

THESIS

PORE FLUID SALINITY EFFECTS ON SEDIMENTATION AND GEOTECHNICAL
PROPERTIES OF FINE-GRAINED SOILS

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ABSTRACT

PORE FLUID SALINITY EFFECTS ON SEDIMENTATION AND GEOTECHNICAL PROPERTIES OF FINE-GRAINED SOILS

The objectives of this study were to evaluate the effects of soluble salt concentration (i.e., salinity) on geotechnical characteristics and sedimentation behavior of fine-grained soils (e.g., mine tailings) and identify test methods applicable for characterizing high-saline soils. Three fine-grained soils were used in this study: soda ash mine tailings, kaolin clay, and bentonite clay. The soda ash mine tailings (sodium carbonate) contained high-saline pore fluid and predominantly sodium on the exchange complex, whereas commercially-available kaolin and bentonite clay were used for comparison with the soda ash tailings. Salinity was controlled in the natural clays via adding salts with different valence (NaCl , CaCl_2 , and FeCl_3) at concentrations ranging between 1 and 1000 mM. Salinity in the soda ash tailings was altered via extracting salts from solution using dialysis to create materials with different soluble salt concentrations.

Sedimentation experiments were conducted in 63.5-mm-diameter by 457-mm-tall glass cylinders to evaluate the sedimentation rate and final solids content. The effects of pore fluid salinity on geotechnical characteristics of soda ash mine tailings and laboratory-prepared, sedimented soils were evaluated via measuring Atterberg limits, specific gravity, and particle-size distribution via hydrometer tests.

Overall, an increase in ionic strength of the sedimentation fluid (i.e., increase in salt concentration) yielded higher sedimentation rates and larger volumes of released

water for experiments on bentonite. In contrast, the sedimentation rate of kaolin was constant for salt concentrations between 1 and 100 mM, and the sedimentation rate decreased at higher salt concentrations. This behavior was attributed to an increase in fluid density and viscosity at high salt concentrations that reduced sedimentation. Soda ash sedimentation behavior was similar to kaolin and characterized by a decrease in sedimentation rate with increase in salt concentration.

Geotechnical characterization of all materials indicated that liquid limit, plastic limit, and clay content decreased with increasing pore fluid salinity. Temporal evaluations of soil plasticity suggest that hydration times of at least two days are required to solubilize salts and capture salinity effects on soil plasticity. Additionally, experimental methods were developed and evaluated for correcting errors in hydrometer and specific gravity tests that may originate in the presence of soluble salts.

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LIST OF SYMBOLS

A_h	Hamaker constant	M_T	Total mass of pycnometer, water, and soil solids
C	Cation concentration	M_w	Water mass
C_0	Ionic concentration	PL	Plastic limit
d	Particle diameter	R	Universal gas constant
D	Thickness of the DDL	T	Absolute temperature
D_v	Yield diameter at which there is no particle settlement out of suspension	v	Settling velocity
e	Unit of electric charge	V_w	Water volume
F_A	Attraction force	w	Water content
F_R	Repulsive force	x	Distance between particles
G_s	Specific gravity	z	Cation valence
K	Boltzmann's constant	ϵ	Dielectric constant
LL	Liquid limit	η	Viscosity
LI	Liquidity index	ρ_s	Soil solids density
M_{s+s}	Mass of salt and soil solids	ρ_w	Water density
M_{salt}	Mass of salt solubilized	M_w	Water mass

CHAPTER 1: INTRODUCTION

1.1 Problem Statement

Increased consumption of raw materials that has been coincident with population growth has increased demand on natural resources. In turn, generation of waste and industrial by-products has increased, which require innovative and sustainable waste management considerations. In the mining industry, waste materials include waste rock discarded from mining operations and fine-grained tailings produced during ore extraction processes. These waste materials are generated in enormous quantities (e.g., > 16 million Mg/yr tailings generation at a single platinum mine) and present relevant engineering and environmental challenges. In particular, mine tailings are generated at high water contents and often contain heavy metals and other potential contaminants that pose risks to human health and the environment. Effective tailings management requires understanding the interactions between pore fluid chemistry, water content, and strength of the tailings, and an improved understanding of physical and chemical interactions of mine tailings can lead to innovative mine waste management strategies.

The addition of soluble salts to mine tailings in slurry form presents an opportunity to enhance sedimentation and strength of deposited materials; however, soluble salts also present challenges to conventional tests methods used to characterize geotechnical properties of fine-grained soils. Atterberg limits and particle-size distribution commonly are used in correlations to a wide variety of engineering properties (e.g., permeability, shear strength, and compressibility). The presence of soluble salts can affect measured Atterberg limits and particle-size distribution via altering interparticle forces, which are a function of van der Waals and diffuse double layer forces. Thus, effects of soluble salt concentration (i.e., salinity) on geotechnical characteristics

and also correction procedures to account for salinity effects on measured properties are required to accurately assess fine-grained soil behavior.

Tailings contain a high percentage of water from ore extraction processes, which results in a low strength material and high potential for contaminant transport. Many mines are located in arid and semiarid regions, and recovering mine process water is advantageous to enhancing environmental sustainability and reducing economic constraints on mine owners. Soluble salts added to high water content mine tailings has the potential to enhance particle flocculation and improve sedimentation and water recovery. Thus, the effects of salinity on sedimentation behavior of fine-grained soils and mine tailings as well as the geotechnical characteristics of these materials was the focus of this study.

1.2 Research Objectives and Tasks

The objectives of this study were to evaluate the effects of soluble salt concentration on geotechnical characteristics and sedimentation behavior of fine-grained soils (e.g., mine tailings) and identify test methods applicable for characterization of high-saline soils. The study included two common clays with differing plasticity, kaolin and bentonite, and saline mine tailings from a soda ash mine in Wyoming, USA. Laboratory-controlled materials (i.e., kaolin and bentonite clay) were used to represent clay with a range of plasticity that can be encountered in mine tailings.

The following research tasks were completed as part of this study:

1. Developed a procedure for correcting errors in hydrometer and specific gravity tests that may originate in the presence of soluble salts;
2. Evaluated the effect of hydration time on Atterberg limits measured on high saline soils and mine tailings;
3. Evaluated the effect of salinity on soil plasticity and particle-size distribution of mine tailings and laboratory-controlled materials; and

4. Evaluated the effects of soluble salt concentration and cation valence on sedimentation behavior of fine-grained soils.

Sedimentation experiments were conducted in 63.5-mm-diameter by 457-mm-tall glass cylinders. Salinity was controlled in the natural clays via adding salts with different valence (NaCl, CaCl₂, and FeCl₃) at concentrations ranging between 1 and 1000 mM. Salinity in the soda ash tailings was altered via dialysis to create materials with different soluble salt concentrations.

CHAPTER 2: EFFECT OF SALINITY ON THE GEOTECHNICAL CHARACTERIZATION OF FINE-GRAINED SOILS AND MINE TAILINGS

2.1 Introduction

Mining operations produce considerable volumes of waste materials during ore extraction processes. The two predominant waste materials that require short- and long-term management are tailings and waste rock (e.g., Bussi re 2007; Blight 2009). Tailings typically are fine grained and have high water contents (low solids contents), whereas waste rock generally is gravel- to cobble-sized material with sand and fines. Disposal and management of mine tailings in impoundment facilities can be challenging due to variability in physical and chemical properties of the tailings (Bussi re 2007). Standardized soil characterization procedures used to classify mine tailings and evaluate geotechnical behavior can be influenced by chemistry of the process water that comprises the liquid fraction of mine tailings.

Common geotechnical characteristics, such as Atterberg limits, particle-size distribution (PSD), and specific gravity (G_s), are used in correlations to estimate engineering properties of soils (e.g., hydraulic conductivity, shear strength, and compressibility). The presence of soluble salts in soils can affect geotechnical characteristics via cation exchange, flocculation, and dispersion of clay particles (Sparks 2003; Mitchell and Soga 2005; Chittaranjan et al. 2011). Thus, the effect of soluble salts (i.e., pore fluid salinity) on geotechnical characterization testing needs to be considered such that appropriate characteristics are quantified to assess engineering properties.

The effect of salinity on the geotechnical characteristics of fine-grained soils, particularly Atterberg limits, has been investigated in numerous studies (Warkentin and Yong 1960; Barbour and Yang 1993; Gleason et al. 1997; Sivapulliah and Savitha 1999; Di maio et al. 2004; Arasan and Yetimoglu 2008; Yukselen-aksoy et al. 2008; Mishra et al. 2009; Shariatmadari et al. 2011;

Spagnoli and Sridharan 2012). Data compiled from these studies are presented in Fig. 2-1 as the normalized difference between liquid limit measured with deionized water (LL_{DI}) and soluble salt solution (LL_{Saline}) versus LL_{DI} . The difference between LL_{DI} and LL_{Saline} is normalized with respect to LL_{DI} to combine literature results ($LL_R = (LL_{DI} - LL_{Saline})/LL_{DI}$). The general trend in the data set is an increasing difference between LL_{DI} and LL_{Saline} as soil plasticity increases (i.e., higher LL_{DI}). Scatter in the data set can be attributed to differences in clay mineralogy, salt composition in the pore fluid, and salt composition on the exchange complex, which combine to yield a range in response with respect to DI-water and changes in salinity.

Warkentin and Yong (1960) reported that LL of bentonite clay decreased as salt concentration in the pore fluid increased. Yukselen-Aksoy et al. (2008) investigated the effect of sea water on LL of 10 soils that included low and high plasticity clays with a range of LL from 25 to 396 % (Fig. 2-1). They reported that the effect of salinity is considerable for higher-plasticity soils, and in particular for $LL > 110$ %. The effect of NaCl solution on different clay minerals was studied by Spagnoli and Sridharan (2012), who observed that LL of smectite decreased in saline water, whereas LL of kaolinite did not change considerably. Arasan and Yetimoglu (2008) reported the opposite effect of soluble salts on low plasticity clay, but did not identify a mechanism contributing to the observed behavior. In general, more pronounced changes in plasticity correspond to higher plasticity soils, which include clay minerals with larger diffuse double layers that are more susceptible to changes in plasticity with fluctuations in salinity.

Warkentin and Yong (1960) also evaluated the effect of initial salt composition on the clay mineral exchange complex and note that the rate of reduction in LL as soluble salt concentration increased was higher in Na-bentonite compared to Ca-bentonite. This can be attributed to an initial higher LL_{DI} for Na-bentonite, which provided a larger LL range for changes in pore fluid salinity to affect soil plasticity. Shariatmadari et al. (2011) evaluated the effect of salt composition (NaCl, $CaCl_2$, and $MgCl_2$) and concentration on LL of natural clay and reported that LL decreased as salt concentration increased in all cases. The rate of LL reduction with

increased salt concentration was higher for salts with divalent cations compared to monovalent cations.

Dunn and Mitchell (1984) performed hydrometer tests on low and high plasticity soil following treatment of the soil with tap water, distilled water, and synthetic Pb-Zn tailings process water. Particle-size distributions for soils treated with Pb-Zn tailings process water indicated coarser particles compared to soils treated with tap water and distilled water. This difference in particle-size distribution was attributed to particle flocculation in the presence of soluble salts, which was more pronounced in the tailings process water. To mitigate salinity effects on particle-size distribution, Kaddah (1975) recommended using an elevated dispersion agent concentration if the soil contains soluble salts or gypsum to overcome flocculated clay particle structures. Alternatively, soluble salts can be leached from the pore fluid via washing a given saline soil or flushing numerous pore volumes of DI-water through the soil.

Noorany (1984) and Nusier et al. (2008) have recommended correction procedures for measuring specific gravity of saline soils. Noorany (1984) recommended removing salts via adding water to a saline soil specimen and subsequently removing that water and soluble salts with a Buchner funnel and vacuum flask. Nusier et al. (2008) recommended the use of kerosene in-place of water in a specific gravity test, since most salts that are soluble in water are insoluble in kerosene. However, removing salts via solubilization and filtration can be time consuming, and there are difficulties associated with measuring the density of kerosene at different temperatures as well as concerns with the use of flammable chemicals in a laboratory.

The objective of this study was to assess the effects of salinity on the geotechnical characterization of a saline mine tailings and two commercially-available clays that include minerals commonly encountered in tailings. The effects of salinity were evaluated by creating soil specimens with a range of soluble salt concentrations and measuring Atterberg limits, particle-size distribution, and specific gravity. The experiments outlined in this study were designed to build on past research and lead to recommendations for a set of laboratory

procedures that can be readily adopted in a soil-testing laboratory to aid in the geotechnical characterization fine-grained saline soils.

2.2 Background

The effect of soluble salts on geotechnical characterization of soils is dependent on interparticle interactions, which can be described with colloidal and double layer theory as applied to clay particles. A colloid consists of small diameter materials (i.e., 0.001-1.0 μm) homogeneously dispersed throughout a medium, and colloidal stability refers to the ability of dispersed materials to remain in suspension (van Olphen 1963). Colloidal stability is controlled by interparticle interactions, which depend on particle and fluid properties. Total interaction potential between particles is dependent on attractive van der Waals forces and repulsive forces due to the diffuse double layer (van Olphen 1963; Mitchell and Soga 2005; Evans and Wennerstrom 1999).

The diffuse double layer (DDL) is an accumulation of water and hydrated ions that surround clay particles to balance the net negative particle charge. The thickness of the DDL (D) can be computed as follows:

$$D = \sqrt{\frac{\varepsilon \cdot K \cdot T}{8\pi \cdot C \cdot e^2 \cdot z^2}} \quad (2-1)$$

where ε is dielectric constant, K is Boltzmann's constant, T is absolute temperature, C is cation concentration (number of ions per cm^3), e is a unit of electric charge, and z is cation valence (van Olphen 1963; Anandrajah and Chen 1994; Shackelford 1994; Mitchell and Soga 2005). Thickness of the DDL decreases with increasing salinity due to increases in C or z . A decrease in D results in a decrease in the repulsive force between neighboring particles. The repulsive force of the DDL (F_R) is computed according to Eq. 2-2:

$$F_R = 16 \cdot \pi \cdot R \cdot T \cdot C_0 \cdot d^2 \cdot e^{\frac{-x}{9}} \quad (2-2)$$

where R is the universal gas constant (8.314 J/(mole·K)), C_0 is ionic concentration, d is particle diameter, and x is distance between particles (Israelachvili 1992; Palomino and Santamarina 2005).

Van der Waals forces are physical forces that remain constant with changes in pore fluid salinity. Electrons surrounding the nucleus of a given atom polarize the atom to generate a fluctuating dipole that results in attraction forces between neighboring particles (Anandarajah and Chen 1997). Van der Waals forces (F_A) are only a function of size, shape, and distance between particles as outlined in Eq. 2-3:

$$F_A = \frac{1}{24} \frac{A_h}{x^3} \cdot d^2 \quad (2-3)$$

where A_h is the Hamaker constant that is independent of pore fluid salinity. With the addition of soluble salts to a colloid, the relative effect of F_A increases due to decreasing repulsive forces (i.e., F_R), which enhances attraction between particles and promotes particle flocculation.

Flocculation is a process that leads to aggregation of clay particles. This process occurs naturally during soil formation via sedimentation (Mitchell 1976; Mitchell and Soga 2005), and is prevalent in all slurry-deposited geomaterials at water contents higher than the LL (e.g., mine tailings). Particles in suspension have a greater propensity to rearrange into a flocculated structure due to greater mobility prior to deposition.

Fine-grained soil particles, in particular clays, typically contain negatively-charged particle surfaces and positively-charged particle edges based on mineralogy. This charge distribution can lead to three main geometric configurations for particle flocculation: (1) face-to-face (FF), (2) edge-to-face (EF), and (3) edge-to-edge (EE) (van Olphen 1963; Mitchell 1976; Mitchell and Soga 2005; Palomino and Santamarina 2005). Face-to-face flocculation usually occurs at low pH where an excess of H^+ ions neutralize particle faces to yield a decrease in repulsion between similarly charged particles. Edge-to-face flocculation is based on Coulombic

attraction between positive edges and negative faces. Edge-to-edge flocculation occurs where van der Waals forces between edges are high and interfacial interactions are repulsive.

2.3 Materials and Methods

2.3.1 Materials

Three types of soil were used in this study: (1) kaolin clay, which consisted predominantly of kaolinite minerals (Thiele Kaolin Company, Georgia, USA), (2) bentonite clay, which consisted predominantly of sodium montmorillonite minerals (Wyoming, USA), and (3) soda ash mine tailings, which was collected from a sodium carbonate mine in Wyoming, USA. The kaolin and bentonite clay were commercially-available materials and received in an air-dried, powdered state. The soda ash mine tailings was collected in an as-generated state from an ore processing plant, and was representative of material discharged to the tailings impoundment.

A summary of the chemical properties and specific gravity of the materials evaluated in this study is in Table 2-1. Salinity of the soda ash tailings pore fluid was modified using dialysis. Dialysis is an effective method for either adding or removing salts within a soil specimen via a semi-permeable molecular membrane. Molecular weight cut-off of the semi-permeable membrane was 6000 - 8000 Da. Natural soda ash tailings at the as-collected water content (T_N) was placed within the membrane and sealed at both ends with clamps. The membrane-filled specimen was then placed in a 7-L container filled with DI water. The container was emptied and refilled with DI water every 24 ± 6 hr (~ 1 d), which constituted one dialysis cycle (Table 2-1). After a targeted number of cycles, tailings were removed from the membrane and air-dried. Five dialyzed tailings specimens were created with varying salinity and are identified as T_1 through T_5 (Table 2-1), where a higher subscript number coincides with higher salinity. Soluble salts also can be removed via washing or permeating soil with a large amount of water;

however, permeation requires considerable time for low hydraulic conductivity soils and washing can lead to peptization of clay particles (Carrado et al. 2006).

The rate of change in electrical conductivity (EC) of water in the dialysis container versus number of cycles for two dialyzed tailings is shown in Fig. 2-2. Soluble salts transferred from the tailings pore fluid into the DI water via diffusion, which was induced by the high soluble salt concentration within the tailings and near zero soluble salt concentration in the DI water. As the number of dialysis cycles increased, the soluble salt concentration within the tailings specimen continuously decreased. The rate of change in EC decreased with increasing cycles due to a diminishing concentration gradient between the tailings pore fluid and DI water (Fig. 2-2). The rate of change in EC approximately was constant after eight cycles, and subsequent dialysis cycles yielded small changes in tailings salinity. The relationship in Fig. 2-2 is illustrative of the dialysis technique used in this study; the relationship will vary as a function of initial pore-fluid chemistry, specimen size, and reservoir volume.

The salinity of kaolin and bentonite clay specimens was modified by mixing NaCl solution and clay in a slurry phase. Salt solution at a target concentration was mixed with dry clay soil, the mixture was thoroughly agitated within a sedimentation cylinder, and clay particles were allowed to settle freely out of suspension. This saline-clay preparation method was used to allow particle flocculation and subsequent sedimentation. Following sedimentation, the remaining soil-free saline solution was removed and the soil was exhumed and air-dried for subsequent characterization testing. The natural, as-received kaolin and bentonite clays are referred to as K_N and B_N , respectively, and higher saline clays include a subscript notation where the subscript value increases with increasing salinity (Table 2-1).

Pore fluid salinity of all materials used in this study was quantified via measuring EC. Electrical conductivity was measured following a mixture technique outlined in Page et al. (1983). Mixtures of air-dried soil and DI water were prepared at a ratio of 1:5 (mass basis) for soda ash tailings and kaolin clay. The mixture ratio for bentonite clay was increased to 1:10

such that free liquid was available in the EC test similar to the other two soils. The 1:10 EC measurement for bentonite was converted to a 1:5 EC for direct comparison with soda ash tailings and kaolin clay. Mixtures for EC measurement were placed in a sealed container and shaken vigorously for 1 min every 30 min over a 2-hr period as outlined in Page et al. (1983). Electrical conductivity was measured on free liquid at the end of the preparation stage using an EC probe (150 A+ Conductivity meter; Thermo Orion, Beverly, MA).

2.3.2 Mineralogy

X-ray diffraction (XRD) was conducted on natural soda ash tailings (non-dialyzed), kaolin clay, and bentonite clay, and x-ray fluorescence (XRF) was conducted on natural and dialyzed soda ash tailings. X-ray diffraction was used to evaluate minerals present in the soils, whereas XRF was used to evaluate chemical composition of dialyzed and non-dialyzed soda ash tailings and to assess effectiveness of the dialysis technique. All analyses were completed by Mineralogy-INC (Tulsa, Oklahoma, USA).

X-ray diffraction results for natural soda ash mine tailings, kaolin clay, and bentonite clay are in Table 2-2. Dolomite and shortite were the predominant minerals in soda ash tailings, with secondary minerals consisting of quartz, potassium-feldspar, and phyllosilicates (clay and mica). Kaolin consisted predominantly of kaolinite minerals, whereas bentonite was primarily montmorillonite minerals with 8 % quartz content. Clay minerals were not quantified in soda ash tailings, but qualitatively identified as illite with mixed layer illite/smectite. Illite has a cation exchange capacity (CEC) ranging between 10 and 40 cmol/kg and specific surface area (SSA) ranging from 65 to 100 m²/g. Kaolinite CEC ranges from 3 to 15 cmol/kg and SSA from 10 to 20 m²/g, whereas CEC of sodium montmorillonite ranges from 80 to 150 cmol/kg and SSA from 50 to 120 m²/g (Mitchell and Soga 2005). Isomorphic substitution in illite occurs in the silica-tetrahedral sheet, whereas isomorphic substitution in montmorillonite occurs in the aluminum-octahedral sheet. The difference in location of isomorphous substitution for illite relative to

montmorillonite produces a net-negative charge that is closer to exchangeable cations, which results in stronger inter-layer bonding and lower CEC and SSA compared to montmorillonite.

Chemical composition of non-dialyzed and dialyzed soda ash tailings specimens based on XRF are in Table 2-3. An additional soda ash specimen was dialyzed for seven cycles to compare chemical composition of non-dialyzed and dialyzed soda ash tailings. Sodium, which was believed to be the predominant cation in the pore fluid, was at a relative contribution that was 3.5 times larger in non-dialyzed soda ash tailings as compared with the dialyzed specimen. Relative percent contributions of all other major cations (e.g., Mg, Si, and Ca) increased with dialysis of soda ash tailings. Thus, the decrease in Na supports the presumption of Na as the predominant cation in soda ash pore fluid and supports that the dialysis technique was effective in reducing pore fluid salinity.

2.3.3 Soil Plasticity

Liquid limit was measured for all materials with a Casagrande cup following ASTM D 4318. Liquid limit was also measured with fall cone penetration following BS 1377 to evaluate the effect of hydration time on LL. Fall cone penetration tests were performed with an 80-g, 30° cone penetrometer. Multipoint measurement procedures were used in both LL tests, and at least five different water contents were used to determine each LL reported herein. The standard soil-thread method was used for measuring the plastic limit (PL) in accordance with ASTM D 4318.

The effect of hydration time on LL of natural soda ash mine tailings and saline bentonite was evaluated using both fall cone penetration and Casagrande cup tests. Air-dried, non-dialyzed tailings were mixed with DI water and placed in six separate sealed containers. Water content of the tailings in the six containers ranged between 30.5 and 40.7 %, which encompassed LL of the tailings (33 %). Five bentonite specimens were prepared with 5 % sodium chloride (by mass) added to the specimens in an air-dried phase. Water content of the

saline bentonite in the five containers ranged between 142 and 193 %, which encompassed the anticipated LL of saline bentonite (159 %). Fall cone penetration and Casagrande cup tests were conducted every 24 ± 1 hr for 5 d. Soil in each container represented one point on a LL plot for each daily test (i.e., water content versus blow count or penetration). Water content of the tailings and bentonite were measured following each daily LL experiment.

Low water content fall-cone specimens (i.e., water content < LL) were prepared following a recommended method in Muntohar and Hashim (2005). Soil was placed on a glass surface such that horizontal and vertical dimensions of the mounded soil were larger than dimensions of the fall-cone specimen cup. The cup was pushed into the soil mound and excess soil around the cup was removed.

2.3.4 Particle-size Distribution

Particle-size distributions of the three materials were evaluated via mechanical sieve and hydrometer tests following appropriate procedures in ASTM D 422 and ASTM D 6913. Sieve analysis only was conducted on a single coarse-grained specimen of soda ash tailings following separation of the coarse- and fine-grained fractions via washing the tailings on a No. 200 sieve. Hydrometer tests were conducted on all materials prepared for this study (Table 2-1) with and without addition of a dispersion agent (i.e., sodium hexametaphosphate). Results from hydrometer tests were used to evaluate the effect of salinity on measured particle-size distributions, which can provide a measure of particle flocculation.

The presence of soluble salts in tailings and saline clay specimens required material-specific assessment of the hydrometer correction factor. Soluble salts increased total salt concentration of the settling fluid in the hydrometer test and yielded higher hydrometer readings due to higher solution densities. Thus, following completion of a given hydrometer test, the settling fluid was filtered through a No. 42 filter paper ($2.5 \mu\text{m}$) into a separate, clean glass sedimentation cylinder to measure a material-specific hydrometer correction factor. A unique

correction factor was determined for each material due to variation in fluid salinity. Al-Amoudi and Abduljawwad (1994) outlined an alternative hydrometer approach using a non-aqueous liquid in-place of DI water in which salt is insoluble. However, the filtration and material-specific hydrometer correction procedure was adopted and evaluated in this study to assess a procedure that is applicable to any soil-testing laboratory.

Material-specific hydrometer correction factors for all materials with and without dispersion agent are shown as a function of $EC_{1:5}$ in Fig. 2-3. Hydrometer correction factors increased with increasing EC for all materials due to higher soluble salt concentrations within the sedimentation fluid. Linear regression of the hydrometer correction factor versus EC relationships reveal different slopes and suggest that correction factor relationships are a function of salt content. The slope of kaolin and bentonite specimens, which included only NaCl, ranged between 0.06 and 0.08. The slope of soda ash tailings trend lines are approximately 0.45. The difference in slopes was due to the difference in salt composition between kaolin and bentonite specimens (NaCl) and soda ash specimens (natural salts). The modest difference in slopes of the kaolin and bentonite regression lines was due to differences in EC of pure kaolin and bentonite (non-saline).

Particle-size distributions from hydrometer tests on T_4 in the presence of a dispersion agent determined with and without applying a material-specific hydrometer correction factor are shown in Fig. 2-4. The testing procedure and correction approach used in the hydrometer test resulted in a coarser PSD. Clay content without the material-specific hydrometer correction factor was three times higher than the actual clay content. This change can be attributed to increased buoyancy of the hydrometer in the presence of additional soluble salts, which increases the sedimentation fluid density and results in higher hydrometer readings.

During hydrometer tests on materials with high soluble salt concentrations, foam formed on the water surface following agitation of the sedimentation cylinder. The presence of foam caused difficulty in recording hydrometer readings during the first 15 to 30 min of the

experiment. Thus, 50 mL of DI water was retained from the total 1-L sedimentation fluid solution and was added via a squirt bottle to suppress foam at the top of the sedimentation cylinder following agitation. This procedure was effective at suppressing the majority of the foam such that hydrometer readings could be recorded within 60 s following agitation.

Specific gravity used in the hydrometer calculations was assumed equal to G_s measured on T_1 (most dialyzed tailings) and non-saline specimens in kaolin and bentonite (K_N and B_N). Higher G_s results in a higher correction factor (α) and lower K value used in hydrometer calculations (ASTM D 422). For a given hydrometer reading, a higher α value yields a higher percent passing, and lower K value yields a smaller particle diameter.

2.3.5 Specific Gravity

Specific gravity of dialyzed and non-dialyzed tailings, saline and non-saline kaolin clay, and non-saline bentonite clay was measured in accordance with ASTM D 854. Soda ash tailings and kaolin clay specimens had unique G_s for each specimen due to differences in pore fluid salinity. The presence of soluble salts in a given soil can result in errors in the measured G_s due to dissolved salts within the pycnometer that increase fluid mass more substantially than the corresponding increase in fluid volume. The effect of salinity on G_s of saline bentonite was not evaluated in this study.

Relationships between total dissolved solids (TDS) and EC of soda ash pore fluid salt and NaCl are shown in Fig. 2-5. Relationships between TDS and EC are slightly nonlinear and dependent on salt composition (Anandarajah and Zhao 2000). These relationships were obtained by adding a known mass of salt (i.e., NaCl or natural salt from the soda ash tailings) to 1 L of DI water and directly measuring EC of the solution. Natural salt from soda ash mine tailings was obtained by filtering pore fluid through a No. 42 filter paper (pore size = 2.5 μm) and evaporating the filtrate. Relationships in Fig. 2-5 were used to correct G_s of soda ash tailings and kaolin clay.

The mass of salt solubilized (M_{salt}) in a given volume of water can be computed based on Eq. 2-4:

$$M_{salt} = TDS \cdot V_w = TDS \left(\frac{M_w}{\rho_w} \right) \quad (2-4)$$

where V_w is water volume, M_w is water mass, and ρ_w is water density. Measurements of initial V_w or M_w added to a pycnometer combined with EC of the pycnometer fluid at the end of a specific gravity test can provide a means to directly compute M_{salt} . Total dissolved solids can be obtained via measuring EC of a soil-water mixture with a known water volume and substituting the measured EC into the TDS-EC relationship (Fig. 2-5). The corrected G_s was then computed via Eq. 2-5:

$$G_s = \frac{M_{s+s} - M_{salt}}{M_{p+w} - (M_T - M_{s+s})} \quad (2-5)$$

where M_{s+s} is mass of salt and soil solids, M_{p+w} is mass of pycnometer and water, and M_T is total mass of pycnometer, water, and soil solids. The volume of dissolved salt in the pycnometer water was assumed negligible in the specific gravity experiment.

2.4 Results

2.4.1 Specific Gravity

Measured and corrected G_s for all soda ash tailings and kaolin specimens are compiled in Table 2-1 and shown as a function of $EC_{1:5}$ in Fig. 2-6. Measured G_s of soda ash tailings ranged from 2.78 for T_N (non-dialyzed tailings) to 2.56 for T_1 , which was the most dialyzed specimen with lowest salinity (Table 2-1). Measured G_s of kaolin clay specimens ranged from 2.81 for K_3 (most saline specimen) to 2.61 for K_N (non-saline, natural kaolin). Specific gravity was not measured on saline specimens of bentonite clay.

Corrected G_s for all soda ash specimens reduced to a narrow range between 2.55 and 2.60 (Fig. 2-6). The correction was small for tailings specimen T_1 (difference of 0.01) due to low

salinity. The negligible difference between measured and corrected G_s for T_1 suggests that the actual G_s of soda ash tailings was approximately 2.55. The close approximation of the corrected G_s for all tailings specimens relative to measured G_s of T_1 (2.55) (Fig. 2-6) suggests that the G_s -correction method developed as a function of TDS is applicable for determining G_s of soil solids for saline soils. A $G_s \approx 2.55$ for soda ash tailings is slightly lower compared to G_s of common soils (e.g., Mitchell and Soga 2005), but compared favorably to G_s of parent rock materials mined for soda ash. Santini et al. (2006) reported that trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) is the most common mineral source mined for soda ash production and has $G_s = 2.17$. Other common minerals mined for soda ash include thermonatrite, wesgsheiderite, and nacholite, which have G_s ranging between 2.20 and 2.35. Thus, residuum from parent rock materials that are mined for soda ash likely contribute to the $G_s \approx 2.55$ for soda ash mine tailings.

Specific gravity corrections applied to kaolin yielded a similar relationship to that observed for soda ash tailings. Corrected G_s ranged between 2.57 and 2.65 (Table 2-1, Fig. 2-6); no correction was applied to kaolin specimen K_N . Specific gravity of K_2 and K_3 decreased 0.01 and 0.24, respectively (Table 2-1), after applying the G_s -correction.

The main source of error when measuring G_s of saline soils is the change in water density due to presence of dissolved salts. The percent difference between measured and corrected G_s increased with increasing salinity (i.e., $EC_{1.5}$ in Fig. 2-6) and exceeded 9 % for T_N (non-dialyzed tailings) and K_3 (most saline specimen). Thus, correcting the mass of soil solids measured in a G_s test for the presence of dissolved salts is important for estimating an appropriate G_s for saline soil.

2.4.2 Plasticity

Relationships between LL and PL versus $EC_{1.5}$ for soda ash tailings, kaolin clay, and bentonite clay are shown in Fig. 2-7. Liquid limit and PL both decrease with increasing EC for all materials. An increase in soluble salts reduces repulsive forces within the DDL, which

decreases water content and leads to an increase in attractive forces and development of a flocculated structure that exhibits lower plasticity properties (van Olphen 1963). Logarithmic trend lines fit to data in Fig. 2-7 suggest that the change in LL is higher in lower salinity. Additionally, the trendlines suggest that the effect of reduced plasticity decreases with increasing salinity and at some magnitude of salinity the DDL is compressed to the extent possible such that subsequent increases in salinity will have negligible effect on LL.

The compilation of LL from literature shown in Fig. 2-1 is reproduced in Fig. 2-8 along with data generated from this study. Data points for this study in Fig. 2-8 are representative of LL_{DI} measured on the lowest salinity materials (T_1 , K_N , and B_N) and LL_{Saline} measured on the highest salinity materials (T_N , K_3 , and B_3). The LL_R ($LL_R = (LL_{DI} - LL_{Saline})/LL_{DI}$) value is 0.8 for bentonite, 0.2 for kaolin, and 0.1 for soda ash mine tailings. The general trend in the data set is an increasing difference between LL_{DI} and LL_{Saline} as soil plasticity increases (i.e., higher LL_{DI}). Regression lines in Fig. 2-8 based on this study and the literature compilation are similar, which lends additional support to the effects of salinity on soil plasticity and geotechnical behavior observed in this study.

The relationship between plasticity index (PI) and pore fluid EC is shown in Fig. 2-9. In soda ash, PI increased with increasing salinity and approximately was constant at 16 % for the four highest saline specimens. However, PI decreased with increasing salinity in kaolin and bentonite. These contrasting relationships were attributed to a more acute sensitivity of PL to changes in pore fluid relative to LL in soda ash tailings, whereas LL was more sensitive than PL in bentonite and the effects of salinity on PL and LL of kaolin were approximately similar (Fig. 2-7).

The effect of hydration time on LL of saline soil was investigated to determine if longer hydration times are needed to capture the effects of soluble salts on plasticity behavior. Temporal trends in LL for non-dialyzed soda ash tailings and saline bentonite are shown in Fig. 2-10. Liquid limit decreased during the first two days of hydration and remained approximately

constant thereafter. As time evolved and more salts dissolved into solution, DDL thickness became increasingly compressed, which resulted in a decrease in LL.

ASTM D 4318 suggests a 16-h hydration time for soil prior to evaluation of Atterberg limits. However, based on the results shown in Fig. 2-10 a 16-h hydration time may be inadequate for saline soil due to time required to dissolve salts into solution. Soda ash mine tailings was a low plasticity soil and the difference in LL between 1-d hydration time and average LL at longer hydration times was approximately 1 %. However, bentonite clay is a high plasticity soil and the difference in LL for 1-d hydration time and average LL at longer hydration times (Day 2 to 5) was approximately 15 %. Thus, the effect of hydration time on LL of saline soils with low plasticity may be negligible, whereas longer hydration times are needed for high plasticity soils. Results from this study suggest that hydration times ≥ 2 d are adequate to assess LL of high-plasticity saline soils. Longer hydration time may be required for saline soils with higher salinity or higher plasticity relative to those evaluated in this study.

2.4.3 Particle-Size Distribution

Particle-size distribution curves for soda ash tailings, kaolin clay, and bentonite clay are shown in Fig. 2-11 for hydrometer tests conducted with dispersion agent and in Fig. 2-12 for hydrometer tests conducted without dispersion agent. All PSDs in Figs. 2-11 and 2-12 were developed using material-specific hydrometer correction factors. Hydrometer tests on non-saline specimens of kaolin (K_N), bentonite (B_N), and soda ash tailings (T_1) in the presence of a dispersion agent (Fig. 2-11) yielded the largest fraction of fine particles. In general, PSDs for all three materials became increasingly coarser for hydrometer tests with dispersion agent as soil salinity increased. Thus, soil salinity can be expected to enhance particle flocculation and yield coarser PSDs even when a dispersion agent is added to mitigate flocculent formation of clay particles in suspension (Dunn and Mitchell 1984).

Hydrometer tests without dispersion agent were used to evaluate the effect of soluble salts on particle flocculation. For all three materials, the coarsest PSD was measured for the highest salinity evaluated (B_3 was not evaluated for bentonite), and in particular, the order-of-magnitude higher salinity used in K_3 versus K_2 (Table 2-1) yielded considerably different PSDs for particles < 0.008 mm (Fig. 2-12). In general, PSDs completed with dispersion agent exhibit a larger fraction of fine-grained particles compared to PSDs without dispersion agent (Figs. 2-11 and 12). Addition of dispersion agent increases pH of the sedimentation fluid, which aids in neutralizing the charge on positive particle edges. This neutralization reduces attraction between negative particle faces and positive particle edges such that the EF flocculated structures break down.

Clay particles were identified as particles < 2 μm , and percent clay content of all materials is shown as a function of pore fluid EC in Fig. 2-13. The clay content percentages in Fig. 2-13 were determined from PSDs with dispersion agent and material-specific hydrometer correction factors. The decreasing relationship in Fig. 2-13 indicates that the measured clay fraction decreased with increasing salinity. Logarithmic trend lines were fit to data in Fig. 2-13, and suggest that the effect of salinity on flocculation of clay particles will diminish as salinity is continuously increased and at some magnitude of salinity measured clay content will remain approximately constant.

The decreasing logarithmic relationships between clay content and EC are attributed to an increasing flocculated structure in kaolin, bentonite, and soda ash particles as salinity increased. The measured clay fraction of the most dialyzed soda ash tailings was 18 %, whereas a clay content of only 6 % was measured for non-dialyzed tailings. The clay content of non-saline kaolin was 70 % and bentonite was 71 %; whereas, measured clay content of the most saline kaolin specimen reduced to 56 % and most saline bentonite reduced to 42 %. The difference in the percent clay content between saline and non-saline materials increased with increasing plasticity for materials evaluated in this study.

2.5 Conclusions

The effects of salinity on geotechnical behavior and characterization of saline mine tailings, kaolin clay, and bentonite clay were evaluated in this study. Laboratory test methods were developed for characterizing saline materials and to correct potential errors arising from salinity in standard soil test methods. The following conclusions were drawn from the study.

- A correction method for specific gravity was developed using a TDS-EC relationship, computing the mass of salt in solution, and neglecting the volumetric contribution of dissolved salt. This correction procedure yielded close comparisons between specific gravity measured on low-salinity materials and specific gravity corrected for high-salinity materials.
- A material-specific hydrometer correction factor can be measured on filtered hydrometer sedimentation fluid following testing of saline soils. Higher salinity corresponded to higher correction factors due to increased fluid density.
- Measured clay content of all materials decreased with increasing salinity due to particle flocculation. Kaolin and bentonite clay content decreased by 14 and 29 %, respectively, with an increase in salinity. The measured clay content of the most dialyzed soda ash tailings increased by 12% relative to non-dialyzed (i.e., saline) tailings.
- Plasticity properties (LL and PL) of all materials decreased with increasing salinity. The decrease in plasticity was more pronounced in bentonite clay, which agreed with a compilation from literature. Liquid limit in kaolin clay decreased by 13 % whereas LL of bentonite clay decreased by 345 %.
- Atterberg limits of soda ash tailings and saline-bentonite clay decreased consistently during the first two days of soil hydration as more salts dissolved and suppressed

plasticity behavior of the materials. The hydration experiments suggest that at least a 48-h hydration time is needed to allow salts to dissolve in the pore fluid.

Table 2.1. Summary of chemical properties and specific gravity of the dialyzed and non-dialyzed soda ash tailings and saline and non-saline kaolin and bentonite.

Sample Name	Material	Salt	No. of Dialysis Cycles	Measured G_s	Corrected G_s
T _N	Soda Ash	Natural salt	0	2.78	2.55
T ₁	Soda Ash	Natural salt	27	2.56	2.55
T ₂	Soda Ash	Natural salt	21	2.57	2.55
T ₃	Soda Ash	Natural salt	10	2.67	2.58
T ₄	Soda Ash	Natural salt	4	2.72	2.60
T ₅	Soda Ash	Natural salt	1	2.75	2.55
K _N	Kaolin	NaCl	NA	2.61	NA
K ₁	Kaolin	NaCl	NA	2.61	2.61
K ₂	Kaolin	NaCl	NA	2.66	2.65
K ₃	Kaolin	NaCl	NA	2.81	2.57
B _N	Bentonite	NaCl	NA	2.75	NA
B ₁	Bentonite	NaCl	NA	NM	NM
B ₂	Bentonite	NaCl	NA	NM	NM
B ₃	Bentonite	NaCl	NA	NM	NM

Note: EC_{1:5} = electrical conductivity relevant to 1 part dry soil to 5 part DI water mixture (mass basis); G_s = specific gravity; NM = not measured, NA = not applicable.

Table 2.2. Mineralogical composition of natural soda ash tailings and kaolin and bentonite clays based on x-ray diffraction.

Mineral	Soda Ash (%)	Kaolin (%)	Bentonite (%)
Montmorillonite	---	---	87
Kaolinite	---	95	---
Plagioclase Feldspar	---	---	2
Chlorite	---	2	---
Dolomite	46	---	---
Shortite	26	---	---
Quartz	11	1	8
Potassium-Feldspar	8	---	---
Clay/Mica	7	---	---
Calcite	2	---	---

Table 2.3. Chemical constituents of non-dialyzed and dialyzed soda ash with seven dialysis cycles based on x-ray fluorescence.

Mineral	Natural Soda Ash Tailings (%)	Dialyzed Soda Ash Tailings (%)
SiO ₂	21.2	26.83
CaO	15.47	18.37
Na ₂ O	11.12	3.18
MgO	6.63	8.02
Al ₂ O ₃	3.9	4.8
K ₂ O	2.18	2.63
Fe ₂ O ₃	1.01	1.16
SO ₃	0.68	0.67
P ₂ O ₅	0.43	0.38
SrO	0.11	0.14
Cl	0.06	0.01
MnO	0.03	0.05
Nb ₂ O ₅	0.01	-

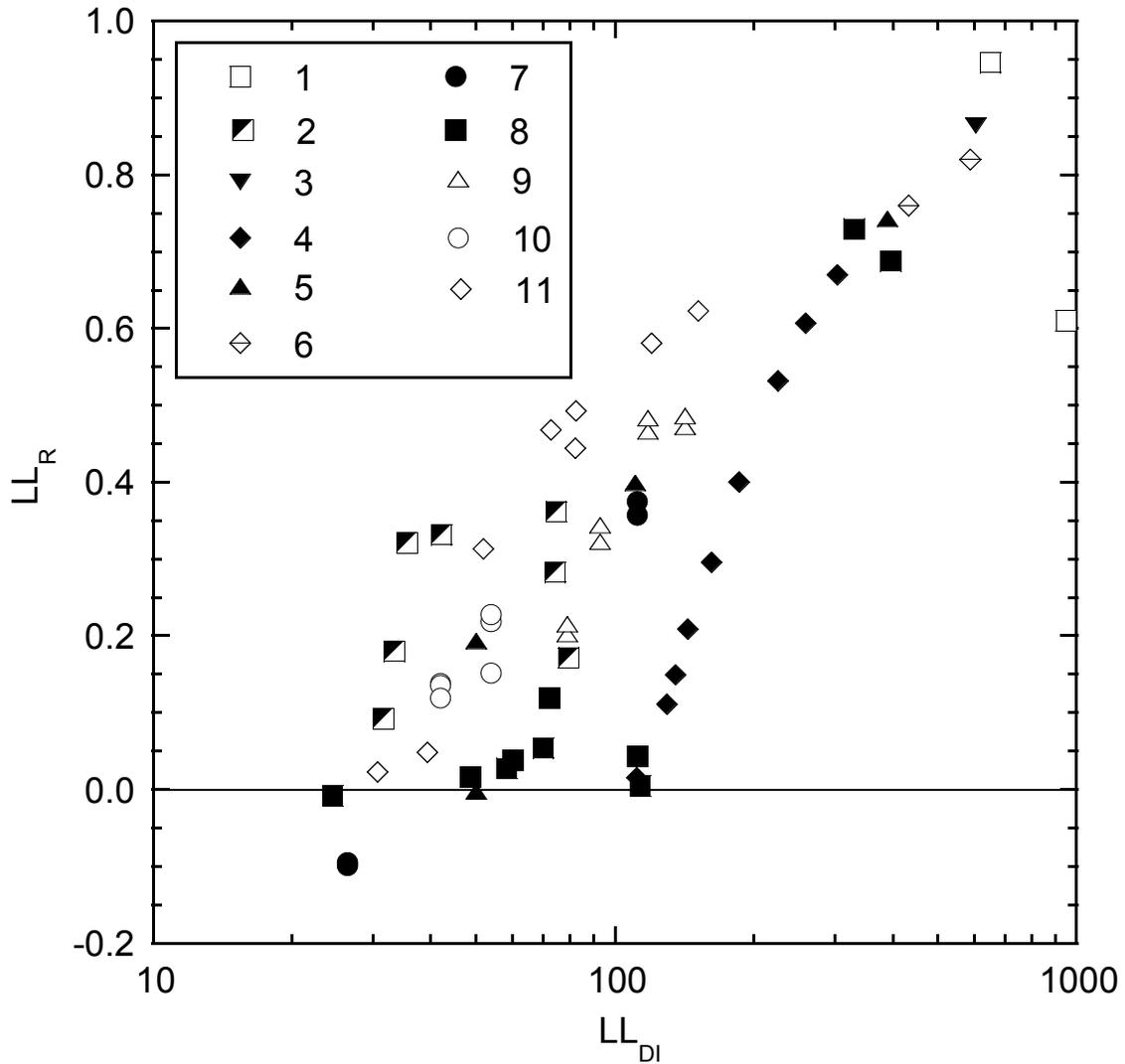


Fig. 2.1. Relationship of the normalized difference between liquid limit measured with deionized water (LL_{DI}) and liquid limit measured in the presence of saline pore fluid (LL_{Saline}) versus LL_{DI} ; $LL_R = (LL_{DI} - LL_{Saline})/LL_{DI}$. References: 1 - Warkentin and Yong (1960), 2 - Barbour and Yang (1993), 3 - Gleason et al. (1997), 4 - Sivapuliah and Savitha (1999), 5 - Di maio et al. (2004), 6 - Lee et al. (2005), 7 - Arasan and Yetimoglu (2008), 8 - Yukselen-aksoy et al. (2008), 9 - Mishra et al. (2009), 10 - Shariatmadari et al. (2011), and 11 - Spagnoli and Sridharan (2012).

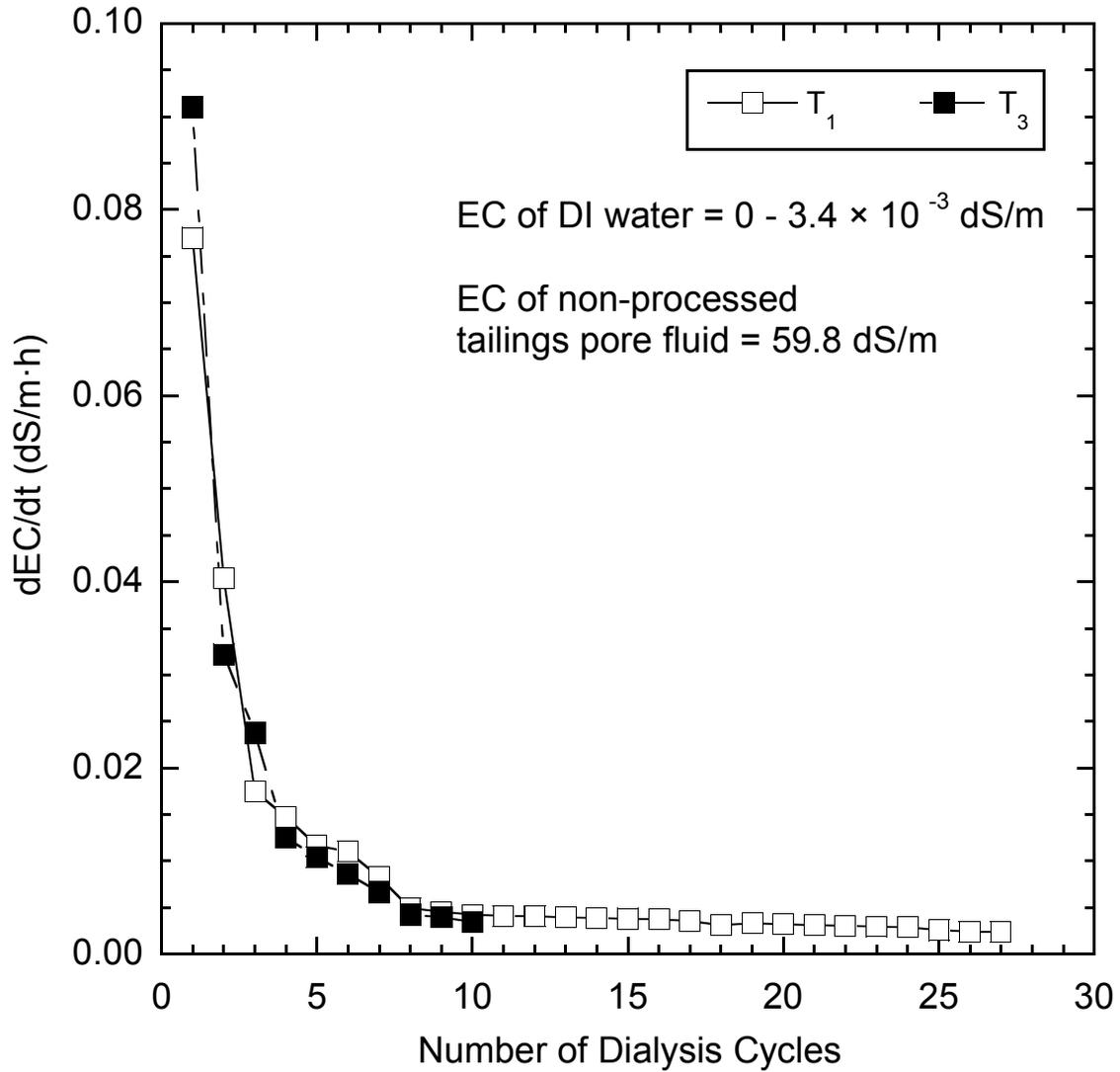


Fig. 2.2. Rate of change in electrical conductivity (EC) of water in the dialysis reservoir during preparation of soda ash tailings specimen T₁ and T₃. Higher subscript number coincides with higher salinity (Table 2-1).

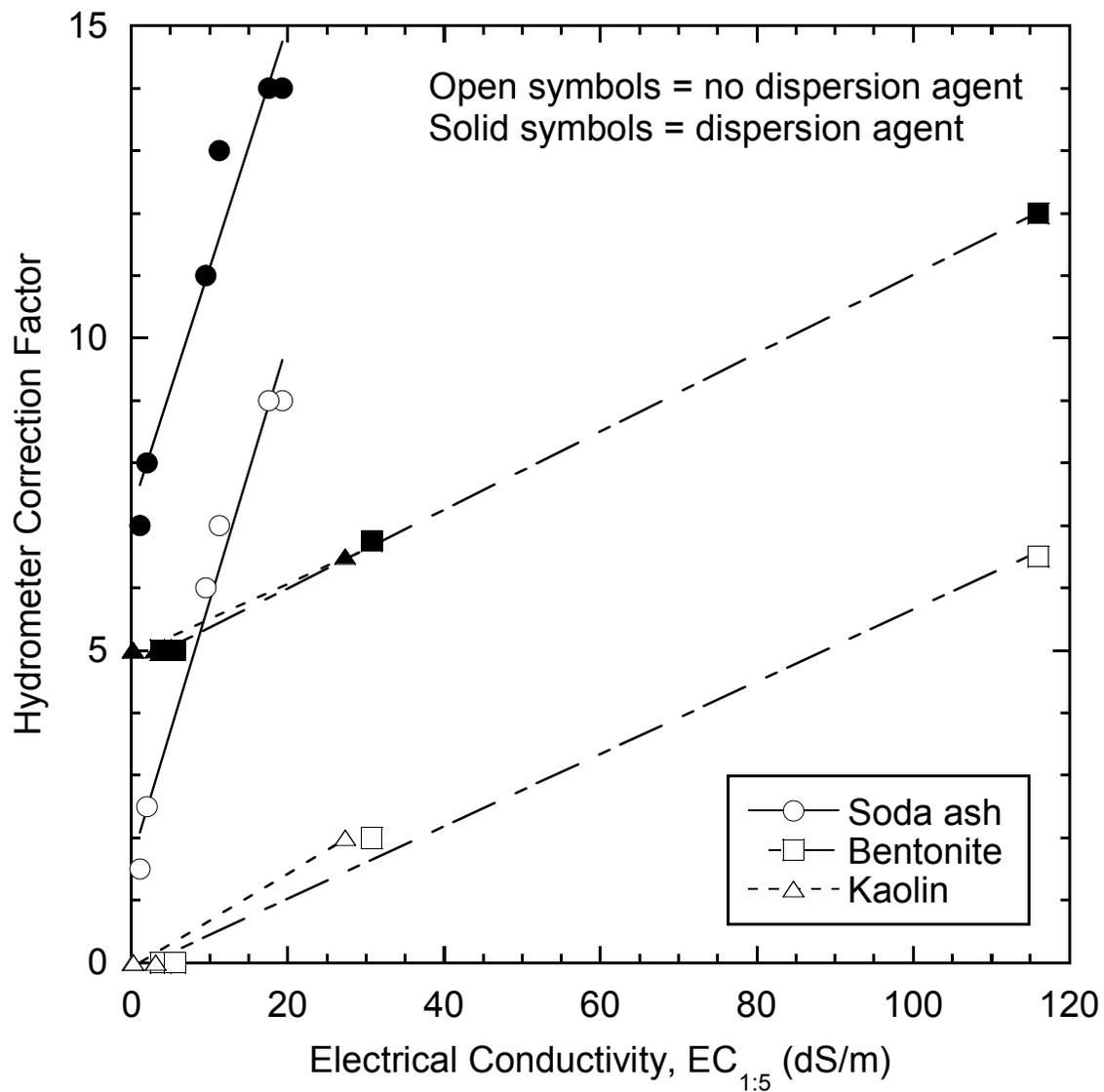


Fig. 2.3. Hydrometer correction factor measured on the sedimentation fluid following experiments conducted with and without dispersion agent (sodium hexametaphosphate) versus electrical conductivity of the soil specimens. Note: coefficients of determination (R^2) are ≥ 0.94 for all linear regression lines.

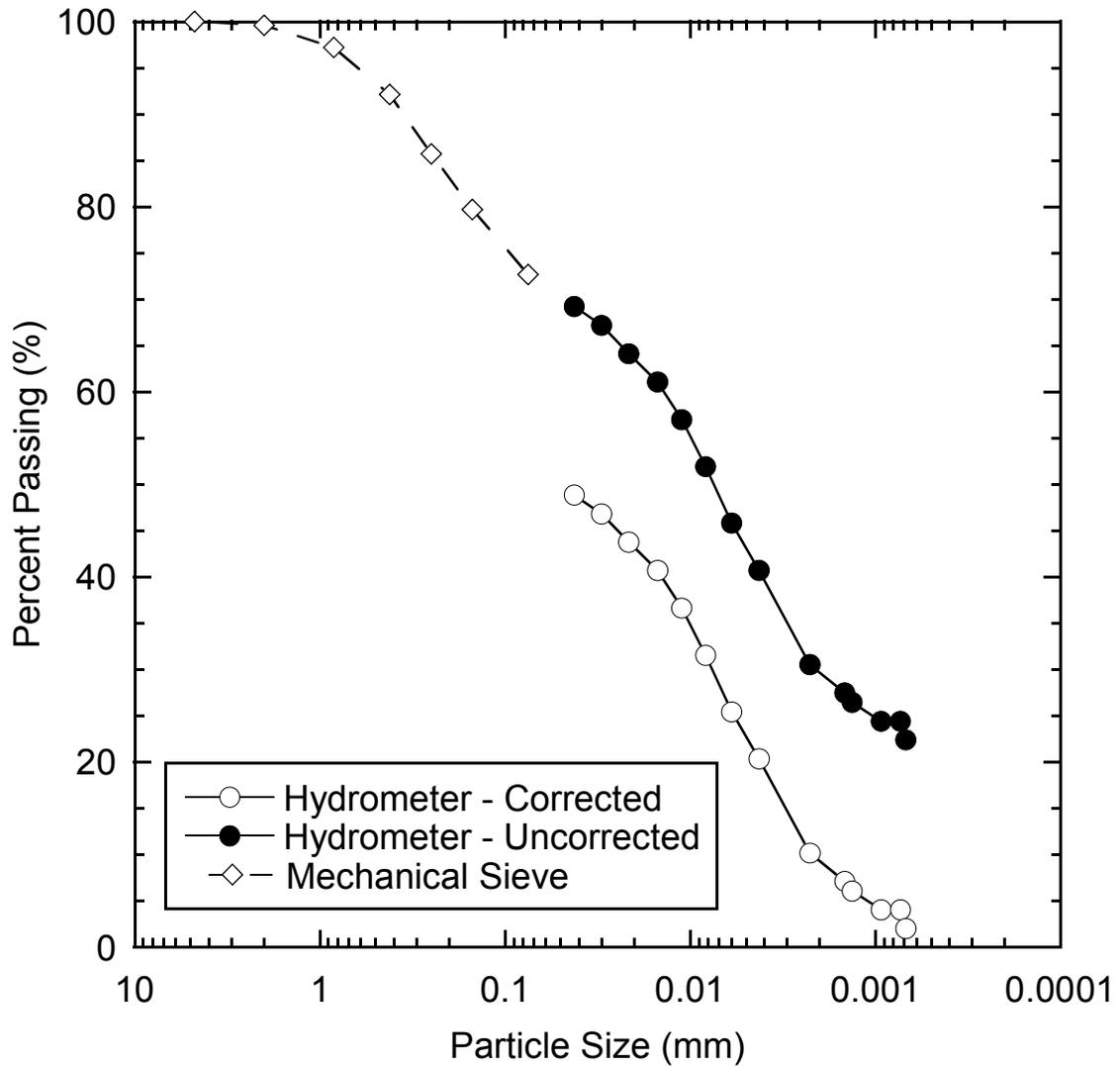


Fig. 2.4. Corrected and uncorrected hydrometer particle-size distribution curves for soda ash tailings specimen T₄ measured with dispersion agent. Mechanical sieve data are for a single coarse-grained soda ash tailings specimen.

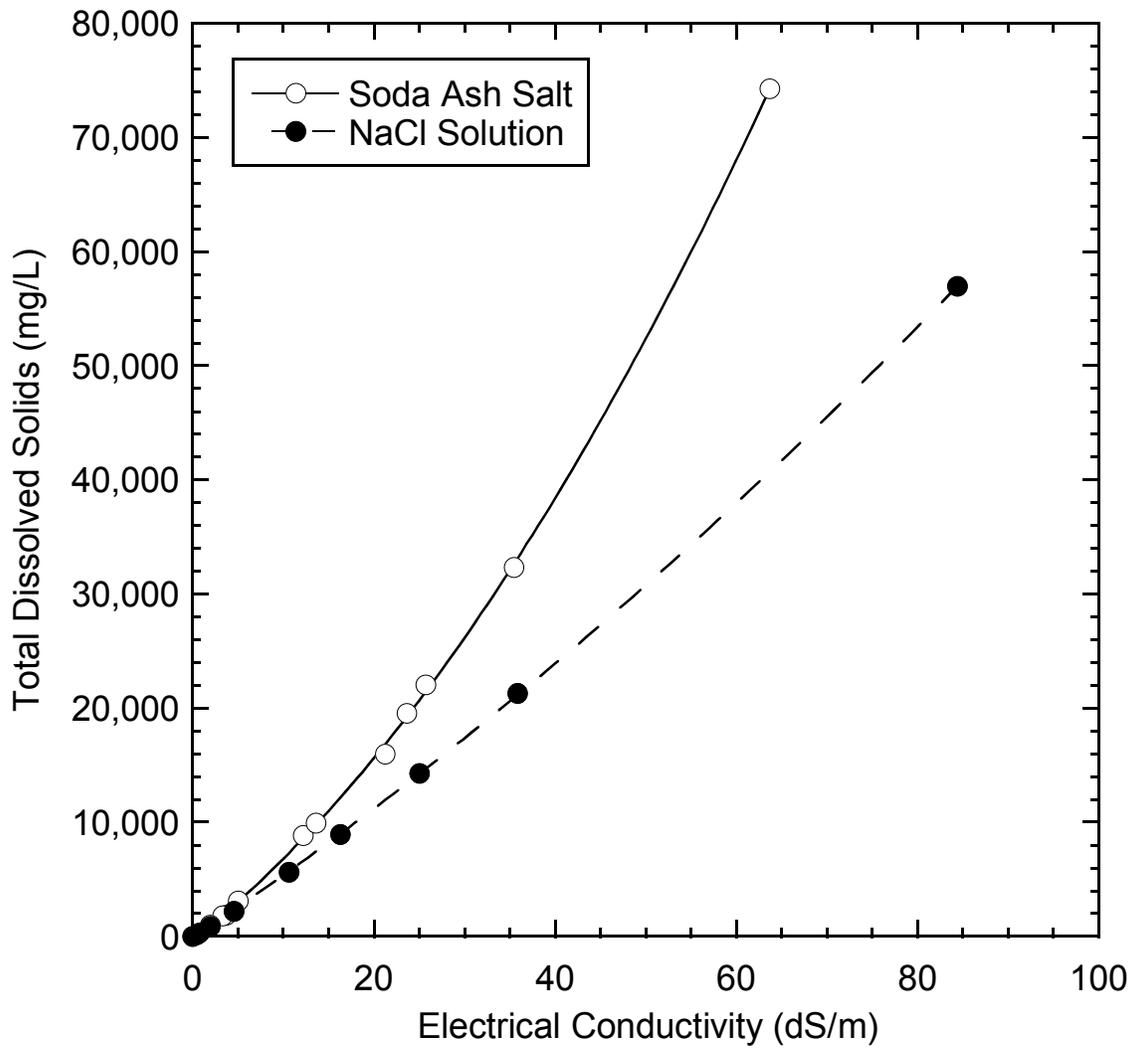


Fig. 2.5. Relationships between total dissolved solids and electrical conductivity for natural soda ash tailings salts and sodium chloride (NaCl).

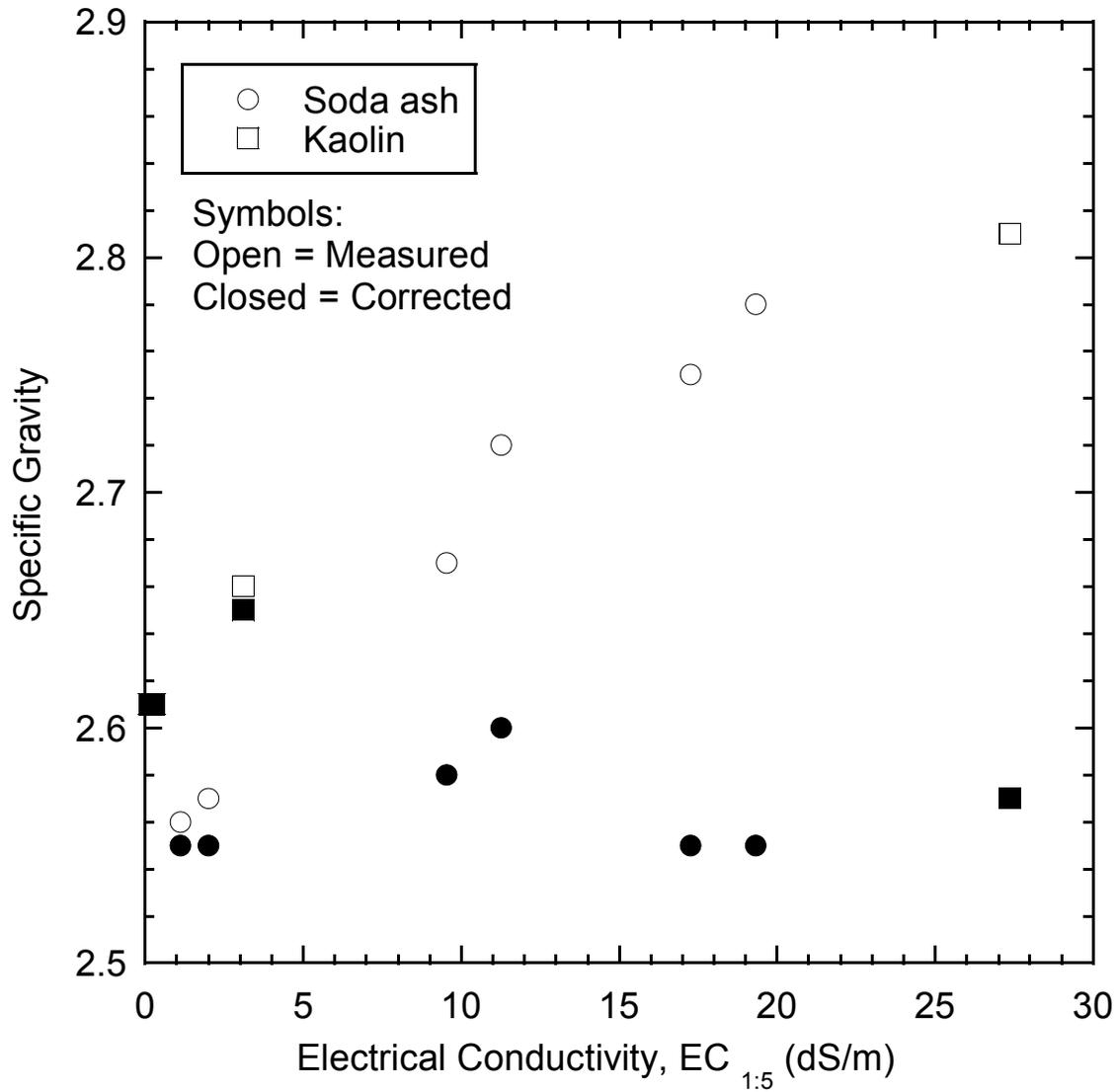


Fig. 2.6. Measured and corrected specific gravity of saline and non-saline kaolin clay and soda ash mine tailings as a function of electrical conductivity measured using the 1:5 soil-to-water mixture method ($EC_{1:5}$).

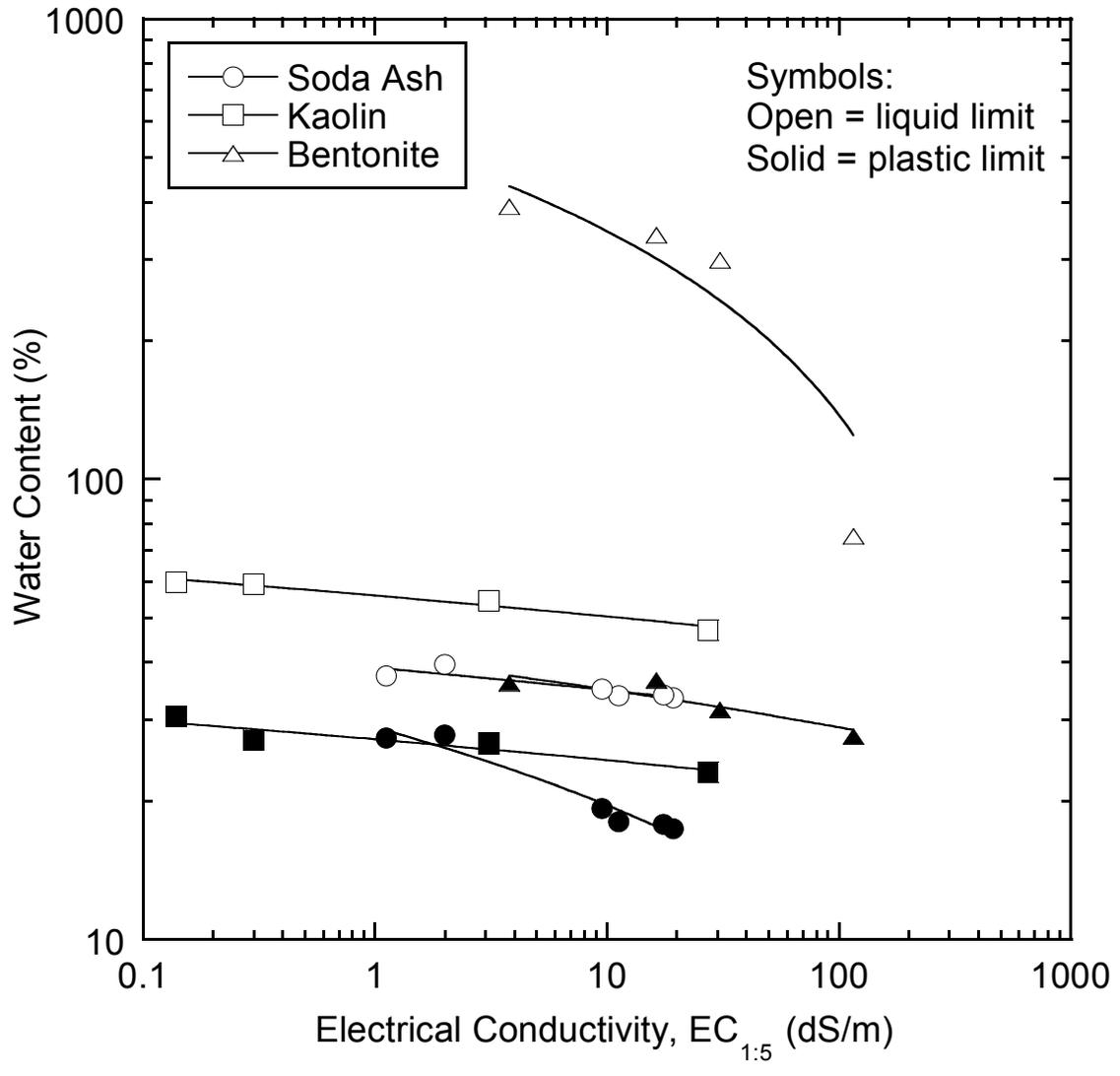


Fig. 2.7. Relationships of liquid limit and plastic limit versus electrical conductivity (EC) measured using the 1:5 soil-to-water mixture method.

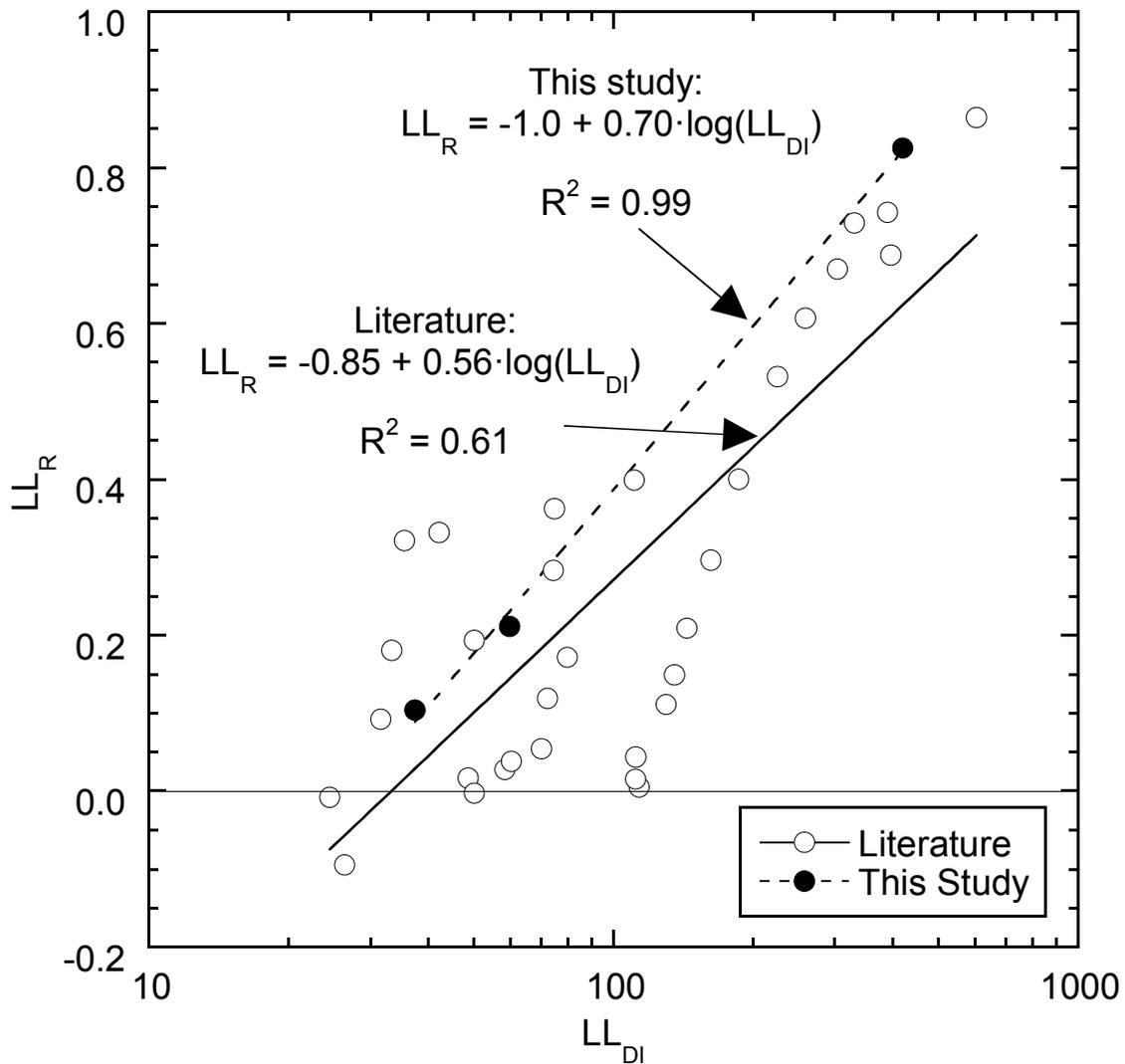


Fig. 2.8. Comparison of the normalized difference between liquid limit measured with deionized water (LL_{DI}) and liquid limit measured in the presence of saline pore fluid (LL_{Saline}) versus LL_{DI} for experiments conducted in this study and compiled from literature; $LL_R = (LL_{DI} - LL_{Saline})/LL_{DI}$. Literature data via Warkentin and Yong (1960), Barbour and Yang (1993), Gleason et al. (1997), Sivapuliah and Savitha (1999), Di maio et al. (2004), Lee et al. (2005), Arasan and Yetimoglu (2008), Yukselen-aksoy et al. (2008), Mishra et al. (2009), Shariatmadari et al. (2011), and Spagnoli and Sridharan (2012).

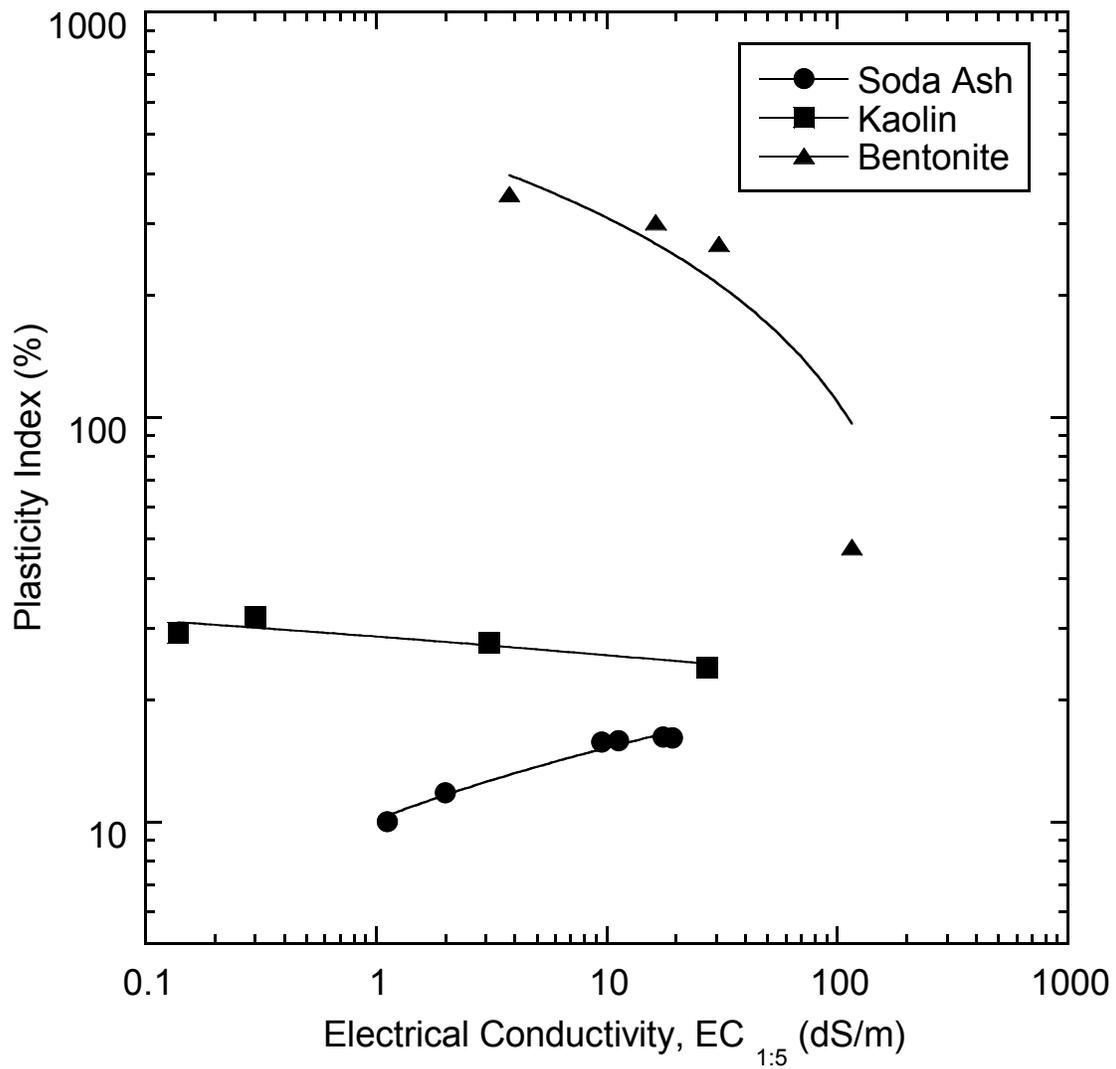


Fig. 2.9. Plasticity index as a function of electrical conductivity (EC) measured using the 1:5 soil-to-water mixture method.

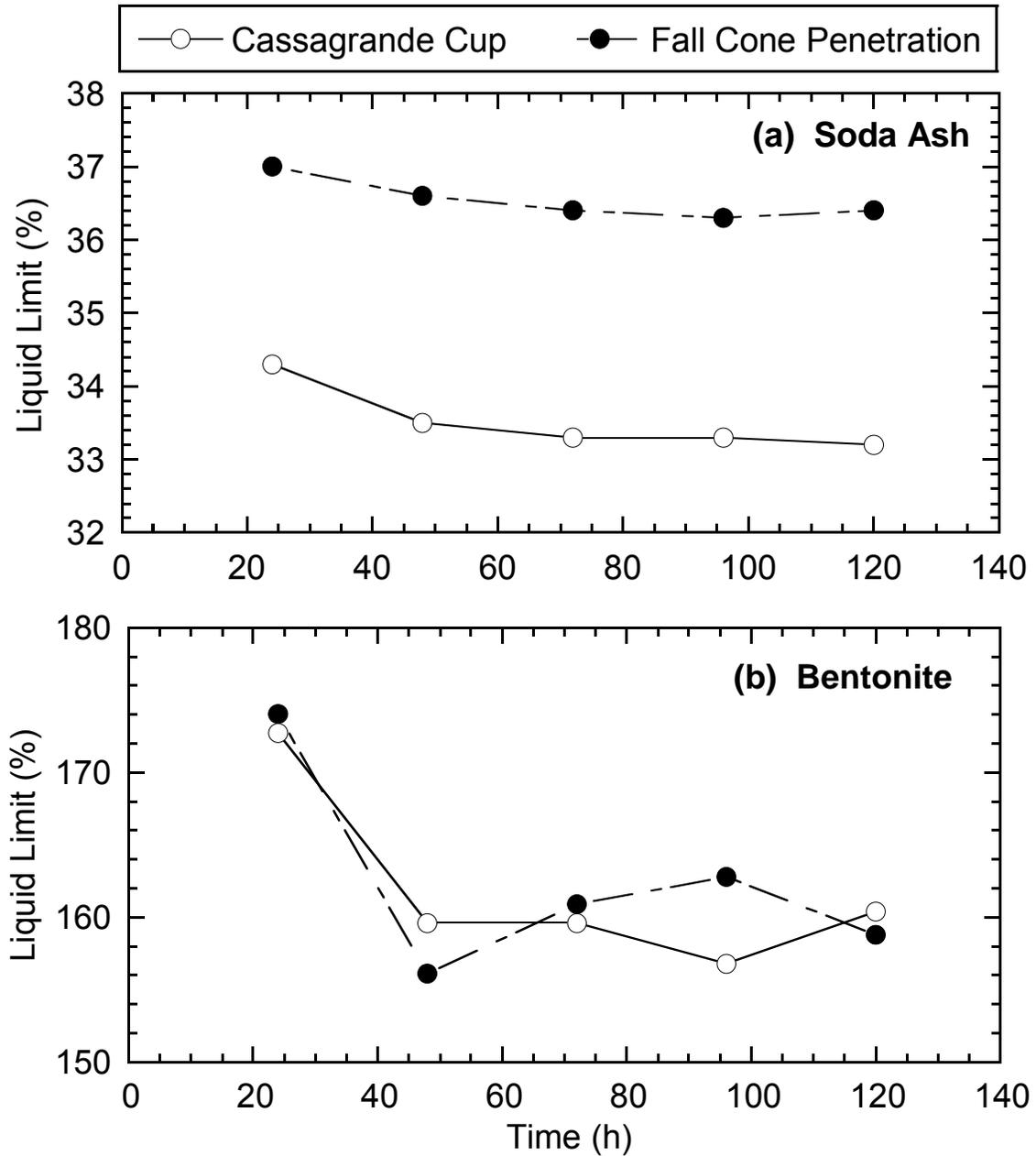


Fig. 2.10. Temporal trends of liquid limit measured with via Casagrande cup and fall cone penetration for (a) non-dialyzed soda ash tailings and (b) saline bentonite.

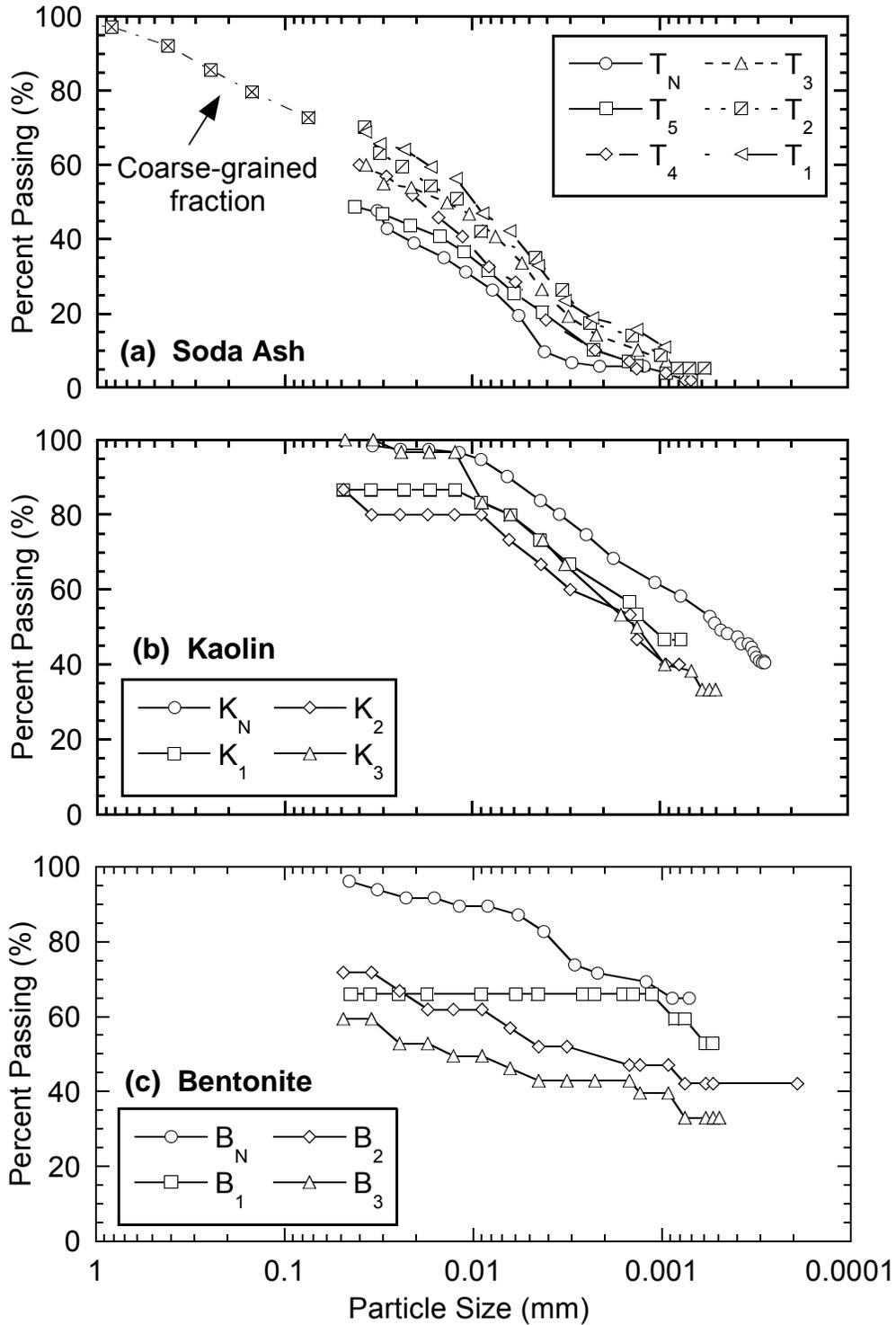


Fig. 2.11. Particle-size distribution curves from hydrometer tests conducted in the presence of dispersion agent on (a) soda ash, (b) kaolin, and (c) bentonite saline and non-saline specimens. Subscript notation for specimens: N = natural soil and higher subscript numbers coincide with higher salinity (Table 2-1).

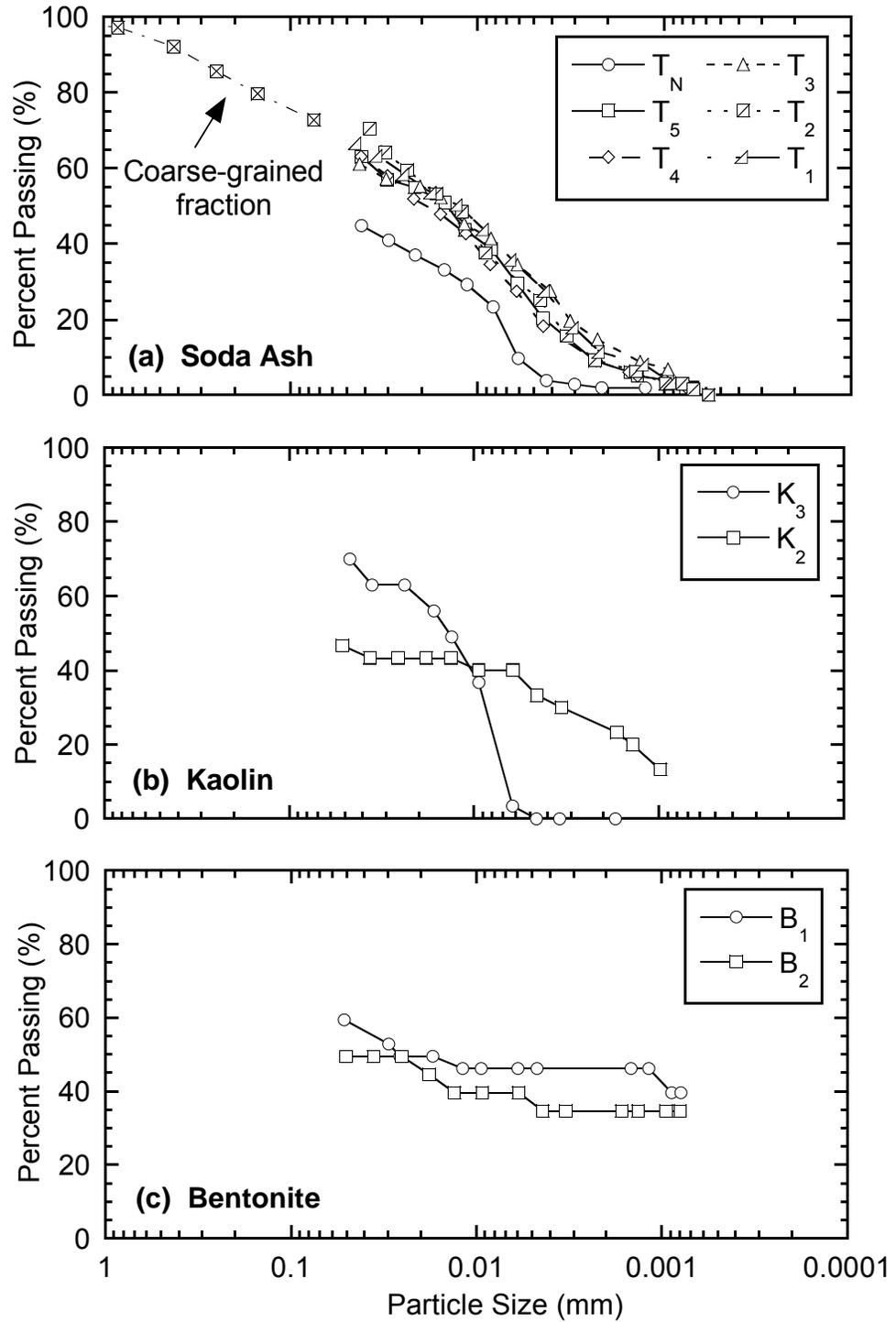


Fig. 2.12. Particle-size distributions from hydrometer tests conducted in the absence of dispersion agent on (a) soda ash, (b) kaolin, and (c) bentonite saline and non-saline specimens. Subscript notation for specimens: N = natural soils and higher subscript numbers coincide with higher salinity (Table 2-1).

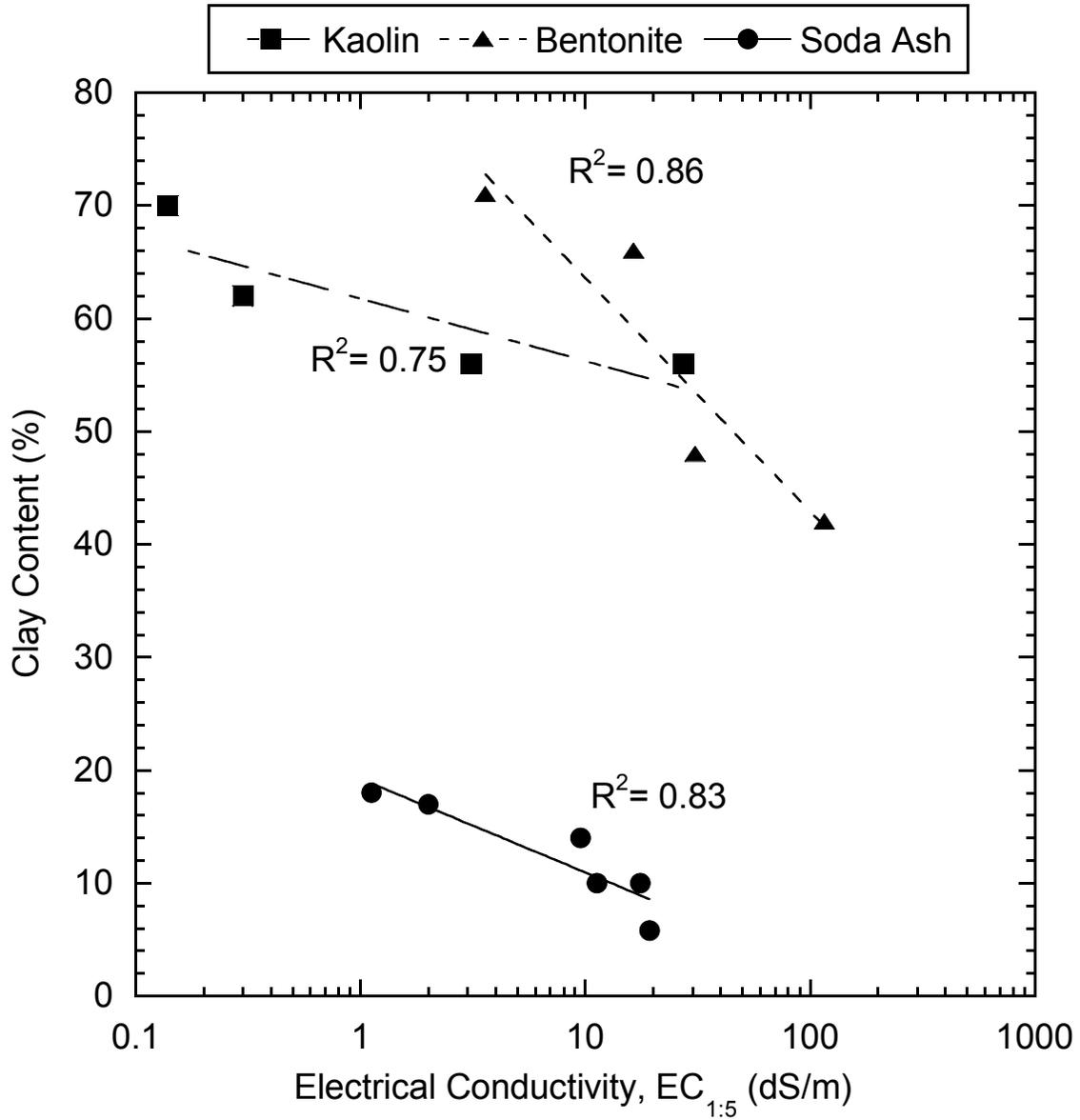


Fig. 2.13. Relationship between clay content and electrical conductivity for kaolin, bentonite, and soda ash mine tailings. Clay contents (i.e., percentage of particles < 0.002 mm) are from hydrometer data generated in the presence of a dispersion agent and using a material-specific hydrometer correction factor.

CHAPTER 3: SALINITY EFFECTS ON SEDIMENTATION BEHAVIOR OF FINE-GRAINED SOILS AND MINE TAILINGS

3.1 Introduction

Mine tailings are residuum from ore extraction processing that contain fine-grained particles of pulverized rock, process water, and uneconomical or unrecoverable ore contents (Blight et al. 2010). Mine tailings generally have high water contents and can be transported through a pipeline for disposal and management in a tailings storage facility (TSF). Long-term colloidal stability of mine tailings (i.e., particle dispersion in solution) is problematic in TSFs due to low shear strength of tailings, limited consolidation and strength gain with time, and difficulty in reclaiming water for subsequent ore processing (Bussière 2007; Blight 2010). The presence of soluble salts in mine tailings can destabilize the colloidal state, which enhances sedimentation and consolidation that promotes strength gain and improves water recovery (van Olphen 1963; Kotylar et al. 1996; Williams et al. 2013).

Sedimentation is the tendency of soil particles to settle out of suspension and is a function of particle-size, shape, and density, and fluid density and viscosity (van Olphen 1963). Particle self-weight is the primary force that controls the behavior of coarse particles in suspension, whereas interparticle forces dominate settling behavior of fine-grained particles in suspension due to low particle weight and high specific surface area (Palomino and Santamarina 2005). Interparticle forces are controlled by specific surface area and charge density of individual particles as well as sedimentation fluid chemistry, which combine to affect the diffuse double layer (DDL) of clay particles and sedimentation fluid density and viscosity.

The effect of soluble salt concentration (i.e., salinity) on the sedimentation behavior of mine tailings primarily has been investigated with respect to mature fine tailings from oil sands. Mature fine tailings contain approximately 30-40 % solids content and the presence of particles $< 0.5 \mu\text{m}$ represents a challenging sedimentation problem for the mining community. Kotylar et

al. (1996) evaluated the effect of NaCl concentration on aggregation of nano-sized particles (20-300 nm) of oil sand tailings in suspension and reported that particle aggregation increased in the presence of salt solution. Sworska et al. (2000) reported that the initial settling rate of oil sand tailings increased with an increase in pH and/or presence of divalent cations (Ca^{2+} and Mg^{2+}). Additionally, they found that the quality of supernatant (i.e., released water during sedimentation) was higher in lower pH solutions or in the presence of divalent cations (Ca^{2+} and Mg^{2+}).

Mine tailings commonly contain clay minerals; for example, oil sand tailings are comprised of 50 to 60 % kaolinite (Sworska et al. 2000; Beier et al. 2013). Montmorillonite minerals are less common in mine tailings; however, the presence of a small amount of montmorillonite can create challenges to mine tailings management due to high charge density and small particle size that results in a tendency to stay dispersed in suspension. The limited extent of sedimentation studies completed on mine tailings, combined with the presence of clay minerals in mine tailings that create sedimentation challenges in TSFs suggests that sedimentation behavior of clay minerals can be coupled with mine tailings to assess the effects of pore fluid salinity and clay mineralogy on tailings sedimentation behavior.

Palomino and Santamarina (2005) presented a fabric map for kaolinite as a function of salinity and solution pH to describe factors influencing particle flocculation and sedimentation behavior. Sedimentation behavior in low salt concentrations (< 100 mM) primarily is affected by pH of the solution. As salt concentrations increase above 100 mM, kaolinite sedimentation behavior becomes independent of pH. Overall, Palomino and Santamarina (2005) observed increased released water and higher initial particle settling velocity in acidic solutions as compared to basic solutions.

Chen and Anandarajah (1998) investigated kaolinite sedimentation in the presence of different salts (monovalent, divalent, and trivalent cations) and concentrations (1 to 1000 mM). They reported that the final sedimented soil volume decreased with an increase in salt

concentration and/or cation valence; however, the initial sedimentation rate of kaolinite decreased in high NaCl concentration (> 100 mM) as compared to lower NaCl concentration (< 100 mM). Williams et al. (2013) investigated the effect of commercially-available salts [NaCl, CaCl₂, MgCl₂, KCl, CaSO₄, Al₂(SO₄)₃] on sedimentation behavior of four sodium bentonites, one calcium bentonite, and one kaolinite. In general, the presence of salt in solution increased clay particle sedimentation relative to a zero concentration condition. The effect of salinity on particle sedimentation was more pronounced in bentonite compared to kaolinite, and aluminum sulfate (Al₂(SO₄)₃) was most effective in enhancing bentonite sedimentation. These effects of salinity on bentonite are in agreement with an investigation by Akhter et al. (2008).

Gumaste et al. (2014) investigated the effects of NaCl and SrCl₂ on sedimentation behavior of a white clay (70% kaolinite), bentonite clay (90% montmorillonite), and natural marine clay (liquid limit = 79 %). They reported that total released water from a bentonite suspension increased by a factor of 87 when ionic strength of the sedimentation fluid increased from 0.1 to 250 mM. In contrast, final released water volume in the white clay and natural marine clay decreased by approximately 10 % for a comparable increase in ionic strength. Results from Williams et al. (2013) and Gumaste et al. (2014) suggest that sedimentation behavior of low-plasticity (e.g., kaolinite) and high-plasticity (e.g., bentonite) clays differ and that there may exist a threshold salt concentration for kaolinite slurries whereupon subsequent increases in salinity do not yield a positive effect on sedimentation.

Past studies have demonstrated the effect of salinity on sedimentation of mine tailings and clay minerals separately, and a combined evaluation of salinity effects on sedimentation behavior of natural clays and mine tailings with a coupled assessment of the role of tailings mineralogy has not been conducted. The objective of this study was to assess the effect of salinity on sedimentation behavior of fine-grained soil and mine tailings. Materials evaluated in this study included kaolin clay, bentonite clay, and soda ash mine tailings. Sedimentation experiments were conducted on all three materials in different ionic strength solutions to

evaluate sedimentation behavior (e.g., initial sedimentation rate and final solids content). Understanding the sedimentation behavior of mine tailings is important for the design, operation, and reclamation of TSFs.

3.2 Background

A colloid consists of small diameter solid materials (0.001 to 1.0 μm) that are homogeneously dispersed throughout a fluid (van Olphen 1963). Colloidal stability refers to the ability of dispersed materials to remain in suspension, which depends on interparticle interactions that are a function of particle and fluid characteristics (van Olphen 1963). Generally, clay particles have negatively-charged particle faces and positively-charged particle edges. Total interaction potential consists of attractive van der Waals forces and repulsive forces due to the DDL. Electrons orbiting the nucleus of an atom create a fluctuating dipole that generates van der Waals forces (F_A) (Anandarajah and Chen 1997), which can be computed via Eq. 3-1 (Palomino and Santamarina 2005):

$$F_A = \frac{1}{24} \cdot \frac{A_h}{x^3} \cdot d^2 \quad (3-1)$$

where A_h is the Hamaker constant, x is distance between two particles, and d is particle diameter. van der Waals forces are attractive, physical forces between soil particles (van Olphen 1963). The Hamaker constant is independent of pore fluid salinity, and thus, van der Waals forces are not directly influenced by changes in ionic strength of sedimentation fluid.

The repulsive force between clay particles (F_R) is due to the DDL and can be computed as,

$$F_R = 16 \cdot \pi \cdot R \cdot T \cdot C \cdot d^2 \cdot e^{\frac{-X}{9}} \quad (3-2)$$

where R is the universal gas constant (8.314 J/mole·K), T is temperature (K), and C is ionic concentration (Palomino and Santamaria 2005). Thus, F_R is a function of pore fluid salinity

whereby an increase in ionic concentration results in a decrease in F_R . Considering that F_A is not directly influenced by changes in salinity, a decrease in F_R corresponds to an increase in F_A , which promotes particle flocculation.

There are two main types of sedimentation behavior: (i) dispersed and (ii) flocculated. Dispersed sedimentation is characterized by slow particle sedimentation, lack of a defined mud line (i.e., the interface between suspended soil particles and clear supernatant), and low supernatant quality. Flocculated sedimentation is characterized by increased sedimentation rates, a defined mud line, and high supernatant quality (Palomino and Santamarina 2005). The separation of positive and negative charges on clay particles can lead to three main types of flocculation: (i) face-to-face (FF), (ii) edge-to-face (EF), and (iii) edge-to-edge (EE). Face-to-face flocculation usually occurs in low pH solution where an excess of H^+ ions neutralize particle faces to yield a decrease in repulsion between similarly charged particles. Edge-to-face flocculation occurs via Coulombic attraction between positively-charged particle edges and negatively-charged particle faces. Edge-to-edge flocculation occurs when van der Waals forces between edges are high and interfacial interactions are repulsive (van Olphen 1963; Palomino and Santamarina 2005).

3.3 Materials and Method

3.3.1 Materials

Three materials were used in this study: (i) kaolin clay, (ii) bentonite clay, and (iii) soda ash mine tailings. Kaolin clay and bentonite clay were used to represent a range of anticipated sedimentation behavior of mine tailings and to compare with previous sedimentation studies conducted on similar materials. Kaolin clay primarily contained kaolinite minerals and was obtained from Thiele Kaolin Company (Georgia, USA). Bentonite clay primarily contained sodium montmorillonite minerals and was a naturally-occurring material obtained from Wyoming, USA. Both kaolin and bentonite clay were obtained as homogenized powders and

used as laboratory-controlled materials. Soda ash mine tailings was generated at a sodium carbonate mine in Wyoming, USA. Process water of the soda ash mine tailings was approximately two to three times the salinity of ocean water (ocean water salinity $\approx 35 \text{ g}\cdot\text{L}^{-1}$).

The soluble salt concentration of soda ash mine tailings was altered using dialysis since the natural tailings pore fluid contained high salinity. A sample of tailings at the as-produced water content (128 %) was placed in a semi-permeable molecular-membrane and sealed at both ends. The membrane was filled with mine tailings, placed in a 7-L deionized (DI) water container, and stirred continuously. The semi-permeable membrane allowed soluble salts to pass out of the tailings pore fluid and into the DI water container via diffusion. The DI water was changed daily to maintain a high concentration gradient between the tailings pore fluid and reservoir fluid.

Electrical conductivity (EC) of soda ash mine tailings was measured following the 1:5 method (1 part dry soil + 5 parts DI water, by mass) described in Page et al. (1983). Three soda ash mine tailings were evaluated in this study that included different pore fluid salinity: T_N = no dialysis with $EC_{1:5} = 19.3 \text{ dS/m}$; T_A = three dialysis cycles with $EC_{1:5} = 16.5 \text{ dS/m}$; and T_B = seven dialysis cycles with $EC_{1:5} = 10.2 \text{ dS/m}$. pH of the soda ash pore fluid was basic (9.50-11.00) and sedimentation behavior was dispersed in initial sedimentation tests, which has also been observed by Palomino and Santamarina (2005). Thus, solution pH was reduced to a neutral range (6.75 - 7.00) via addition of hydrochloric acid (HCl) to all soda ash sedimentation tests. This pH adjustment was necessary to change sedimentation behavior of soda ash mine tailings from dispersed to flocculated, which was the main focus of this study. pH and EC were measured using a pH probe (Ross Ultra Triode, Thermo Scientific Orion, Waltham, MA) and EC probe (DuraProbe Conductivity Cell, Thermo Scientific Orion, Waltham, MA) connected to a Thermo Scientific Orion Versa Star multi-function meter (Waltham, MA).

3.3.2 Sedimentation Tests

Sedimentation tests were performed in 1-L glass cylinders commonly used for hydrometer testing (ASTM D422). The cylinders were 63.5-mm in diameter by 457-mm tall and filled to a height corresponding to 1 L. Three salts with different cation charges were used to evaluate the effect of cation valence on sedimentation behavior of kaolin and bentonite clay: (i) sodium chloride (NaCl), (ii) calcium chloride (CaCl_2), and (iii) ferric chloride (FeCl_3). A constant anion (i.e., chlorine) was used in all tests to reduce the number of variables between sedimentation experiments. Salts were added to deionized (DI) water to create solutions with salt concentration ranging from 1 to 1000 mM for sedimentation tests conducted on kaolin and salt concentration ranging from 10 to 1000 mM for sedimentation tests on bentonite clay.

A summary of sedimentation tests conducted as part of this study is in Table 3-1. A total of 13 sedimentation tests were conducted on kaolin, ten on bentonite, and three on soda ash mine tailings. These tests were conducted to evaluate the effects of salt concentration, cation valence, and clay mineralogy on sedimentation behavior. Tests on kaolin at a concentration of 1 mM were conducted to evaluate sedimentation behavior at low salt concentrations. Sedimentation tests with 34-mM CaCl_2 and 17-mM FeCl_3 were conducted to evaluate the effect of cation valence in comparable ionic strength solutions ($I = 100 \text{ mM}$) to the 100 mM NaCl solution.

Kaolin clay suspensions were prepared with 50 g of dry soil dispersed in 1 L of solution (5 % by weight mixture), which is similar to recommendations for hydrometer testing (ASTM D 422). Bentonite clay suspensions were prepared with 25 g of dry soil dispersed in 1 L of solution (2.5 % by weight). The solid mass for bentonite sedimentation tests was reduced due to the high water affinity of bentonite. Soda ash mine tailings suspensions were prepared with 75 g of dry soil dispersed in 1 L of solution (8 % by weight). The additional mass used for soda ash mine tailings experiments was to increase the mass of clay particles in solution as only 18 % of soda ash tailings was clay-sized particles.

All sedimentation tests initially were prepared via mechanically blending the solid fraction with 300 mL of solution. Mixtures subsequently were poured in sedimentation cylinders and solution was added to reach 1 L. The sedimentation cylinder was sealed with a rubber stopper and agitated vigorously for 1 min. The cylinder was then placed on a laboratory table and elapsed time was referenced as time since placement. The interface between the settling suspension and supernatant liquid is referred to herein as the mud line. Mud-line height above the base of the sedimentation cylinder was recorded at 1 min and continued on a logarithmic scale for 24 hr; after 24 hr, daily mud-line heights were measured. Measurements were recorded until no change was observed for three sequential readings. Typical testing durations were 2 d for soda ash, 3 d for kaolin, and 10 d for bentonite, which included the period of three sequential readings of constant mud-line height.

The effect of sidewall friction on sedimentation of kaolinite was investigated by Michaels and Bolger (1962), who derived the following equation for the effect of cylinder diameter on particle sedimentation:

$$D_v = \frac{4 \cdot \tau_v}{g \cdot (\rho_s - \rho_l) \cdot \phi_k} \quad (3-3)$$

where D_v is yield diameter at which there is no particle sedimentation out of suspension, τ_v is yield stress, g is the gravitational constant, ρ_l is fluid density, ρ_s is soil solid particle density, and ϕ_k is volumetric fraction of the soil. The ratio of D_v to diameter of a TSF would be near zero due to the size of TSFs (e.g., Blight 2010). Thus, the presumptive error between sedimentation in a cylinder and sedimentation in a TSF can be taken as the ratio of D_v to diameter of the cylinder (Michaels and Bolger 1962). The computed error was 6 % for kaolin assuming $\tau_v = 0.3$ Pa. A similar analysis completed for bentonite assuming $\tau_v = 0.42$ Pa yielded an error of 16%.

3.3.3 Solid and Liquid Chemical Analysis

Chemical analyses were performed on the solid and liquid fractions of soda ash tailings, and on the solid fraction of kaolin and bentonite clays. Analysis of the liquid phase of the soda ash tailings was performed to quantify salt type and concentration. Analyses on the solid fraction of all three materials were conducted to evaluate mineralogical composition. An additional assessment was conducted on the solid fraction of soda ash tailings to determine chemical constituents of the dried salts to supplement liquid chemistry.

Cation concentrations in the pore fluid of non-dialyzed soda ash tailings were analyzed using inductively coupled plasma-atomic emission spectrometry (IRIS® Advantage/1000 ICAP Spectrometer, Thermo Jarrel Ash Co., Franklin, MA). Anion concentrations in the pore fluid of non-dialyzed soda ash tailings were analyzed with ion chromatography (Dionex® 4000i IC Module, Dionex Co., Sunnyvale, CA). Concentrations of cations and anions present in the soda ash pore fluid at the natural tailings water content are in Table 3-2. Sodium (Na^+) and phosphate (PO_4^{3-}) were the predominant cation and anion in the soda ash tailings pore fluid, with secondary ions consisting of potassium (K^+) and sulfate (SO_4^{2-}).

X-ray diffraction (XRD) was conducted on natural soda ash tailings (non-dialyzed), kaolin clay, and bentonite clay, and x-ray fluorescence (XRF) was conducted on natural and dialyzed soda ash tailings. X-ray diffraction was used to evaluate minerals present in the materials, whereas XRF was used to assess chemical composition of dialyzed and non-dialyzed soda ash tailings and also to evaluate effectiveness of the dialysis technique. All analyses were completed by Mineralogy-INC (Tulsa, Oklahoma, USA).

X-ray diffraction results for natural soda ash mine tailings, kaolin clay, and bentonite clay are in Table 3-3. Dolomite and shortite were the predominant minerals in soda ash tailings, with secondary minerals consisting of quartz, potassium-feldspar, and phyllosilicates (clay and mica). Kaolin consisted predominantly of kaolinite minerals, whereas bentonite was primarily montmorillonite minerals with 8 % quartz content. Clay minerals were not quantified in soda ash

tailings, but qualitatively identified as illite with mixed layer illite/smectite. Illite has a cation exchange capacity (CEC) ranging between 10 and 40 cmol/kg and specific surface area (SSA) ranging from 65 to 100 m²/g. Kaolinite CEC ranges from 3 to 15 cmol/kg and SSA from 10 to 20 m²/g, whereas CEC of sodium montmorillonite ranges from 80 to 150 cmol/kg and SSA from 50 to 120 m²/g (Mitchell and Soga 2005). Isomorphic substitution in illite occurs in the silica-tetrahedral sheet, whereas isomorphic substitution in montmorillonite occurs in the aluminum-octahedral sheet. The difference in location of isomorphous substitution for illite relative to montmorillonite produces a net-negative charge that is closer in proximity to exchangeable cations, which results in stronger inter-layer bonding and lower CEC compared to montmorillonite.

Chemical composition of non-dialyzed and dialyzed (i.e., specimen T_B) soda ash tailings based on XRF are in Table 3-4. Sodium, which was the predominant cation in the pore fluid (Table 3-3), was 3.5 times larger in non-dialyzed soda ash tailings as compared with the dialyzed specimen. Relative percent contributions of all other major cations (e.g., Mg, Si, and Ca) increased with dialysis of soda ash tailings (Table 3-4). Thus, the decrease in Na in the dialyzed soda ash tailings relative to the non-dialyzed tailings validates that the dialysis technique was effective in reducing pore fluid salinity.

3.4 Results

3.4.1 Sedimentation Tests on Kaolin and Bentonite

Temporal trends of mud line height from sedimentation tests conducted on kaolin and bentonite with different salt concentrations are shown in Fig. 3-1. Dispersed behavior with no sedimentation was observed for both clays mixed in DI water. The addition of salt to the sedimentation solution initiated particle sedimentation in all kaolin and bentonite experiments.

Addition of salt at a low concentration of 1 mM altered interparticle interactions of kaolin from dispersed to flocculated and initiated particle sedimentation (Fig. 3-1). The presence of a

low salt concentration decreases repulsive forces between particles due to a decrease in DDL thickness (Chen and Anandarajah 1998). This decrease in repulsive forces is counteracted by an increase in the relative magnitude of attractive van der Waals forces. The relative change in magnitude between the attractive and repulsive forces initiated particle flocculation and ultimately sedimentation as clay particle flocculants are heavier and settle faster relative to individual clay particles. Chen and Anandarajah (1998) and Palomino and Santamarina (2005) both observed particle flocculation and subsequent sedimentation for kaolin mixed in a 0.1-mM-NaCl solution.

The surface charge on kaolin particles is pH dependent at low salt concentration. Palomino and Santamarina (2005) reported that the flocculated structure of kaolin present at pH = 3.0 to 5.0 for a 0.1-mM-NaCl solution changed to dispersed structure with limited particle sedimentation for an increase in pH to 9.0 in a comparable strength NaCl concentration. In a neutral pH solution, positively-charged particle edges and negatively-charged particle faces lead to EF flocculation. As pH increases, excess OH^- is present in high pH solution that can lead to edge neutralization of clay particles and increase the DDL. These changes combine to decrease Coulombic attractive forces between particle edges and particle surfaces and change suspended particle interaction from flocculated to dispersed.

A salt concentration of 10 mM initiated particle flocculation and sedimentation in all bentonite experiments (Figs. 3-1b, 3-1d, and 3-1f). An increase in salinity from 10 mM to 1000 mM yielded more rapid sedimentation in bentonite for all salts evaluated. The addition of salt suppressed the DDL thickness in bentonite similar to kaolin. However, as a given salt concentration increased in the bentonite experiments, a more pronounced increase in sedimentation was evident with increasing salt concentration. Higher salt concentrations continued to enhance flocculation in bentonite due to an initial larger DDL that decreased in size over a broader range of salinity as compared to kaolin (Mitchell 1976). Similar results have been reported by Shackelford (1994) and Gumaste et al. (2014).

Temporal trends of sedimentation rates for kaolin and bentonite are shown in Fig. 3-2. Sedimentation rates were calculated as the difference in mud-line height between two consecutive readings divided by elapsed time. In general, the sedimentation rate of bentonite was lower than kaolin due to smaller particles and higher particle charge density. Although the rate of sedimentation varied with time, sedimentation predominantly occurred in the first 200 min for kaolin and in the first day for bentonite.

Two parameters of interest were derived from sedimentation data shown in Figs. 3-1 and 3-2 to quantify sedimentation behavior: (1) initial sedimentation rate, which relates to the water release rate, and (2) final solids content, which increases for higher density deposits and larger total volumes of released water. In kaolin with no salt addition, a thin sediment layer began to form at the bottom of the sedimentation cylinder after approximately 2 min, which slowly increased with time as sedimentation continued. In bentonite with no salt addition, a very thin layer of settled particles was observed at the bottom of the sedimentation cylinder after approximately 4 min, and the layer thickness remained nearly constant with time. Thus, initial sedimentation rates were not evaluated for kaolin and bentonite in the absence of soluble salts (Table 3-1).

3.4.1.1 Initial Sedimentation Rate

The initial sedimentation rate was computed via a graphical procedure described in Palomino and Santamarina (2005). Examples of this graphical procedure for kaolin and bentonite clay in 100 mM-CaCl₂ solution are shown in Fig. 3-3. In this approach, mud-line height plots (e.g., Fig. 3-1) were reproduced with elapsed time on an arithmetic axis and a straight line was drawn from the origin (time = 0) that follows initial sedimentation behavior. The slope of the straight line represents the initial sedimentation rate.

3.4.1.1.1 Kaolin Sedimentation Behavior

The relationship between initial sedimentation rate and salt solution concentration for kaolin is shown in Fig. 3-4. Data in Fig. 3-4 are from this study as well as sedimentation tests reported in Shackelford (1994), Chen and Anandarajah (1998), and Palomino and Santamarina (2005). An approximately constant initial sedimentation rate for kaolin was observed in each study for salt solution concentrations less than 100 mM (Fig. 3-4). Exponential regression lines fit to each individual data set in Fig. 3-4 all have coefficients of determination (R^2) ≥ 0.83 . These exponential regression lines suggest that a critical concentration (C_{cr}) exists whereupon there is a transition in sedimentation behavior. For $C < C_{cr}$, sedimentation rates are approximately constant for kaolin in a given set of experiments, whereas for $C > C_{cr}$, the sedimentation rate decreases. The C_{cr} for kaolin is approximately 100 mM based on data compiled in Fig. 3-4.

Palomino and Santamarina (2005) report that EF flocculation in kaolin occurs at low salt concentrations of 0.1 mM. These low concentrations are sufficient to suppress the DDL thickness, and subsequent increases in salt concentration do not considerably change the DDL thickness due to low specific surface area of kaolinite and relatively thin initial DDL. Furthermore, sedimentation fluid density and viscosity do not change considerably when salt concentration increases from 1 to 100 mM (ρ_t in Table 3-1). As a result, the initial sedimentation rate nearly is constant for a given set of experiments for salt concentrations ranging between 0.1 and 100 mM (Fig. 3-4).

As salt concentration increased from 100 to 1000 mM (Fig. 3-4), additional suppression of the DDL thickness likely did not occur in kaolin due to an initial thin DDL that was sufficiently suppressed in the presence of a low salt concentration (1 mM). However, sedimentation fluid density and viscosity increased with an increase in salt concentration from 100 mM to 1000 mM (Table 3-1). Physical properties of the sedimentation fluid (i.e., density and viscosity) are influenced by the presence of soluble salts. The settling velocity of particles out of suspension (v) can be computed as,

$$v = \frac{(\rho_s - \rho_\ell) \cdot d^2}{18 \cdot \eta_\ell} \quad (3-6)$$

where η_ℓ is fluid viscosity (Das 2001). An increase in ρ_ℓ and/or η_ℓ for a mixture with constant particle diameter (d) reduces the settling velocity (Eq. 3-6). Thus, the C_{cr} in kaolin sedimentation experiments was attributed to increases in ρ_ℓ and η_ℓ , which combine to decrease the rate of particle sedimentation.

A comparison of v for kaolin in low and high salinity sedimentation fluids was conducted to evaluate the hypothesis that the decrease in sedimentation rate observed in kaolin for $C > C_{cr}$ was due to a change in fluid properties. A ratio of v relative to $C = 1$ mM (v_1) and $C = 1000$ mM (v_{1000}) was computed as follows:

$$\frac{v_1}{v_{1000}} = \frac{(\rho_s - \rho_{\ell 1}) \cdot \eta_{1000}}{(\rho_s - \rho_{\ell 1000}) \cdot \eta_1} \quad (3-7)$$

where $\rho_{\ell 1}$ and $\rho_{\ell 1000}$ are the solution densities at 1-mM and 1000-mM salt concentration, respectively, and η_1 and η_{1000} are the solution viscosities at 1-mM and 1000-mM salt concentration, respectively.

Settling velocity ratios for sedimentation tests on kaolin in the three sedimentation fluids used in this study are in Table 3-5. The calculated velocity ratios in Table 3-5 were based on Eq. 3-7 and included fluid densities computed from mass-volume relationships and viscosities for the different salt concentrations and salt types obtained from Zaytsev and Aseyev (1992). The measured velocity ratios were based on the assumption that the measured initial sedimentation rate (ISR in Table 3-1) was equivalent to v . Both the measured and calculated velocity ratios support the hypothesis and indicate that a decrease in sedimentation velocity of kaolin in high salt concentrations can be attributed to changes in sedimentation fluid density and viscosity (Table 3-4).

The initial sedimentation rate of kaolin in 1000-mM-FeCl₃ solution ($C > C_{cr}$) decreased by a factor of 15 relative to initial sedimentation rates at $C < C_{cr}$ (i.e., 1, 10, and 100 mM). The

decrease in sedimentation rate for $C > C_{cr}$ for CaCl_2 and NaCl solutions was approximately 4 to 5. The higher reduction in sedimentation rate for FeCl_3 was attributed to a more pronounced change in sedimentation fluid density due to higher molar mass of FeCl_3 in comparison with CaCl_2 and NaCl (Table 3-1).

The initial sedimentation rate in kaolin for $C < C_{cr}$ increased with an increase in cation valence for solutions with comparable molarity (Figs. 3-2 and 3-4). pH of the FeCl_3 solutions were low (Table 3-1) and excess H^+ ions present in solution neutralized negative clay particle faces and reduced the repulsive DDL force between particles (Palomino and Santamarina 2005). These chemical interactions produced FF flocculation that resulted in denser particle arrangements compared to EF or EE flocculation (Palomino and Santamarina 2005), which yielded higher settling rates in FeCl_3 compared to CaCl_2 and NaCl . Flocculated particles in CaCl_2 solution settled faster than NaCl solution due to a higher charge valence that more effectively suppressed the DDL and decreased pH.

Additional sedimentation tests were performed with comparable ionic strength solutions of 100 mM (i.e., 100 mM NaCl , 34 mM CaCl_2 , 17 mM FeCl_3) to further assess the effect of cation valence on sedimentation behavior of kaolin (Table 3-1). The initial sedimentation rate of kaolin increased with an increase in cation charge, and the rates in CaCl_2 and FeCl_3 solutions were two and four times higher than NaCl solution, respectively. The higher initial sedimentation rate for FeCl_3 solution in comparison with CaCl_2 solution was due to the acidic environment of the sedimentation fluid (Table 3-1). Shackelford (1994) and Palomino and Santamarina (2005) reported that presence of H^+ ions in acidic solutions neutralize the face of kaolin particles and decreased the repulsive force between kaolin particle faces. As a result, FF flocculation in kaolin resulted in more rapid sedimentation. Solution density and viscosity of CaCl_2 was lower than NaCl in the same ionic strength solution (Table 3-1), which likely contributed to higher initial sedimentation rates in CaCl_2 .

3.4.1.1.2 Bentonite Sedimentation Behavior

The relationship between initial sedimentation rate of bentonite and sedimentation solution salinity is shown in Fig. 3-5a. Data in Fig. 3-5a are compiled from this study and sedimentation tests reported in Shackelford (1994) and Gumaste et al. (2014). The compilation of bentonite sedimentation test data supports a trend of increasing sedimentation rate with increasing salt concentration. Bentonite consists of considerably smaller clay particles compared to kaolin, which have a larger specific surface area and DDL (Mitchell and Soga 2005). Increasing the salt concentration within a range from 0.1 to 1000 mM (Fig. 3-5a) continuously suppressed the DDL thickness in bentonite (Akhter et al. 2008), which enhanced particle flocculation via reduction in repulsive forces between particles. The range in initial sedimentation rate for a given salinity (e.g., 10 mM in Fig. 3-5a) may be attributed to variation in soil mass used in sedimentation experiments completed in the different studies as well as differences in mineralogical composition of the bentonite.

The mass of bentonite used in a given sedimentation test can alter sedimentation behavior via increasing or decreasing interparticle interactions. Initial sedimentation rates normalized with respect to soil mass are shown as a function of sedimentation solution ionic strength in Fig. 3-5b. The normalized initial sedimentation rate was an attempt to combine the compiled bentonite sedimentation data into a single relationship to evaluate the effect of salinity. Overall, the normalized initial sedimentation rate (Fig. 3-5b) reduced some of the scatter in Fig. 3-5a. A single power-function regression line was fit to all data in Fig. 3-5b and two additional trend lines are included that represent the 95 % confidence interval of the regression line. Data in Fig. 3-5b exhibit a trend of increasing initial sedimentation rate of bentonite with increasing ionic strength of the sedimentation solution.

Sedimentation tests performed with bentonite and salt solutions at comparable ionic strength of 100 mM (i.e., 100 mM NaCl, 34 mM CaCl₂, 17 mM FeCl₃) are in Table 3-1. In bentonite, the initial sedimentation rate in CaCl₂ and FeCl₃ was 5.7 and 4.0 times larger than

NaCl, respectively. The higher initial sedimentation rate of CaCl₂ solution was attributed to cation exchange between divalent cations in solution and Na⁺ ions on the exchange complex of montmorillonite minerals (Lee et al. 2005). Water holding capacity and swell potential of Ca-montmorillonite are lower than Na-montmorillonite, which results in increased DDL suppression in CaCl₂ solutions and higher sedimentation rates. Ferric chloride solutions produced an acidic environment (Table 3-1), which typically leads to FF flocculation. However, Fe³⁺ cations will be precipitated in the form of Fe(OH)₃ following FeCl₃ dissolution (Crittenden et al. 2012) and there likely was limited Fe³⁺ cations available in solution to participate in cation exchange within the DDLs of bentonite particles. Shackelford (1994) reported an increase in bentonite sedimentation with a decrease in pH. However, the initial sedimentation rate in CaCl₂ solution that was greater than FeCl₃ solution suggests that cation exchange had a more pronounced effect on bentonite flocculation and sedimentation relative to solution pH.

3.4.1.2 Final Solids Content of Sedimented Soils

The relationship between final solids content and sedimentation solution ionic strength for kaolin is shown in Fig. 3-6. Data in Fig. 3-6 are from this study as well as sedimentation tests reported in literature. Data from Shackelford (1994), Palomino and Santamarina (2005) (pH = 7), Kaya et al. (2006), and this study support a decreasing trend between solids content and ionic strength. In contrast, data from Chen and Anandarajah (1998), Palomino and Santamarina (2005) (pH = 5), and Gumaste et al. (2014) support an increasing trend between solids content and ionic strength. These contrasting trends between final solids content and ionic strength were attributed to achieving a minimum DDL thickness at low ionic strength in kaolin combined with the observation that pore fluid density and viscosity do not affect final sedimented volume. In general, ionic strength (i.e., salinity) does not have a considerable effect on final solids content in kaolin.

Normalized final solids content for bentonite as a function of ionic strength from this study and results obtained by Shackelford (1994), Lee et al. (2005), and Gumaste et al. (2014) are shown in Fig. 3-7. Data in Fig. 3-7 were normalized with respect to soil mass used in sedimentation tests reported in each study. Final solids content increased with an increase in ionic strength due to enhanced flocculation of clay particles. Measured final solids contents from experiments conducted in this study are in Table 3-1. Bentonite solids content was 3 % for sedimentation in DI water and increased to 6 % for 1000-mM NaCl and 16 % for 1000-mM CaCl₂ and FeCl₃ solutions. Flocculated particles in saline solutions occupy a smaller total volume relative to dispersed particles, which increases the volume of released water and final solids content of the sedimented material. This behavior suggests larger volumes of water will be released with an increase in pore fluid salinity of montmorillonite-rich materials.

Final solids content measured in bentonite sedimentation tests in salt solutions at comparable ionic strength of 100 mM (i.e., 100 mM NaCl, 34 mM CaCl₂, 17 mM FeCl₃) are in Table 3-1. Final solids content in NaCl, CaCl₂, and FeCl₃ in the same ionic strength solution are approximately constant (3-4 %), which suggests that ionic strength and not cation valence is a better predictor of final solids content in bentonite.

3.4.2 Sedimentation Behavior of Soda Ash Mine Tailings

Sedimentation rates for non-dialyzed soda ash tailings and the two dialyzed tailings specimens are shown in Fig. 3-8. In general, sedimentation behavior of the three soda ash tailings specimens was similar and initial sedimentation rates determined for the three experiments were comparable in the range of 9 to 10 mm/min (Table 3-1). Soda ash tailings contained a high fraction of sand and silt (82 % by mass), which likely contributed to a sedimentation rate of approximately zero in all soda ash experiments after 25 min (Fig. 3-8). Sand and silt particles do not flocculate similarly to clay particles, and soluble salts can be assumed to have negligible effect on sedimentation of sand and silt particles beyond changes in

sedimentation fluid density and viscosity (Eq. 3-6). Thus, mud-line heights measured for soda ash tailings (Fig. 3-8) primarily correspond to sedimentation of the 18 % clay content of the tailings.

Salt concentrations of the soda ash sedimentation fluids were estimated based on a relationship between total dissolved solids (TDS) and EC of soda ash pore fluid salt dissolved in DI water. This TDS-EC relationship yielded salt concentrations of 4620 mg/L for T_N , 3881 mg/L for T_A , and 2176 mg/L for T_B (Table 3-1). Salt concentrations used in the kaolin and bentonite sedimentation experiments also are listed in Table 3-1 in mg/L. Salinity of the soda ash tailings sedimentation fluid falls within the range of 37 to 79 mM for pure NaCl solutions, which corresponds to salinities that are below the C_{cr} (100 mM) identified for kaolin (Fig. 3-4). In general, soda ash tailings sedimentation behavior was similar to kaolin sedimentation behavior for $C < C_{cr}$ and contrary to sedimentation behavior of bentonite. These comparisons support the observation that for the range of salinity achieved in the soda ash tailings experiments, salinity had a limited effect on initial sedimentation rate in soda ash tailings and there was no effect of salinity on final solids content (Table 3-1).

Although clay minerals were not quantified in soda ash tailings, illite was qualitatively identified as the dominant clay mineral. Sedimentation results from the soda ash experiments suggest that illite and kaolin exhibit similar sedimentation behavior. Whitehouse et al. (1960) performed sedimentation tests with sea water on kaolinite, illite, and montmorillonite and reported that the settling velocity of kaolinite was approximately constant for salt concentrations ranging from 900 to 32,500 mg/L, which agrees with results obtained in this study. However, the settling velocity of montmorillonite particles increased by a factor of 37 for a comparable increase in salt concentration. Whitehouse et al. (1960) also report that the sedimentation behavior of illite was similar to kaolin and that with an increase in salt concentration from 900 mg/L to 32,500 mg/L the settling velocity only increased by a factor of 0.2. Findings from this

study are in agreement with those reported in Whitehouse et al. (1960) and support the observation that illite sedimentation behavior is comparable to kaolin.

Tailings pore fluid salinity is a function of parent rock and mining extraction processes. The presence of soluble salts in montmorillonite-rich mine tailings can increase the sedimentation rate and volume of released water. Furthermore, the subsequent addition of soluble salts to increase salinity in montmorillonite-rich mine tailings can have a positive effect on enhancing sedimentation. The presence of soluble salts in mine tailings that contain high kaolinite content, and potentially illite, can also enhance initial sedimentation rate and final solids content. However, results from this study and data compiled from literature suggest that the subsequent addition of soluble salts to increase sedimentation fluid salinity of kaolinite-rich mine tailings will have negligible effect on sedimentation behavior.

3.5 Conclusions

Sedimentation tests were conducted to assess the effects of salt concentration and salt type on sedimentation behavior of kaolin and bentonite suspensions and to evaluate behavior of a natural saline mine tailings. Sedimentation rate and final solids content were evaluated in the presence of NaCl, CaCl₂, and FeCl₃. The following conclusions were drawn from this study.

- Kaolin sedimentation behavior changed from dispersed in DI water to flocculated in the presence of a low salinity solution (1 mM). Sedimentation rates did not change with increasing salinity from 1 mM to 100 mM, but subsequently decreased regardless of salt type for salinity > 100 mM. This change in sedimentation behavior was attributed to increased sedimentation solution density and viscosity for salinity > 100 mM, which contributed to decreased rates of particle sedimentation.
- Kaolin clay particles settled faster in FeCl₃ solution in comparison with CaCl₂ and NaCl solution at similar ionic strength due to the acidic nature of the FeCl₃ solution. Final

solids content of sedimented kaolin was similar in all three salt solutions at the same ionic strength; thus, although cation valence increased sedimentation rates, cation valence did not influence final solids content of kaolin clay in comparable ionic strength solutions.

- Sedimentation rates in bentonite suspensions increased with increasing salinity for all salts evaluated in this study. This increasing trend was attributed to an initial large diffuse double layer in bentonite that was suppressed over a broad range of salinity that continuously enhanced particle flocculation and sedimentation with increasing salinity.
- The clay content of soda ash tailings was qualitatively identified as illite via x-ray diffraction and the sedimentation behavior of soda ash tailings was comparable to kaolin. Constant sedimentation rates were measured for different salt concentrations in the soda ash tailings experiments, and all salt concentrations were less than critical concentration identified for kaolin. Thus, findings suggest that kaolin and illite may exhibit similar sedimentation behavior, but additional experiments are warranted on pure illite to support this observation.
- Addition of salt to montmorillonite-rich mine tailings can be used to enhance sedimentation rates and promote tailings dewatering. However, salt addition to kaolinite-rich mine tailings in concentrations ranging between 1 and 100 mM will not affect sedimentation rates, whereas addition of salt to concentrations > 100 mM likely will decrease sedimentation rates due to elevated sedimentation fluid density and viscosity.

Table 3-1. Summary of sedimentation experiments conducted on kaolin and bentonite clay and soda ash mine tailings, including sedimentation fluid characteristics, initial sedimentation rate, and final solids content.

Soil	Salt	C (mM)	C (mg/L)	I (mM)	pH ^a	EC ^a (dS/m)	ρ_t (kg/m ³)	ISR (mm/min)	FSC (%)
Kaolin	NA	0	0	0	4.63	0.10	997.1	0	5
	NaCl	1	58	1	5.13	0.30	997.1	2.53	35
		10	584	10	4.61	1.3	997.5	2.50	37
		100	5840	100	4.98	11	1001.5	2.50	33
		1000	58,400	1000	6.28	82	1041.2	0.57	30
	CaCl ₂	1	111	3	4.67	0.30	997.2	4.90	35
		10	1110	30	NM	NM	997.9	5.15	35
		34	3774	100	4.24	5.7	999.9	4.77	33
		100	11,100	300	NM	NM	1005.4	9.83	31
		1000	111,000	3000	5.80	NM	1082.4	1.09	32
	FeCl ₃	1	162	6	3.80	0.30	997.2	1.0	31
		10	1622	60	NM	NM	998.3	5.1	32
		17	2757	100	2.40	4.4	999.2	9.83	32
		100	16,220	600	NM	NM	1009.2	4.98	32
		1000	162,200	6000	1.20	78	1126.5	0.63	26

Notes: C = concentration; I = ionic strength; EC = electrical conductivity; ρ_t = sedimentation fluid density; ISR = initial sedimentation rate; FSC = final solids content; NM = not measured

^a pH and EC were measured on the supernatant after finishing a given sedimentation test.

Table 3-1. Summary of sedimentation experiments conducted on kaolin and bentonite clay and soda ash mine tailings, including sedimentation fluid characteristics, initial sedimentation rate, and final solids content (continued).

Soil	Salt	C (mM)	C (mg/L)	I (mM)	pH ^a	EC ^a (dS/m)	ρ_t (kg/m ³)	ISR (mm/min)	FSC (%)	
Bentonite	NA	0	0	0	7.14	NM	997.1	0	3	
	NaCl	10	584	10	NM	NM	997.5	0.01	3	
		100	5840	100	7.85	12	1001.5	0.01	3	
		1000	58,400	1000	7.75	60	1041.2	0.12	6	
	CaCl ₂	10	1110	30	7.75	3.6	997.9	0.02	3	
		34	3774	100	7.70	6.1	999.9	0.08	4	
		100	11,100	300	7.65	46	1005.4	0.03	4	
		1000	111,000	3000	NM	NM	1082.4	3.6	16	
	FeCl ₃	10	1620	60	2.87	2.9	998.3	0.01	3	
		17	2757	100	2.36	5.0	999.2	0.05	3	
		100	16,220	600	NM	NM	1009.2	0.63	8	
		1000	162,200	6000	1.22	84	1126.5	2.05	16	
	Soda ash	Natural salt ^b	—	4620	—	6.80	7.2	—	9.0	36
			—	3881	—	6.80	6.2	—	9.0	35
—			2176	—	7.00	3.8	—	10	35	

Notes: C = concentration; I = ionic strength; EC = electrical conductivity; ρ_t = sedimentation fluid density; ISR = initial sedimentation rate; FSC = final solids content; NM = not measured

^a pH and EC were measured on the supernatant after finishing a given sedimentation test.

^b Soda ash salt concentrations estimated from relationship between total dissolved solids versus EC developed via dissolving extracted soda ash salts into known volumes of DI water. Millimolar concentration, I, and ρ_t not determinable for soda ash mine tailings.

Table 3-2. Ion name, formula, charge, and concentration of non-dialyzed tailings pore fluid measured via inductively coupled plasma-atomic emission spectrometry and ion chromatography.

Ion		Concentration (mg/L)
Name	Chemical Formula and Charge	
Sodium	Na ⁺	1061
Potassium	K ⁺	49
Calcium	Ca ²⁺	3
Magnesium	Mg ²⁺	2
Silicon	Si ⁴⁺	17
Phosphate	PO ₄ ³⁻	760
Sulfate	SO ₄ ²⁻	272
Fluorine	F ⁻	127
Chlorine	Cl ⁻	42
Nitrate	NO ₃ ⁻	1

Table 3-3. Mineralogical composition of natural soda ash tailings and kaolin and bentonite clays based on x-ray diffraction.

Mineral	Soda Ash (%)	Kaolin (%)	Bentonite (%)
Montmorillonite	---	---	87
Kaolinite	---	95	---
Plagioclase-feldspar	---	---	2
Chlorite	---	2	---
Dolomite	46	---	---
Shorite	26	---	---
Quartz	11	1	8
Potassium-feldspar	8	---	---
Clay/Mica	7	---	---
Calcite	2	---	---

Table 3-4. Chemical constituents of non-dialyzed and dialyzed soda ash with seven dialysis cycles based on x-ray fluorescence.

Mineral	Natural Soda Ash Tailings (%)	Dialyzed Soda Ash Tailings (%)
SiO ₂	21.20	26.83
CaO	15.47	18.37
Na ₂ O	11.12	3.18
MgO	6.63	8.02
Al ₂ O ₃	3.90	4.8
K ₂ O	2.18	2.63
Fe ₂ O ₃	1.01	1.16
SO ₃	0.68	0.67
P ₂ O ₅	0.43	0.38
SrO	0.11	0.14
Cl	0.06	0.01
MnO	0.03	0.05
Nb ₂ O ₅	0.01	-

Table 3-5. Comparison of kaolin clay particle settling velocities in low (1 mM) and high (1000 mM) salinity fluids.

Salt	Calculated settling velocity ratios, v_1 / v_{1000} ^a	Measured settling velocity ratios, ISR_1 / ISR_{1000} ^b
NaCl	1.12	4.42
CaCl ₂	1.18	4.50
FeCl ₃	2.38	14.49

^a Settling velocity ratios (v) computed via Eq. 3-7, where v_1 is for 1 mM solution and v_{1000} is for 1000 mM solution.

^b Computed assuming the measured initial sedimentation rate (ISR) equals the settling velocity (v), where ISR_1 is for 1 mM solution and ISR_{1000} is for 1000 mM solution.

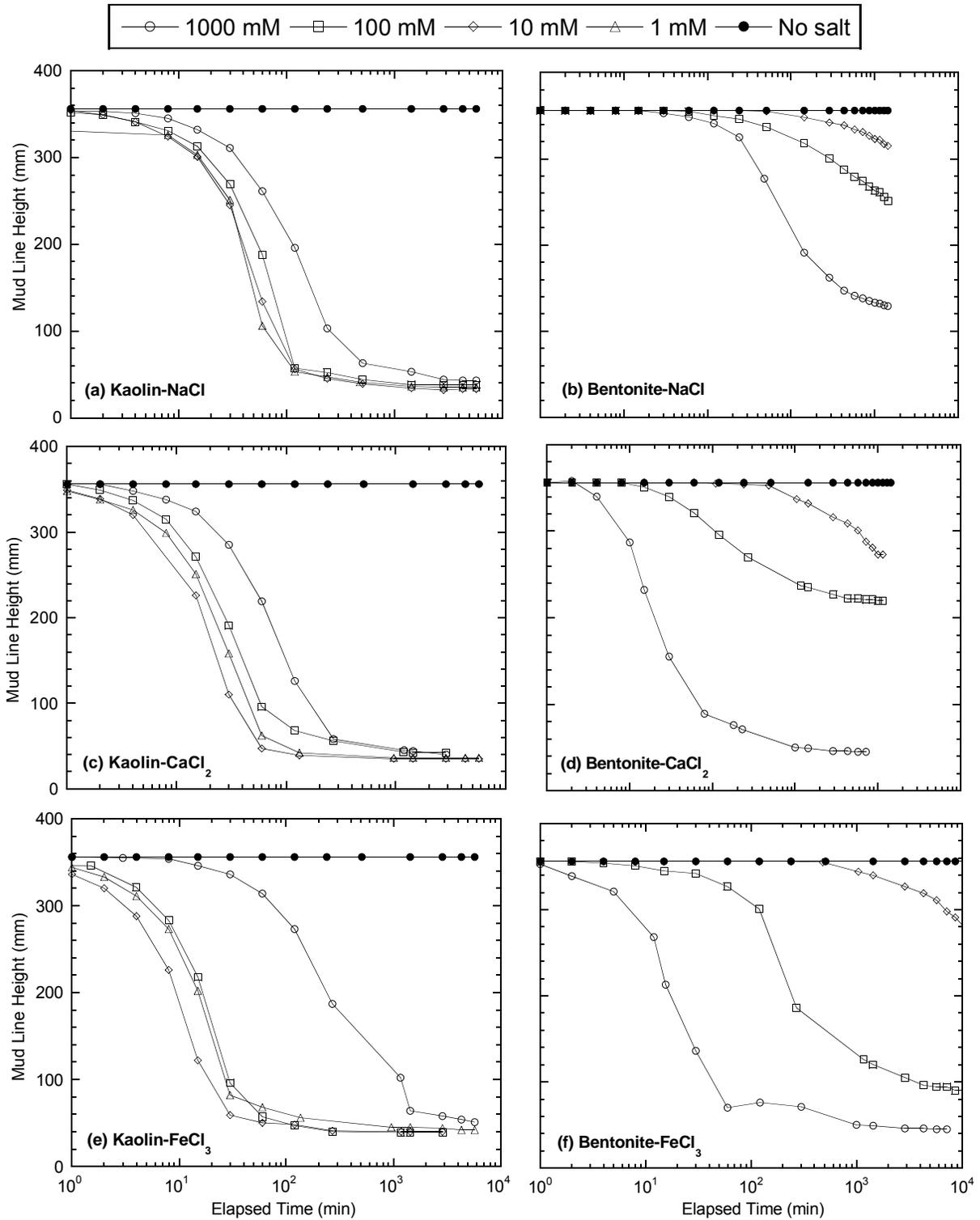


Fig. 3.1. Temporal relationships of mud-line height for kaolin and bentonite clay as a function of salt type and concentration: (a) kaolin-NaCl, (b) bentonite-NaCl, (c) kaolin-CaCl₂, (d) bentonite-CaCl₂, (e) kaolin-FeCl₃, and (f) bentonite-FeCl₃.

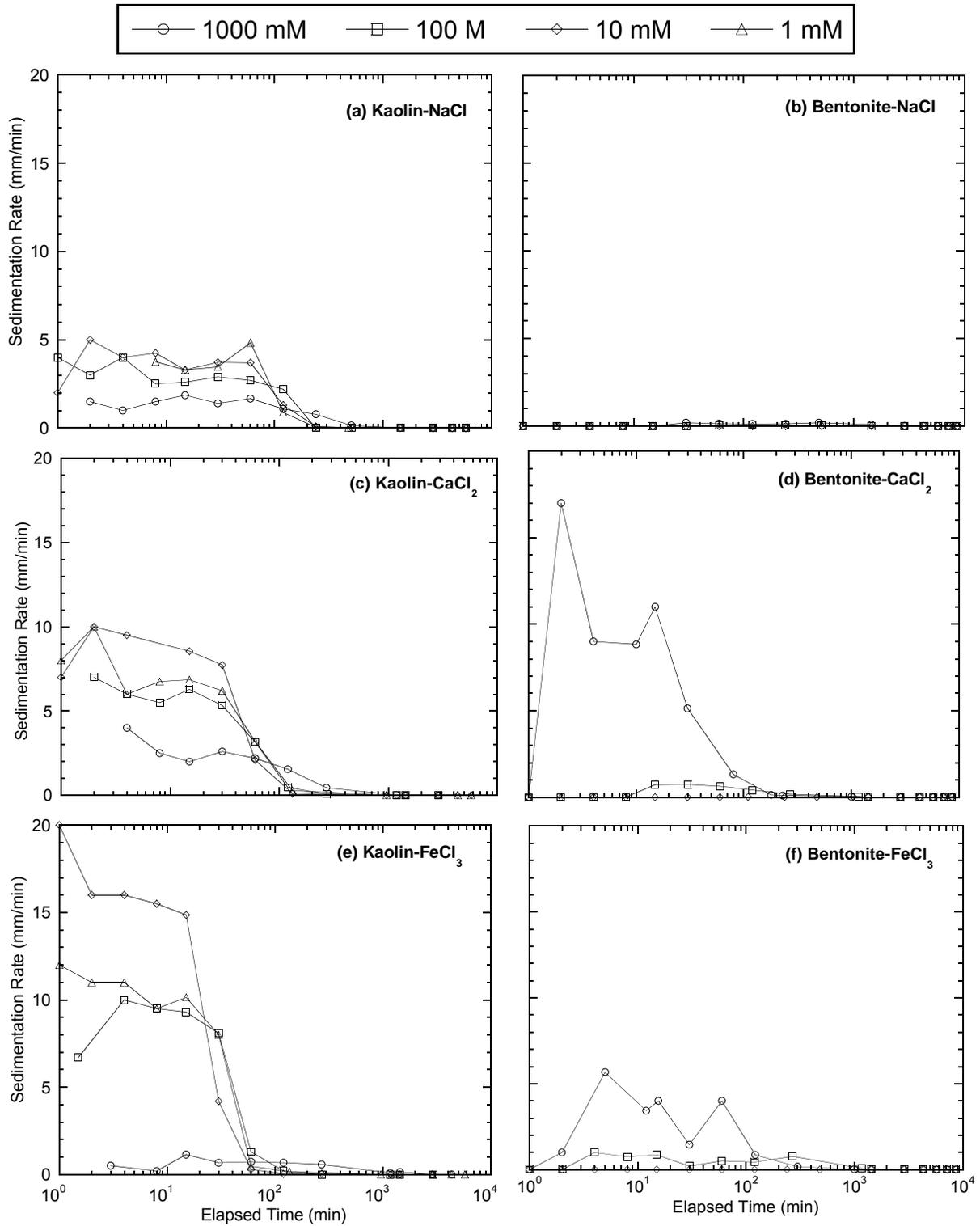


Fig. 3.2. Temporal relationships of sedimentation rate for kaolin and bentonite clay as a function of salt type and concentration: (a) kaolin-NaCl, (b) bentonite-NaCl, (c) kaolin-CaCl₂, (d) bentonite-CaCl₂, (e) kaolin-FeCl₃, and (f) bentonite-FeCl₃.

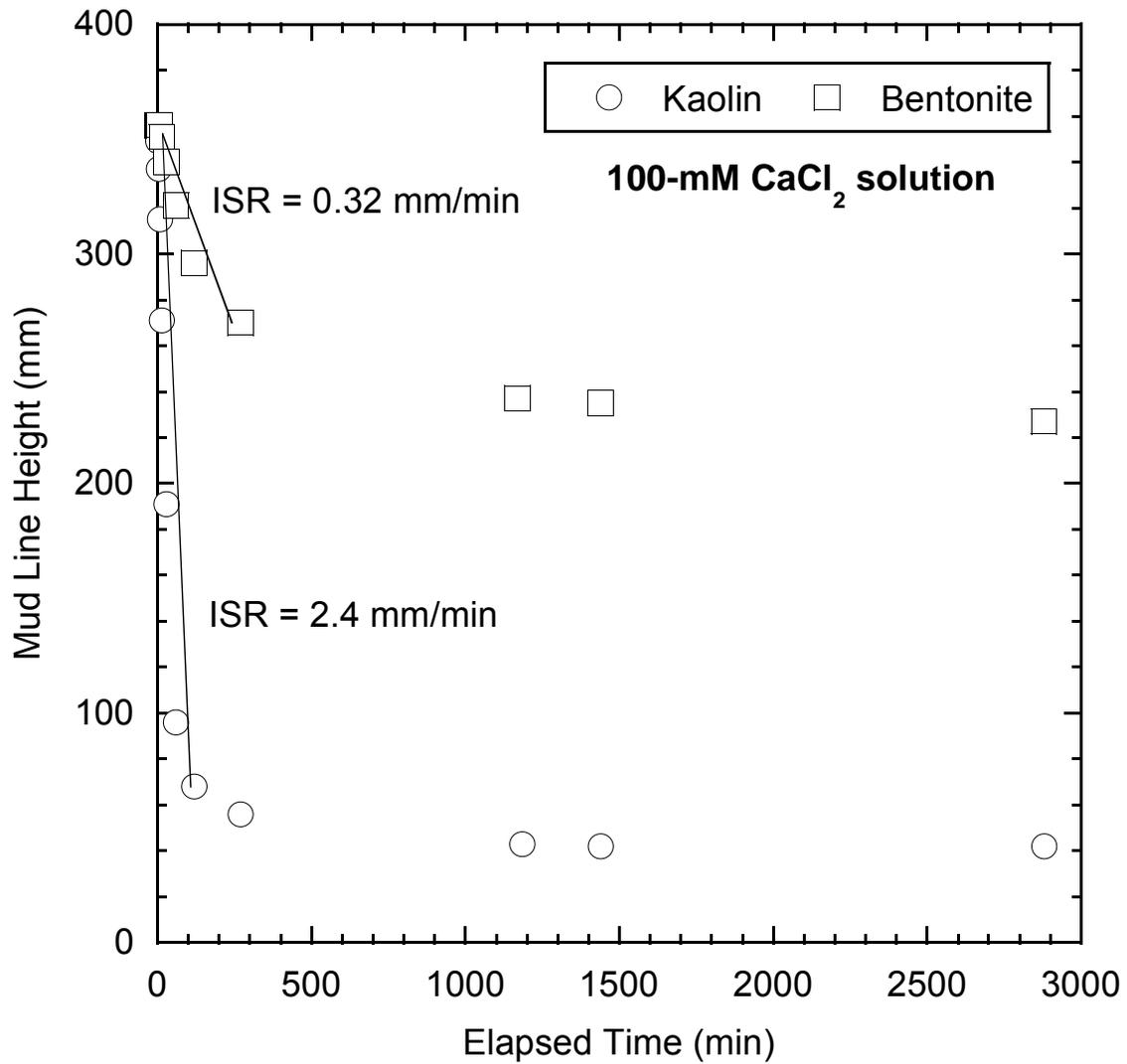


Fig. 3.3. Graphical method for computing the initial sedimentation rate adopted from Palomino and Santamarina (2005) for 1000-mM NaCl solution for kaolin and bentonite.

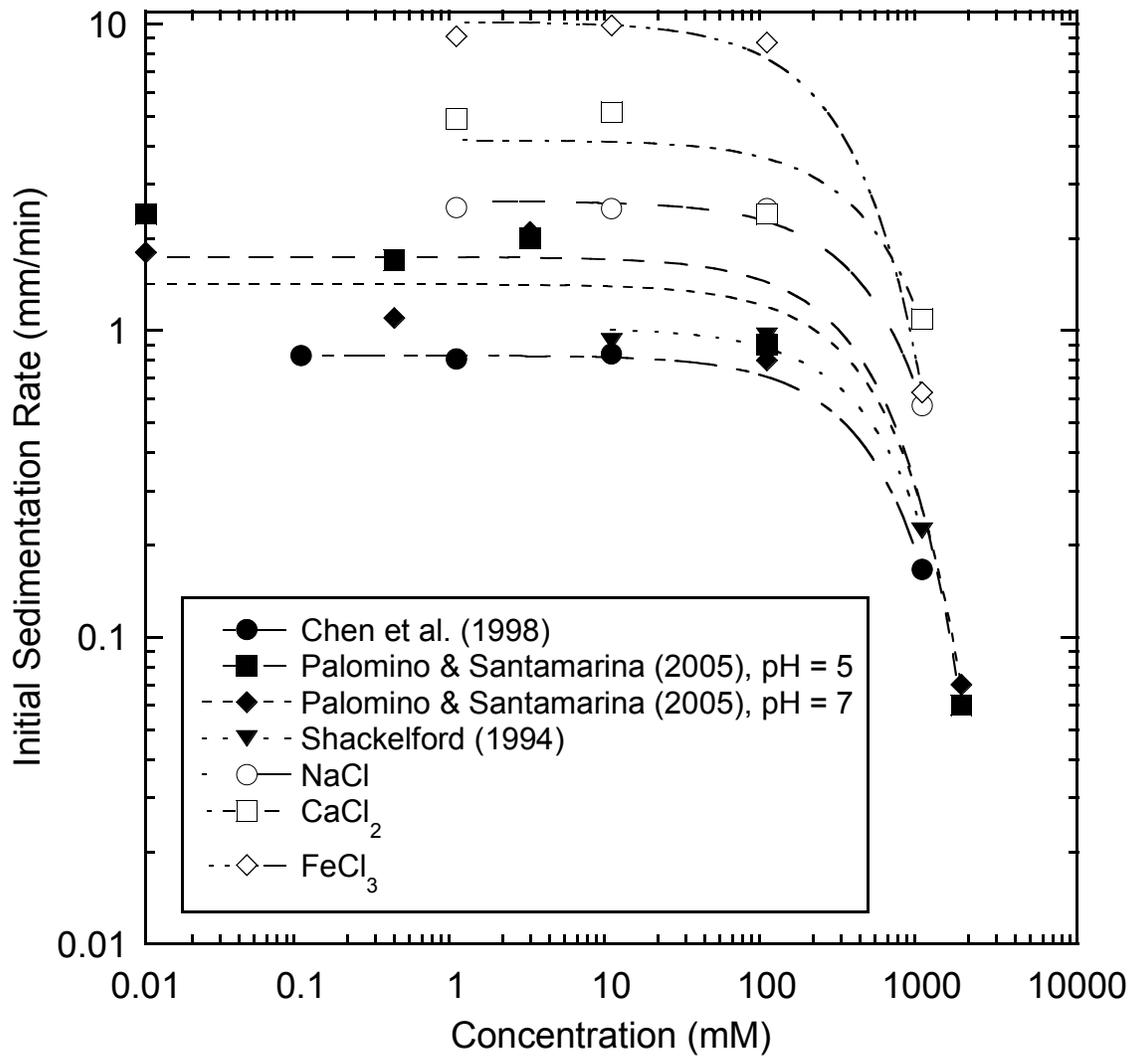


Fig. 3.4. Effect of salt type and concentration (NaCl, CaCl₂, and FeCl₃) on initial sedimentation rate of kaolin clay for experiments conducted in this study and compiled from literature.

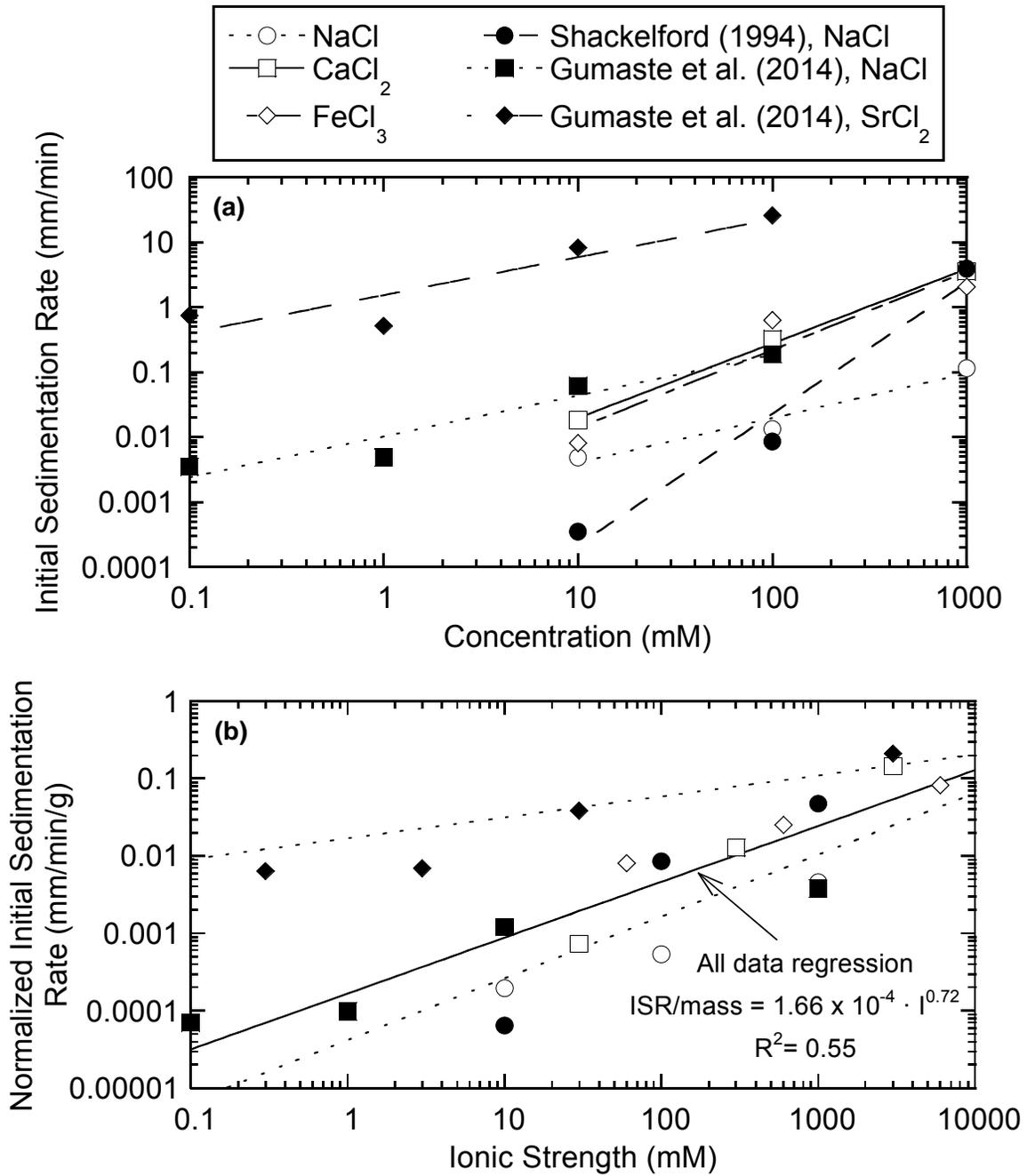


Fig. 3.5. Relationships of (a) initial sedimentation rate versus salt solution concentration and (b) normalized initial sedimentation rate with respect to specimens mass versus ionic strength for bentonite clay. Dashed lines in (b) represent upper and lower 95% confidence bounds for the all data regression line.

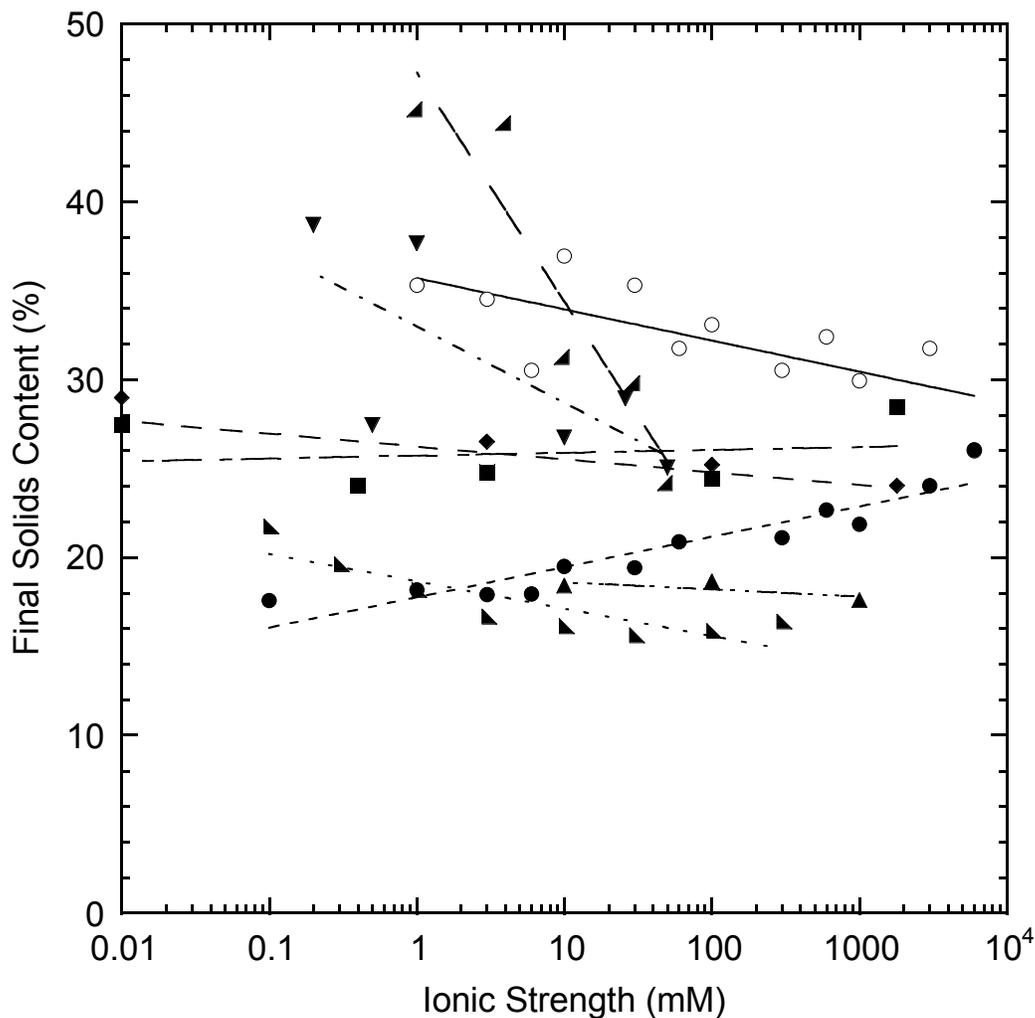
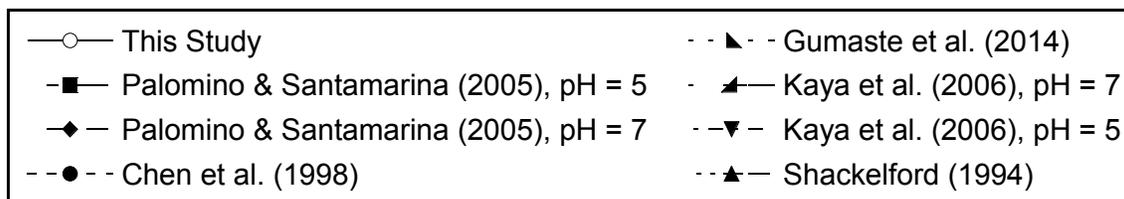


Fig. 3.6. Relationship between final solids content of kaolin and ionic strength of the sedimentation fluid for experiments conducted in this study and compiled from literature.

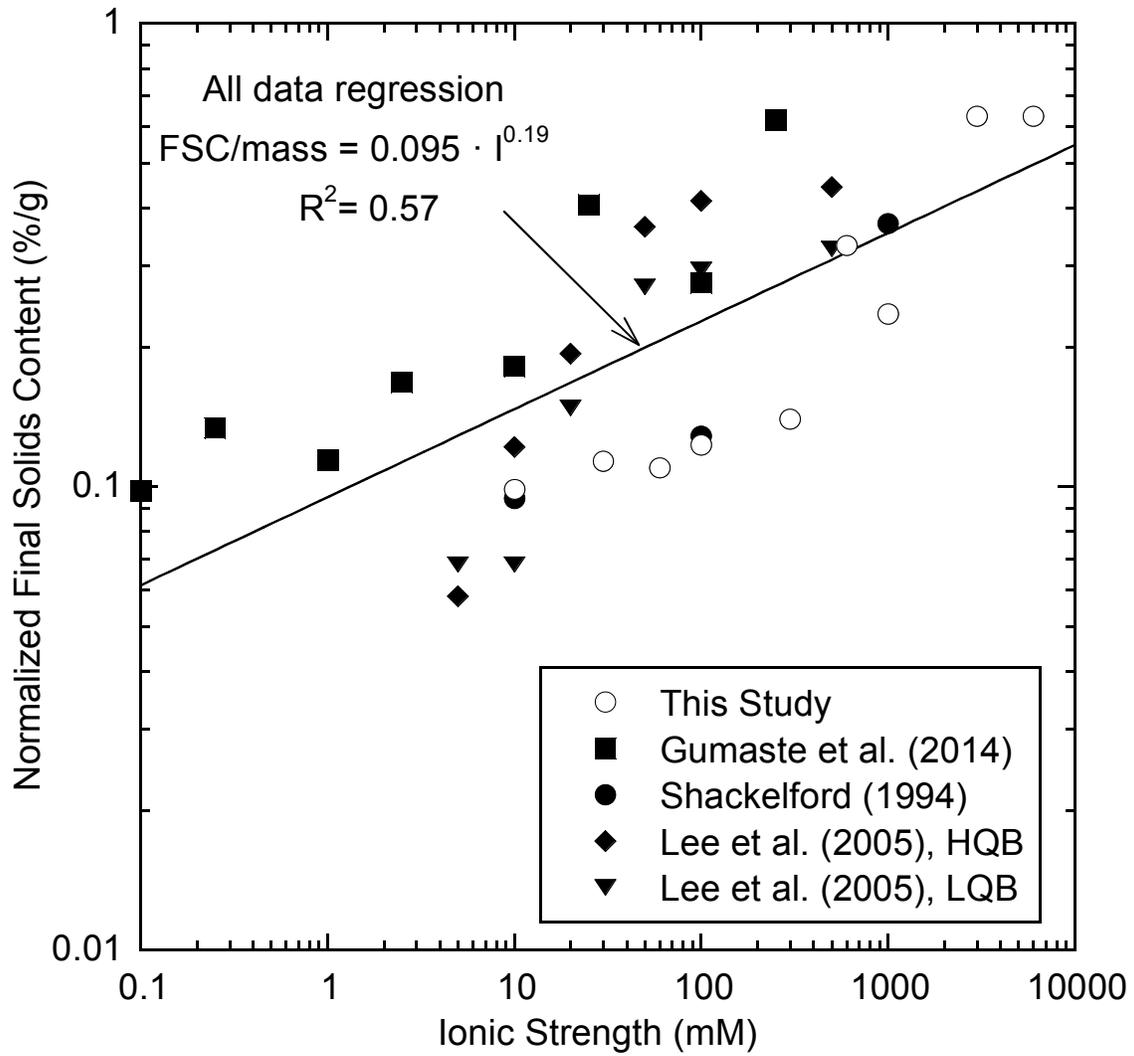


Fig. 3.7. Relationship between final solids content of bentonite normalized with respect to specimen mass and ionic strength of the sedimentation fluid for experiments conducted in this study and compiled from literature. Data compiled from Lee et al. (2005) includes high quality bentonite (HQB) and low quality bentonite (LQB).

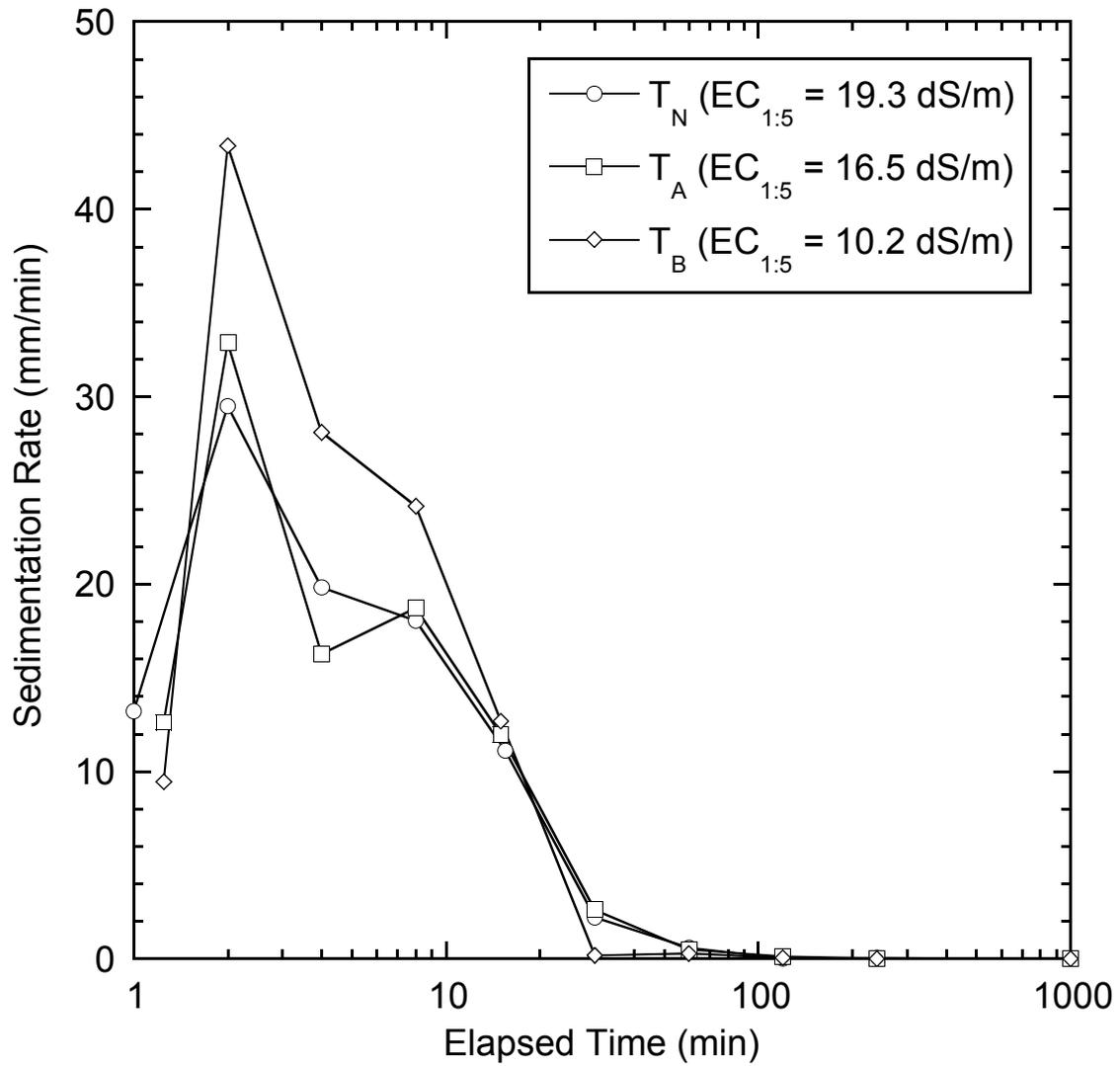


Fig. 3.8. Temporal relationships of sedimentation rate of soda ash mine tailings for three different sedimentation fluid salinities. Subscripts: N is representative of natural tailings, and A and B are representative of dialyzed specimens.

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