD are not intrinsic. The difference in the PSD from NaHMP dispersion and overnight soaking is not so significant for illite, but there is difference for kaolinite. Therefore, it is reasonable to conclude that the kaolinite PSD obtained by NaHMP dispersion represents the intrinsic one and the illite PSD obtained by overnight soaking or NaHMP is intrinsic.

For the swelling clay minerals, primary particles should be the individual particles at their non-swollen state. The PSD obtained in water-based dispersions (e.g., DI water, NaHMP solution, glycerol in water solution) also reflect the swollen particles. Additionally, powdery clay minerals cannot be fully dispersed in dry mode. The use of an interlayer expanding agent, glycerol, certainly alters the original particle thickness. Therefore, the PSD of the two montmorillonites dispersed in ethyl alcohol, a much less polar liquid where they do not readily swell, are regarded as intrinsic. This is due to the fact that dispersion in a less polar liquid avoid swelling (due to intercalation of water molecules into interlayers), cation exchange between the clay mineral and solution, and exfoliation. Table 5 summarizes the intrinsic PSD parameters for all four clay minerals.

3.6 Practical implications

PSD are one of the most fundamental physical properties of soils. It is required by current soil classification standards (e.g., the unified soil classification system). Based on the above analyses, relatively strong clay mineral-based flocculi of 10-20 μm in size are quite resistant to mechanical disaggregation and chemical dispersion and can exist in different types of clay

minerals. As such, this type of clay mineral aggregates is usually counted toward the silt-sized fraction, which may lead to misleading soil classifications or incorrect soil properties (e.g., activity). On the other hand, better dispersion techniques that can disaggregate clay mineral flocculi should be developed in future studies.

In addition, several other factors warrant more thorough considerations when selecting appropriate sample preparation methods for PSD analysis. First, soaking in water for sufficient time (e.g., overnight) should be always performed for most soils, especially those containing a significant fraction of kaolinite or other low charge clay minerals; Second, caution should be taken when Na^+ -based dispersants are used, particularly for soils with non-sodium based smectites, although NaHMP is specified in the ASTM or other standard methods for PSD analysis. As a general guideline, when selecting proper dispersants for soils containing Ca or other divalent cation dominant smectites, cation exchange between smectites and dissolved dispersants that can lead to alteration to the particle size should be avoided; Finally, the solvent used to prepare soil dispersions should not be limited to water only, and other polar or less polar liquids may also be selected to prevent the unnecessary clay mineral-water or clay mineral-solvent interactions.

4. Conclusions

An experimental study was conducted to evaluate the PSD and their variability of four source clay minerals, kaolinite, illite, Ca^{2+} -Mt, and Na^+ -Mt, under different dispersion methods, including dry dispersion in pressurized air and wet dispersion in water and EA with and without an interlayer expanding agent, glycerol, along with ultrasound disaggregation and NaHMP dispersion. Based on the results and above discussion, the following conclusions can be drawn:

- Overnight soaking in water should always be included in the preparation of clay mineral dispersions for PSD analysis, especially for kaolinite or other low charge clay minerals.
- Prolonged ultrasound disaggregation should be avoided in sample preparation for PSD measurement in order to prevent unnecessary particle exfoliation.
- Dry dispersion in pressurized air is not effective to disperse clay mineral aggregates for PSD analysis.
- A much less polar solvent such as EA should be used to prepare the dispersions of swelling clay minerals for PSD analysis.
- Most clay minerals contain relatively strong clay mineral-based flocculi of 10-20 μm in size that is resistant to disaggregation, and hence the resulting PSD overestimate the silt-sized fraction, but underestimate the clay-sized fraction.
- The intrinsic PSD of kaolinite and illite should be obtained by NaHMP dispersion, while those of the two smectites can be obtained by dispersing in EA or other less- or non-polar solvents.
- In general, caution should be taken in selecting an appropriate chemical dispersant for PSD analysis, especially when selecting a Na^+ -based dispersant for soils containing non-sodium based smectites.
- The PSD of most clay minerals show a multimodal lognormal distributions with local maxima representing $<2 \mu\text{m}$ primary clay mineral particles, 10-20 μm flocculi, and sometimes 50-500 μm microflocs.

Notations:

θ – Diffraction angle

D – Volume moment based mean diameter of particles within a given size range

n – Number of particles
 l – Diameter of a particle in that given size range
 d – Basal spacing of clay minerals
 P – Percent finer of particles by number
 F – Frequency as a percentage of a particle in the whole sample

Acknowledgments

This work was partially supported by the Office of Naval Research through Naval Research Laboratory base funding under Award No. N00173-10-1-G013 as part of the NRL ARI “Biogeochemical Influences on Cohesive Sediment Strength in Marine and Estuarine Environments (PE No. 061153N)”. The facilities used in this study were purchased using the fund from the Louisiana Board of Regents Enhancement Program.

REFERENCES

- Anderson, R.L., Ratcliffe, I., Greenwell, H.C., Williams, P.A., Cliffe, S. & Coveney, P.V. (2010) Clay swelling - a challenge in the oilfield. *Earth-Science Reviews*, **98**, 201-216.
- ASTM. (2007) Standard test method for particle-size analysis of soils. Pp. D422-463, ASTM International, West Conshohocken, PA.
- Bihannic, I., Tchoubar, D., Lyonnard, S., Besson, G. & Thomas, F. (2001) X-ray scattering investigation of swelling clay fabric: 1. The dry state. *Journal of Colloid and Interface Science*, **240**, 211-218.
- Brindley, G.W., Wiewiora, K. & Wiewiora, A. (1969) Intracrystalline swelling of montmorillonite in some water-organic mixtures (clay-organic studies. Xvii). *American Mineralogist*, **54**, 1635-1644.
- Burt, R. (2004) Soil survey laboratory methods manual. Pp. 735, 42, *Soil Survey Investigations Report No. 42* Version 4.0, Lincoln, NE: Natural Resources Conservation Service, U.S. Department of Agriculture.
- Celis, R. & Koskinen, W.C. (1999) Sorption and desorption of triadimefon by soils and model soil colloids. *Journal of Agricultural and Food Chemistry*, **47**, 776-781.

569 Chipera, S.J. & Bish, D.L. (2001) Baseline studies of the clay minerals society source clays:
570 Powder x-ray diffraction analyses. *Clays and Clay Minerals*, **49**, 398-409.

571 Chipera, S.J., Guthrie, G.D. & Bish, D.L. (1993) Preparation and purification of mineral dusts.
572 *Reviews in Mineralogy*, **28**, 235-249.

573 Costanzo, P.M. (2001) Baseline studies of the clay minerals society source clays: Introduction.
574 *Clays and Clay Minerals*, **49**, 372-373.

575 Crowley, M.S. & Welch, A.P. (1954) Clay-particle dispersion by ultrasounds. *Journal of The*
576 *American Ceramic Society*, **37**, 433-439.

577 Daoud, Y. & Robert, M. (1992) Influence of particle size and clay organization on hydraulic
578 conductivity and moisture retention of clays from saline soils. *Applied Clay Science*, **6**, 293-
579 299.

580 de Boer, G.B., de Weerd, C., Thoenes, D. & Goossens, H.W. (1987) Laser diffraction
581 spectrometry: Fraunhofer diffraction versus mie scattering. *Particle Characterization*, **4**, 14-
582 19.

583 Du, J., Morris, G., Pushkarova, R.A. & Smart, R.S. (2010) Effect of surface structure of kaolinite
584 on aggregation, settling rate, and bed density. *Langmuir*, **26**, 13227-13235.

585 Franco, F., Perez-Maqueda, L.A. & Perez-Rodriguez, J.L. (2004) The effect of ultrasound on the
586 particle size and structural disorder of a well-ordered kaolinite. *Journal of Colloid and*
587 *Interface Science*, **274**, 107-117.

588 Frenkel, H., Levy, G.J. & Fey, M.V. (1992) Clay dispersion and hydraulic conductivity of clay-
589 sand mixtures as affected by the addition of various anions. *Clays and Clay Minerals*, **40**,
590 515-521.

591 Furukawa, Y., Watkins, J.L., Kim, J., Curry, K.J. & Bennett, R.H. (2009) Aggregation of
592 montmorillonite and organic matter in aqueous media containing artificial seawater.
593 *Geochemical Transactions*, **10**.

594 Genrich, D.A. & Bremner, J.M. (1972a) Effect of probe condition on ultrasonic dispersion of
595 soils by probe-type ultrasonic vibrators. *Soil Sci. Soc. Am. Proc.*, **36**, 975-976.

596 -. (1972b) A reevaluation of the ultrasonic-vibration method of dispersing soils. *Soil Sci. Soc. Am.*
597 *Proc.*, **36**, 944-947.

598 Goldberg, S., Forster, H.S. & Godfrey, C.L. (1996) Molybdenum adsorption on oxides, clay
599 minerals, and soils. *Soil Science Society of America Journal*, **60**, 425-432.

600 Gupta, V., Hampton, M.A., Stokes, J.R., Nguyen, A.V. & Miller, J.D. (2011) Particle
601 interactions in kaolinite suspensions and corresponding aggregate structures. *Journal of*
602 *Colloid and Interface Science*, **359**, 95-103.

603 Güven, N. (1992) Molecular aspects of clay-water interactions. Pp. In N. Güven, and R. Pollastro,
604 Eds. *Clay-water interface and its rheological implications*, CMS workshop lectures, 4, Clay
605 Minerals Society.

606 Harvey, C.C. & Murray, H.H. (1997) Industrial clays in the 21st century: A perspective of
607 exploration, technology and utilization. *Applied Clay Science*, **11**, 285-310.

608 Helmy, A.K. (1998) The limited swelling of montmorillonite. *Journal of Colloid and Interface*
609 *Science*, **207**, 128-129.

610 Hill, P.S. (1998) Controls on floc size in the sea. *Oceanography*, **11**, 13-18.

611 Hower, J. & Mowatt, T.C. (1966) The mineralogy of illites and mixed-layer
612 illite/montmorillonites. *American Mineralogist*, **51**, 825-854.

613 Jouyban, A., Soltanpour, S. & Chan, H.K. (2004) A simple relationship between dielectric
614 constant of mixed solvents with solvent composition and temperature. *International Journal*
615 *of Pharmaceutics*, **269**, 353-360.

616 Kiliaris, P. & Papaspyrides, C.D. (2010) Polymer/layered silicate (clay) nanocomposites: An
617 overview of flame retardancy. *Progress in Polymer Science*, **35**, 902-958.

618 Kinter, E.B. & Diamond, S. (1958) Gravimetric determination of monolayer glycerol complexes
619 of clay minerals. *Clays and Clay Minerals*, **5**, 318-333.

620 Kjellander, R., Marcelja, S., Pashley, R.M. & Quirk, J.P. (1988) Double-layer ion correlation
621 forces restrict calcium clay swelling. *Journal of Physical Chemistry*, **92**, 6489-6492.

622 Kleijn, W.B. & Oster, J.D. (1982) A model of clay swelling and tactoid formation. *Clays and*
623 *Clay Minerals*, **30**, 383-390.

624 Lagaly, G. (2006) Chapter 5. Colloid clay science. Pp. 141-245. In B.K.G.T. Faïza Bergaya, and
625 L. Gerhard, Eds. *Developments in clay science*, Volume **1**, Elsevier.

626 Lagaly, G. & Ziesmer, S. (2003) Colloid chemistry of clay minerals: The coagulation of
627 montmorillonite dispersions. *Advances in Colloid and Interface Science*, **100**, 105-128.

628 Laird, D.A. (2006) Influence of layer charge on swelling of smectites. *Applied Clay Science*, **34**,
629 74-87.

630 Lapides, I. & Yariv, S. (2004) The effect of ultrasound treatment on the particle-size of wyoming
631 bentonite in aqueous suspensions. *Journal of Materials Science*, **39**, 5209-5212.

632 Lee, B.J., Fettweis, M., Toorman, E. & Molz, F.J. (2012) Multimodality of a particle size
633 distribution of cohesive suspended particulate matters in a coastal zone. *Journal of*
634 *Geophysical Research-Oceans*, **117**, 17.

635 Levy, G.J., Shainberg, I., Alperovitch, N. & Vandermerwe, A.J. (1991) Effect of na-
636 hexametaphosphate on the hydraulic conductivity of kaolinite-sand mixtures. *Clays and Clay*
637 *Minerals*, **39**, 131-136.

- 638 Mackinnon, I.D.R., Uwins, P.J.R., Yago, A. & Page, D. (1993) Kaolinite particle sizes in the < 2
639 micron range using laser scattering. *Clays and Clay Minerals*, **41**, 613-623.
- 640 Moore, D.M. & Reynolds, R.C. (1997) *X-ray diffraction and the identification and analysis of*
641 *clay minerals*. Pp. 378, Oxford University Press, New York.
- 642 Murray, H.H. (1999) Applied clay mineralogy today and tomorrow. *Clay Minerals*, **34**, 39-49.
- 643 -. (2000) Traditional and new applications for kaolin, smectite, and palygorskite: A general
644 overview. *Applied Clay Science*, **17**, 207-221.
- 645 Neumann, M.G., Gessner, F., Schmitt, C.C. & Sartori, R. (2002) Influence of the layer charge
646 and clay particle size on the interactions between the cationic dye methylene blue and clays
647 in an aqueous suspension. *Journal of Colloid and Interface Science*, **255**, 254-259.
- 648 Olejnik, S., Posner, A.M. & Quirk, J.P. (1974) Swelling of montmorillonite in polar organic
649 liquids. *Clays and Clay Minerals*, **22**, 361-365.
- 650 Pavlidou, S. & Papaspyrides, C.D. (2008) A review on polymer-layered silicate nanocomposites.
651 *Progress in Polymer Science*, **33**, 1119-1198.
- 652 Posner, A.M. & Quirk, J.P. (1964) Changes in basal spacing of montmorillonite in electrolyte
653 solutions. *Journal of Colloid Science*, **19**, 798-812.
- 654 Pruett, R.J. & Webb, H.L. (1993) Sampling and analysis of kga-1b well-crystallized kaolin
655 source clay. *Clays and Clay Minerals*, **41**, 514-519.
- 656 Quirk, J.P. & Aylmore, L.A.G. (1971) Domains and quasi-crystalline regions in clay systems.
657 *Soil Science Society of America Proceedings*, **35**, 652-654.
- 658 Rengasamy, P., van Assche, J.B. & Uytterhoeven, J.B. (1976) Particle size of wyoming bentonite
659 and its relation to the cation exchange capacity and the homogeneity of the charge density.
660 *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed*
661 *Phases*, **72**, 376-381.
- 662 Segad, M., Jonsson, B., Akesson, T. & Cabane, B. (2010) Ca/na montmorillonite: Structure,
663 forces and swelling properties. *Langmuir*, **26**, 5782-5790.
- 664 Theng, B.K.G. (1982) Clay-polymer interactions - summary and perspectives. *Clays and Clay*
665 *Minerals*, **30**, 1-10.
- 666 Vandeven, T.G.M. & Hunter, R.J. (1977) Energy-dissipation in sheared coagulated sols.
667 *Rheologica Acta*, **16**, 534-543.
- 668 Walling, D.E. & Moorehead, P.W. (1989) The particle size characteristics of fluvial suspended
669 sediment: An overview. *Hydrobiologia*, **176/177**, 125-149.
- 670 Wu, W.J. (2001) Baseline studies of the clay minerals society source clays: Colloid and surface
671 phenomena. *Clays and Clay Minerals*, **49**, 446-452.

672 Yariv, S. & Lapidot, I. (2003) Laser shadow analysis of particle-size distribution of
673 montmorillonites in aqueous suspensions. *Clays and Clay Minerals*, **51**, 23-32.

674 Zbik, M. & Smart, R.S.C. (1998) Nanomorphology of kaolinites: Comparative SEM and AFM
675 studies. *Clays and Clay Minerals*, **46**, 153-160.

676 Zbik, M. & Smart, R.S.C. (2002) Dispersion of kaolinite and talc in aqueous solution: Nano-
677 morphology and nano-bubble entrapment. *Minerals Engineering*, **15**, 277-286.

678 Zbik, M.S. & Frost, R.L. (2009) Micro-structure differences in kaolinite suspensions. *Journal of*
679 *Colloid and Interface Science*, **339**, 110-116.

680 Zhang, G., Germaine, J.T. & Whittle, A.J. (2005) An evaluation of the mechanical and chemical
681 dispersion methods for a tropical old alluvium. *Geotechnical Testing Journal*, **28**, 123-132.

682 Zhang, G., Germaine, J.T., Whittle, A.J. & Ladd, C.C. (2004) Index properties of a highly
683 weathered old alluvium. *Geotechnique*, **54**, 441-451.

684 Zhang, Z.P., Liao, L.B. & Xia, Z.G. (2010) Ultrasound-assisted preparation and characterization
685 of anionic surfactant modified montmorillonites. *Applied Clay Science*, **50**, 576-581.

686

687

688

Table Captions

Table 1. Origins and basic properties of the four clay minerals^a.

Table 2. Summary of all clay mineral dispersions prepared by different methods.

Table 3. Parameters of dry mode dispersion for the four clay minerals.

Table 4. Dielectric constant of different solvents at 25 °C.

Table 5. Intrinsic PSD parameters of the four clay minerals.

Table 1. Origins and basic properties of the four clay minerals^a.

Name	Origin	CEC ^b (meq/ 100g)	Layer charge ^c (unbalanced charge)		SSA ^d (m ² /g)	pH ^e	Chemical formula
			T	O			
Kaolinite (KGa-1b)	Washington County, Georgia	2.00	-0.06 (0)		10.05	5.97	(Mg _{.02} Ca _{.01} Na _{.01} K _{.01}) [Al _{3.86} Fe ³⁺ _{.02} Mn _{tr} Ti _{.11}] [Si _{3.83} Al _{.17}]O ₁₀ (OH) ₈
			-0.17	+0.11			
Illite (IMt-1)	Silver Hill, Montana	15.00 ^f	-1.68 (0)		30.00 ^g or 24.9 ^h	8.61	(Mg _{.09} Ca _{.06} K _{1.37}) [Al _{2.69} Fe ³⁺ _{.76} Fe ²⁺ _{.06} Mn _{tr} Mg _{.43} Ti _{.06}] [Si _{6.77} Al _{1.23}]O ₂₀ (OH) ₄
			-1.23	-0.44			
Ca ²⁺ -Mt (STx-1b)	Gonzales County, Texas	84.40	-0.68 (-0.08)		83.79	7.32	(Ca _{.27} Na _{.04} K _{.01}) [Al _{2.41} Fe ³⁺ _{.09} Mn _{tr} Mg _{.71} Ti _{.03}][Si _{8.00}] O ₂₀ (OH) ₄
			0	-0.68			
Na ⁺ -Mt (SWy-2)	Crook County, Wyoming	76.40	-0.55 (+0.05)		31.82	6.44	(Ca _{.12} Na _{.32} K _{.05}) [Al _{3.01} Fe ³⁺ _{.41} Mn _{.01} Mg _{.54} Ti _{.02}] [Si _{7.98} Al _{.02}]O ₂₀ (OH) ₄
			-0.53	-0.02			

^a All data except those noted are taken from the Clay Minerals Society Source Clay Data Sheets.

^b CEC = cation exchange capacity.

^c The layer charge is based on per O₁₀(OH)₈ for kaolinite and O₂₀(OH)₄ for the other three clay minerals; O: charge from octahedral sheet; T: charge from tetrahedral sheets.

^d SSA = specific surface area.

^e pH of the suspension at a concentration of 0.4 g/L in deionized water at room temperature (23 °C) obtained by a pH meter (Thermo Scientific Orion StarTM Series).

^f Data from Hower and Mowatt (1966), and Kinter and Diamond (1958).

^g Data from Celis and Koskinen (1999).

^h Data from (Goldberg et al., 1996).

Table 2. Summary of all clay mineral dispersions prepared by different methods.

Method		Sample preparation	Samples	Purpose
I (Liquid mode)	A	Probe-type ultrasound for 15 mins, followed by 3.5 hrs settling	All 4 clay minerals	Obtain the <2 μm fractions
	B	Unsoaking vs. overnight soaking in water	All 4 clay minerals	Investigate the influence of overnight soaking
	C	Probe-type ultrasound for 15 mins	All 4 clay minerals	Evaluate mechanical disaggregation
	D	Disperse in a 40g/L sodium hexametaphosphate solution	All 4 clay minerals	Evaluate a chemical dispersant
	E	3 solvents: EA, 2 vol.% glycerol in EA, and 2 vol.% glycerol in DI water	Only Ca^{2+} -Mt and Na^{2+} -Mt	Investigate the influence of swelling
II (Dry mode)		Dispersed in and transported by pressurized dry air	All 4 clay minerals	Evaluate dry dispersion

Table 3. Parameters of dry mode dispersion for the four clay minerals.

Sample	Mass of sample per measurement (g)	Obscuration rate	Vibration frequency (Hz)	Cyclic ratio of vibration	Air pressure (mbar)
Kaolinite	1.8	18%	50	40%	400
Illite	1.0	14%	50	35%	350
Ca ²⁺ -Mt	2.0	16%	50	40%	500
Na ²⁺ -Mt	3.0	14%	50	40%	400

Table 4. Dielectric constant of different solvents at 25 °C.

Solution or solvent	Dielectric constant
Deionized water	80.3
Ethyl alcohol	24.3
Glycerol	42.5
2 vol.% glycerol in deionized water	79.5*
2 vol.% glycerol in ethyl alcohol	24.7*

* Dielectric constant estimated based on a relationship proposed by (Jouyban et al., 2004).

Table 5. Intrinsic PSD parameters of the four clay minerals.

Sample	Dispersion method	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	$C_u = \frac{D_{60}}{D_{10}}$	$C_c = \frac{(D_{30})^2}{(D_{10} * D_{60})}$
Kaolinite	Dispersed in NaHMP solution	0.63	3.56	19.41	14.44	0.39
Illite	Overnight soaking / Dispersed in NaHMP solution	0.76	6.37	15.94	11.32	0.81
Ca^{2+} -Mt	Dispersed in alcohol	1.87	12.98	32.75	8.56	2.14
Na^{+} -Mt	Dispersed in alcohol	1.56	12.26	31.91	9.94	2.03

C_u is the coefficient of uniformity, defined as the ratio of D_{60} to D_{10} ; C_c is the coefficient of curvature, defined as the ratio of squared D_{30} to the product of D_{10} and D_{60} .

Figure Captions

Figure 1. X-ray diffraction pattern of the processed illite powdery sample.

Figure 2. Schematic diagram showing the dry mode system (left) and liquid dispersion and circulation system with an inverted microscope for particle imaging (right) of the Cilas PSA.

Figure 3. PSD curves of the $<2\ \mu\text{m}$ fraction of the four clay minerals. Note: P refers to the cumulate percentage, while F refers the occurrence frequency of each size. Same for other figures.

Figure 4. Schematic diagram showing the swelling of mixed $\text{Ca}^{2+}/\text{Na}^{+}$ -montmorillonite in water.

Figure 5. Effect of overnight soaking in water on the PSD of the four clay minerals.

Figure 6. Optical microscope images of clay minerals: (a) kaolinite in DI water, (b) illite in DI water, (c) Ca^{2+} -Mt in DI water, (d) Na^{+} -Mt in DI water, (e) Ca^{2+} -Mt in EA, and (f) Na^{+} -Mt in EA (Scale bar: $50\ \mu\text{m}$).

Figure 7. PSD curves of the four clay minerals obtained by different dispersion methods.

Figure 8. PSD curves of two montmorillonites in different dispersion solvents.

Figure 1. X-ray diffraction pattern of the processed illite powdery sample.

Figure 2. Schematic diagram showing the dry mode system (left) and liquid dispersion and circulation system with an inverted microscope for particle imaging (right) of the Cilas PSA.

Figure 3. PSD curves of the $<2 \mu\text{m}$ fraction of the four clay minerals. Note: P refers to the cumulate percentage, while F refers the occurrence frequency of each size. Same for other figures.

Figure 4. Schematic diagram showing the swelling of mixed $\text{Ca}^{2+}/\text{Na}^{+}$ -montmorillonite in water.

Figure 5. Effect of overnight soaking in water on the PSD of the four clay minerals.

Figure 6. Optical microscope images of clay minerals: (a) kaolinite in DI water, (b) illite in DI water, (c) Ca²⁺-Mt in DI water, (d) Na⁺-Mt in DI water, (e) Ca²⁺-Mt in EA, and (f) Na⁺-Mt in EA (Scale bar: 50 µm).

Figure 7. PSD curves of the four clay minerals obtained by different dispersion methods.

Figure 8. PSD curves of two montmorillonites in different dispersion solvents.

Evaluation of the particle sizes of four clay minerals

Graphical Abstract