

THE EFFECTS OF SALINITY AND SHEAR HISTORY ON THE RHEOLOGICAL CHARACTERISTICS OF ILLITE-RICH AND Na-MONTMORILLONITE-RICH CLAYS

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Abstract—Particle–particle interactions in natural clays can be evaluated by their rheological behavior, but the results are often affected by the physicochemical properties of the clays. The behaviors of two fundamentally different types of clays (low-activity and high-activity) differ with respect to salinity and a time factor (duration of shearing at a given shear rate): illite-rich Jonquiere clay (low-activity clay, Canada) and montmorillonite-rich Wyoming bentonite (high-activity clay, USA). The purpose of the present study was to investigate these different behaviors. Most natural clays exhibit shear-thinning and thixotropic behavior with respect to salinity and the volumetric concentration of the solids. Natural clays also exhibit time-dependent non-Newtonian behavior. In terms of index value and shear strength, low-activity and high-activity clays are known to exhibit contrasting responses to salinity. The geotechnical and rheological characteristics as a function of salinity and the shearing time for the given materials are compared here. The clay minerals were compared to estimate the inherent shear strengths, such as remolded shear strength (which is similar to the yield strength). Low-activity clay exhibits thixotropic behavior in a time-dependent manner. High-activity clay is also thixotropic for a short period of shearing, although rare cases of rheopectic behavior have been measured for long periods of shearing at high shear rates. The change from thixotropic to rheopectic behavior by bentonite clay has little effect at low shearing speeds, but appears to have a significant effect at higher speeds.

Key Words—Low-activity Clay, High-activity Clay, Salinity, Rheopectic, Thixotropic, Yield Strength.

INTRODUCTION

The important types of clay minerals encountered in engineering are illites and montmorillonites. Illite is the most common clay mineral in postglacial marine and lacustrine soft clays and silt deposits (Terzaghi *et al.*, 1996). Illites commonly show some interstratification with smectites, including montmorillonite. Natural bentonite contains mainly montmorillonite and is used in many applications: drilling muds, slurry shield tunneling, horizontal directional drilling, jet grouting (Besq *et al.*, 2003), and as geosynthetic clay liners (GCL) for the waste-disposal management of municipal solid waste (Alther, 1987; Petrov and Rowe, 1997; Dixon *et al.*, 1999) or for the disposal of radioactive wastes (Churchman *et al.*, 2002). Bentonite has been used to improve structural strength and has resulted in significant economic returns. Here, illite is considered to be a low-activity clay, and montmorillonite is considered to be a high-activity clay. Even on the basis of particle shape, generalizations about illites and montmorillonites

are difficult to construct. Illite is found in sediments, and montmorillonite is found in clay deposits, as reported by Jeong *et al.* (2010).

Rheological measurements have been used to evaluate the interactions between the particles and the mode of association. According to previous studies, the rheological properties of natural clays are affected by particle size, pH, electrolyte concentration, solid concentration, and shear history. Thus, understanding the rheological properties is essential to determine the optimal production conditions for the application of these materials (Heller and Keren, 2001; Liang *et al.*, 2010). Yield stress and viscosity have been used to describe the degree and change in the mode of the particle–particle association (Lagaly, 1989; Heller and Keren, 2001; Malfoy *et al.*, 2003; Laribi *et al.*, 2006). Yield stress and viscosity depend on the rate of increase in the shear rate, irrespective of the clay minerals in the aqueous colloidal dispersions. Contradicting results concerning the effects of pH and the electrolyte concentration on the rheology of colloidal dispersions are often reported (Kelessidis *et al.*, 2007). The rheological properties of low-activity and high-activity clays, particularly with respect to salinity and time dependence, are not fully understood (Heath and Tadros, 1983; Vali and Bachmann, 1988; Lagaly, 1989; Besq *et al.*, 2003; Malfoy *et al.*, 2003). The present study

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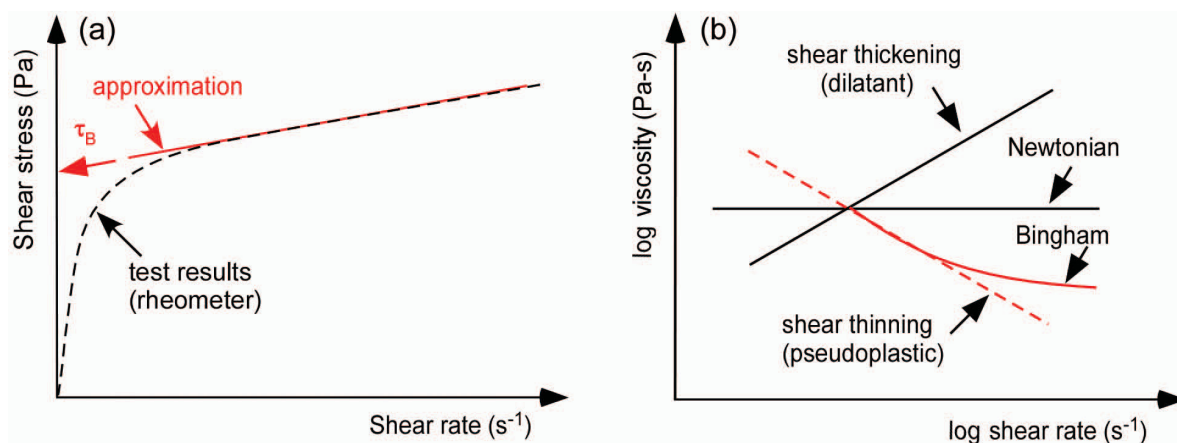


Figure 1. Rheology of the clays: (a) Bingham approximation with test results; and (b) types of fluids, including Newtonian, Bingham, shear thinning, and shear thickening.

attempts to provide insight into the similarities and differences in the geotechnical and rheological characterizations based on the solid concentration, salinity, and shearing time. A rheological study of the products of natural alteration of different parent materials, *i.e.* illite-rich and montmorillonite-rich clays, was undertaken and the test results are reported here.

Natural clays exhibit a shear thinning behavior (Figure 1); under shear they become yield stress materials and have been modeled as Herschel-Bulkley fluids (Coussot and Piau, 1994; Bekkour *et al.*, 2005; Kelessidis *et al.*, 2006). The flow behavior is similar to a Bingham fluid at low solid concentrations (Jeong *et al.*, 2010). The Bingham and Herschel-Bulkley models are given as follows.

$$\begin{aligned} \text{Bingham equation} \quad \tau &= \tau_B + \eta_h \cdot \dot{\gamma} & (1) \\ \text{Herschel-Bulkley equation} \quad \tau - \tau_y &= K(\dot{\gamma})^n & (2) \end{aligned}$$

where τ is the shear stress (Pa). In equation 1, τ_B is the Bingham yield stress (Pa), η_h is the plastic viscosity (Pa-s), and $\dot{\gamma}$ is the shear rate (s^{-1}). In equation 2, τ_y is the Herschel-Bulkley yield stress (Pa), K is the consistency coefficient (Pa-s), and n is the flow behavior index (dimensionless). Different flow types are often observed in different colloidal dispersions (Figure 1b).

In this paper, the geotechnical and rheological

characteristics of natural soft clays from a data compilation by Jeong (2006) are reviewed and the effects of the solids concentration and salinity on the rheological properties are then discussed. Some general conclusions are drawn about the similarities and differences between the low-activity and high-activity clays in the context of the index properties (especially for the liquid state) and the rheological responses (yield strength and viscosity). Particular emphasis is placed on the time-dependent behavior of the two types of clays.

MATERIALS AND METHODS

Test materials

Two types of materials were selected: an illite-rich clay (*i.e.* Jonquiere clay) and a montmorillonite-rich clay (*i.e.* Wyoming bentonite clay). The data set compiled by Jeong (2006) was used. The geotechnical properties of the selected materials are summarized in Table 1.

Low-activity clay: illite-rich Jonquiere clay, Québec, Canada. Jonquiere clays are leached postglacial marine sediments from eastern Canada that were sampled in the Jonquiere area ~200 km north of Québec City (Perret *et al.*, 1996). Quantitative mineralogical determination of the Jonquiere clays at its natural salinity (0.1 g/L NaCl

Table 1. Physico-chemical properties of illite-rich Jonquiere and montmorillonite-rich clays.

Soil	w_L	w_p	I_p	SSA	S	CF	A_c	CEC
Jonquiere	51.3	22.3	29.2	63–67 ⁺ (83*)	0.1	58–61	0.5	7–10
Bentonite	353.4 140.5	53.9 51.3	299.5 89.2	602.1* 126.6*	0 30	77	3.9 1.2	N.D.

A_c = activity (= I_p/CF), CEC = cation exchange capacity (meq/100 g), CF = clay fraction (%), I_p = plasticity index, N.D. = no data provided, SSA = specific surface area (m^2/g), S = salinity (g/L), w_L = liquid limit (%), and w_p = plastic limit (%).

⁺ determined from the Methylene Blue method, * determined from Atterberg limits (Santamarina *et al.*, 2002).

equivalent) revealed ~15% clay minerals by weight of the dry suspension, whereas the <2 μm fraction of particles made up 60%. According to Perret *et al.* (1996), illite is the most common clay mineral, based on X-ray diffraction (XRD) and chemical analysis of this postglacial rock flour. Vermiculite and traces of an interstratified mineral (probably illite/vermiculite) have also been detected. The tested material consisted of silty clays (CH in United States Geological Survey (USGS) classification), none of which was retained on a 400 μm mesh, so only fine-sized particles ($\leq 75 \mu\text{m}$) were present. The organic matter was <0.5%. No changes were assumed to have occurred in the chemical characteristics of the mud during testing. For the illite-containing Jonquiere clays (Perret *et al.*, 1996), the specific surface area was determined by the methylene blue method and ranged from 63 to 67 m^2/g . Compared to the high-activity clays, the specific surface areas are very small. The specific surface area is thought to be due to the small percentage of vermiculite and montmorillonite, which have the most prominent specific surface areas. The Jonquiere clays are a good example of clayey sediment types that are frequently encountered in Québec, Canada.

High-activity clay: Na-montmorillonite-rich Wyoming bentonite clay. Bentonite, a natural Na-rich montmorillonite clay, was supplied by Black Hills Bentonite, LLC (Wyoming, USA). This clay is highly plastic and swells readily in water to form a thixotropic gel. The grain-size distribution was conducted according to the American Society for Testing and Materials (ASTM) D 422 standard. The distribution of particle sizes of <75 μm was determined by a sedimentation process using a 152H hydrometer. The bentonite sample, which exhibited a water content of ~8%, was oven dried. Forty grams of the oven-dried bentonite that had washed through a No. 200 sieve (75 μm) was weighed out. A dispersing agent of 4% sodium hexametaphosphate (known commercially as Calgon®, a suitable and convenient dispersant) solution (125 mL) was mixed with the sample. Approximately 80% of the actual particle-size distribution of the bentonite (as determined by sedimentation analysis) consisted of particles of <2 μm . X-ray diffraction showed that the mineralogy of the bentonite consisted mainly of montmorillonite and trace amounts of other minerals. The specific gravity of the bentonite sample tested was 2.6, which is lower than that of common bentonite but is within the range reported by Mitchell (1993). No data were provided for the specific surface area of the bentonite sample. The specific surface areas for montmorillonite-containing bentonite were calculated as 126.6 m^2/g for salt water and 602.1 m^2/g for fresh water (Table 1). These values were calculated from the relationship between the specific surface area and the Atterberg limits (Santamarina *et al.*, 2002).

Consistency and free swelling tests

In general, the Casagrande plasticity chart is used to classify clays (Mitchell, 1993). Both of the samples in the present study are located between the U line and the A line in that classification system. The U line is the upper limit of the relationship between the plasticity index and the liquid limits, and it lies above the A line. The Jonquiere clays are located in the boundary zone of natural soft clays without any swelling capacity. The liquid and plastic limits are the two most commonly used Atterberg limits. The liquid and plastic limits of Jonquiere clay are 51% and 22%, respectively. For the bentonite clays, the liquid limits are in the range of 100 to 360%. The plasticity indices (I_p) are in the range 80–300% for bentonite hydrated with 0 and 30 g/L NaCl solution, respectively. By definition, the liquid limit (w_L) is the water content at which the clay behavior changes from plastic to liquid. The plastic limit (w_p) is the water content at which clay starts to exhibit plastic behavior. The difference between these limits is given by I_p (the plasticity index), which is a measure of the plasticity of a clay. The liquidity index (I_L) is used for scaling the water content of a clay sample to the limits: $I_L = (w - w_p)/I_p$, where w is the water content. The liquidity index indicates the state of the clays in the field. The activity (A_c , defined as the ratio of the plasticity index to the content of clay fraction) of the bentonite is >1.2. Jonquiere clay exhibited a relatively low activity value. As expected, the high activity value of bentonite clay, 1.2 for 30 g/L and 3.9 for 0 g/L, signifies the possibility of large volume changes when wetted, and it is very reactive chemically.

Regarding the swelling capacity of bentonite, the as-received bentonite (air-dried) powder was immersed in jugs that contained either fresh water (0 g/L) or salt water (10 g/L and 30 g/L NaCl). The powder was allowed to swell freely for 24 h after dispersion. No change was observed when the clay was left for an additional six days. The swelling volumes were recorded within 24 h after the free dispersion (Table 2). Additional

Table 2. Free-swell capacity of montmorillonite-rich clay with different salinities.

No.	I	II	III
Salinity (g/L)	0	10	30
Bentonite (2 g)	1.9	1.9	1.9
Water (mL)	100	100	100
Volume (mL)	25	23	12
Free swell (%)	1216	1111	532

Free-swell tests after 7 days of hydration. Swelling capacity of bentonite hydrated with different salinities (0, 10, and 30 g/L NaCl equivalent). After 24 h of hydration, no significant change was observed.

observations were made after seven days (Jeong, 2006). When the samples were dispersed into the cylinder, the bentonite in salt water sedimented more rapidly than the bentonite in fresh water. The free swell of the powdered bentonite, as defined by ASTM D 5890, was 25 mL/2 g (0 g/L) in fresh water and 23 mL/2 g (10 g/L) and 12 mL/2g (30 g/L) in salt water. The swelling bentonite exhibits free swell values of up to 1200%. A simple measurement of the swelling capacities of bentonite in fresh water and salt water showed that bentonite swells up to twice as much in fresh water as in salt water. Similar findings were reported by Marr *et al.* (2001).

Geotechnical and rheological techniques

Basic geotechnical tests were performed on the consistency and shear strength of clays using the 60 g, 60° Swedish fall cone. The liquid limit and undrained shear strength, such as the yield strength in rheology, are best measured with the fall cone apparatus (Hansbo, 1957; Leroueil *et al.*, 1983; Locat, 1997). The rheological analysis of the natural soft clays was conducted using a Rotovisco RV-12 coaxial cylinder viscometer, which was used to apply shear rates that ranged from 0.1 to 1200 s⁻¹. Ten different rotational speeds (revolutions per minute, rpm) were used, which ranged from 1 to 512 rpm. The viscometer can operate at shear rates as high as 1200 s⁻¹ but only for fine-grained suspensions (silt and clay mixtures). The apparatus consists of two coaxially mounted cylinders in which a sample is sheared between them. The inner cylinder (rotor or bob) is equipped for measuring the torque applied on the fluid, which is contained within the outer cylinder (drum). The latter (including the temperature vessel and stand) is fixed and ensures the control of the temperature (~7°C) during shearing. Before conducting the rheological tests, the bentonite powder was dispersed progressively in either fresh or salt water (NaCl solution), and the samples were then mixed thoroughly for >10 min to ensure complete homogenization. All of the samples were mixed using a blender at a high spin rate (~3000 rpm) until the mixtures were homogeneous. Then, the samples were allowed to rest for at least 30 min to allow hydration of the clay particles. The samples were placed in a jug for 24 h, allowing sufficient time to ensure uniform mixing and build-up of the gel-like structure before testing. Except for the swelling test, the illite-rich Jonquiere clays were tested the same way. For every rheological measurement, the liquidity index (or concentration of the solid) was slowly increased up to the next desired value at a given constant salinity. All of the measurements were made at room temperature (~21°C). The procedure was described by Locat and Demers (1988). Three types of tests are generally performed: (1) steady state, (2) dynamic response, and (3) hysteresis. However, the primary intent of this work was to examine the time-dependent shear stress, which is a thixotropic feature.

RESULTS AND DISCUSSION

Flow behavior as a function of the solid concentration

Natural soft clays behave as non-Newtonian yield-stress fluids (Coussot *et al.*, 2002). The relationship between shear stress (τ) and shear rate ($\dot{\gamma}$) is shown in the linear and logarithmic plots (called flow curves) for the Jonquiere (Figure 2) and Wyoming bentonite clays (Figure 3) at the same state of liquid but with different salinities. The geotechnical and rheological properties of the selected clays are summarized in Table 3. The rheological tests of the Jonquiere clay were performed at the same liquidity index (3 g/L) and with salinities from 0.1 to 30 g/L (Figure 2). The shear stress increases rapidly toward a yield stress before increasing more slowly. Referring to the Bingham model for a given liquidity index and salinity, the yield stress and viscosity can be determined graphically. The Bingham model describes relatively well the rheological behavior at strain rates >20 s⁻¹, but it overestimates the shear stress at lower strain rates (Figures 1, 2).

As for the effect of salinity on natural inorganic clays, Locat and Demers (1988) showed that flow behavior evolves from a Bingham-like to a Casson

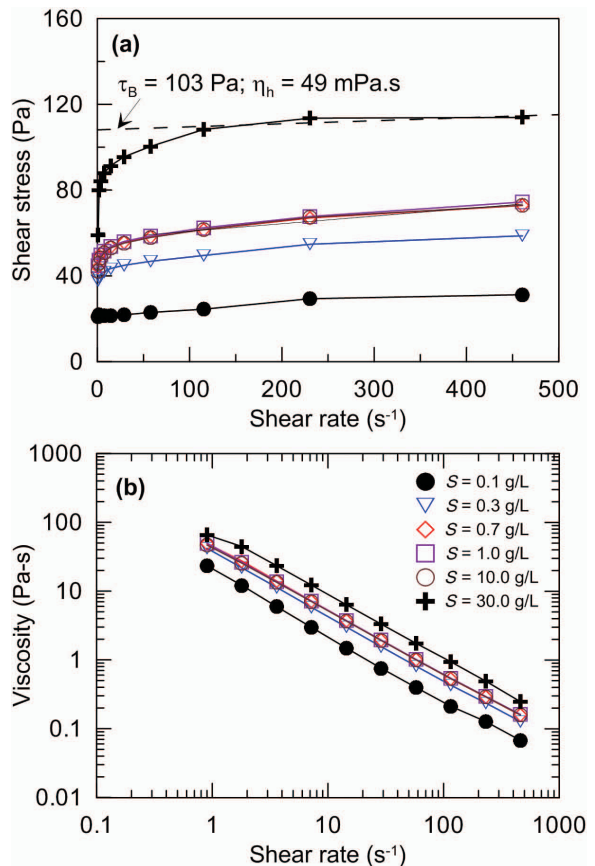


Figure 2. Flow curves of illite-rich Jonquiere clay as a function of salinity.

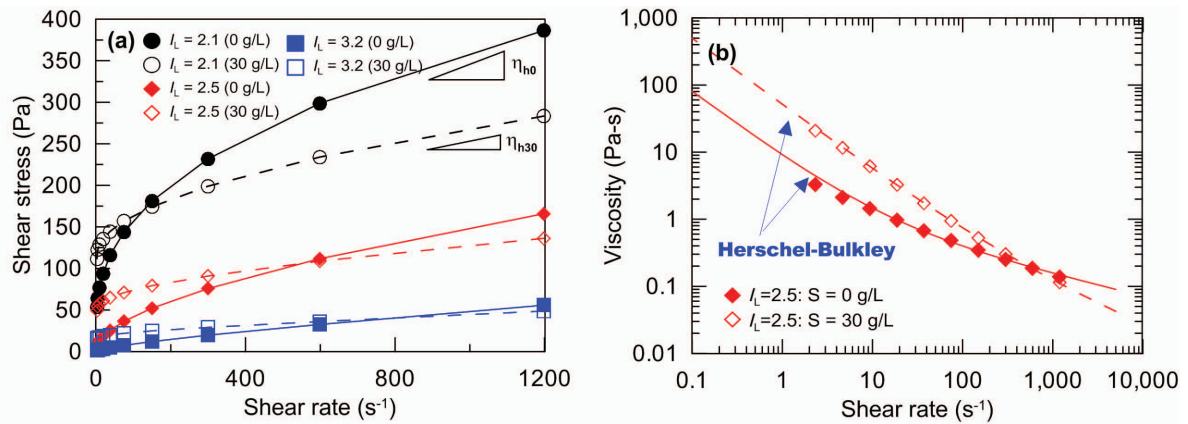


Figure 3. Flow curves of montmorillonite-rich Wyoming bentonite clay with respect to the liquidity index and salinity. η_{h0} and η_{h30} are the plastic viscosities with 0 g/L and 30 g/L, respectively.

(pseudoplastic) fluid as the salinity is increased. The illite-rich Jonquiere clay exhibited characteristics of a pseudoplastic (shear-thinning) fluid with a flow behavior index (n) that ranged from 0.1 to 0.4 for salinities ranging from 0.1 to 30 g/L with a liquidity index of 3. The rheological behavior of Jonquiere clays at low salinity (*i.e.* 0.1 g/L) shows Bingham-like behavior, but it exhibits shear-thinning behavior for increased salinity (*i.e.* 30 g/L), which may increase the critical yield values. From the rheological compilations obtained from illitic soils (Locat, 1997), a simple relationship is observed between the yield stress (τ_B , in Pa) and plastic viscosity (η_h , in mPa-s), *i.e.* $\tau_B / \eta_h = 1000$. For a given concentration of solid and similar physical boundaries, the plastic viscosity of illite-rich Jonquiere clays is given approximately by a linear relationship with the shearing resistance (Jeong, 2006). This relationship can be

obtained when the material is assumed to obey the Bingham constitutive equation.

Montmorillonite-rich clay also exhibited characteristics of a shear-thinning fluid with n values that ranged from 0.4 to 0.9 for salinities of 0 g/L (BF, bentonite in fresh water with $n = 0.4$ to 0.9) and 30 g/L (BS, bentonite in salt water with $n = 0.4$ to 0.6). The BS may result in extensive interactions between the particles and in the formation of a strong structural network relative to that formed by BF. The rheological behavior of bentonite depends, therefore, on the salt concentration and on the concentration of the particles. This finding agrees with numerous experimental works (*e.g.* Churchmann *et al.*, 2002). The rheological behavior of bentonite clays may, however, be modified in several ways. According to Van Olphen (1963, 1964), yield stress is very sensitive to small modifications in the

Table 3. The rheological properties of illite-rich Jonquiere and montmorillonite-rich clays.

I_L	S	τ_B	η_h	r^2	τ_y	K	n	r^2
Jonquiere								
3	0.1	23.5	17.9	0.934	15.0	4.8	0.165	0.791
3	0.3	47.5	25.2	0.854	37.7	1.9	0.393	0.976
3	0.7	58.6	31.6	0.824	44.1	4.2	0.306	0.997
3	1.0	59.0	34.0	0.831	44.7	3.3	0.360	0.997
3	10	58.8	31.5	0.789	42.1	3.8	0.349	0.975
3	30	103.2	48.7	0.707	44.0	8.5	0.228	0.985
Bentonite								
2.1	0	148.4	255.6	0.891	53.5	8.3	0.534	0.991
2.5	0	48.6	98.9	0.954	7.7	1.5	0.670	0.996
3.1	0	8.1	34.4	0.989	1.3	0.2	0.823	0.995
2.1	30	192.1	159.9	0.904	133.6	7.1	0.481	1.000
2.6	30	77.1	49.8	0.929	48.9	2.9	0.471	0.999
3.2	30	22.7	21.7	0.961	15.1	0.6	0.564	0.997

I_L = Liquidity index, S = Salinity (g/L), τ_B = Bingham yield stress (Pa), η_h = Bingham viscosity (mPa-s), τ_y = Herschel-Bulkley yield stress, K = Consistency, n = flow behavior index (sometimes referred to as the 'strength parameter').

initial conditions of pH and electrolyte concentration. For example, when bentonite drilling fluids are adjusted, bentonite is added to water in quantities that vary from 3 to 7 wt.% (Kelessidis *et al.*, 2007). At the same solid concentration, this flow behavior can be characterized by salinity. The similarities and differences between illite-rich and montmorillonite-rich clays in terms of geotechnical and rheological behavior are discussed in the following section.

Flow behavior as a function of salinity

The flow behavior of illite-rich Jonquiere clay showed that the difference induced by an increase in salinity is somewhat small, even though uncertainty exists in the measurement of the viscosity at the lowest shear rate of $\sim 1 \text{ s}^{-1}$ (Figure 2b). In most cases, natural inorganic clays (illitic and montmorillonitic clays) behave as pseudoplastic fluids (*i.e.* the viscosity decreases with increasing shear rate), which is consistent with the Herschel-Bulkley model with an n exponent of < 1 . Compared to the behavior of the illite-rich clay, the montmorillonite-rich clay demonstrated that the structural change induced by the addition of salinity is significant for a given state of clay (*i.e.* the same liquidity indices of 2.1, 2.5, and 3.2). The BF exhibited characteristics of being intermediate between the Bingham and shear-thinning fluid. However, the rheological behavior of BS was most likely to be pseudoplastic (*i.e.* shear-thinning with no yield stress value), which indicates that the bentonite clay exhibited special characteristics, such as negative electric charge, grain size, very large specific surface area, and high sensitivity to hydration. A significant increase in the yield stress occurs as a result of an increase in the salinity of bentonite and assuming that the materials behave as the Bingham fluid. However, the opposite result is observed

for the variation in the plastic viscosity. The viscosity of BF exhibited a larger value than that of BS, particularly for relatively low and high shear rates (dashed line in Figure 3a). For the bentonite clay with a liquidity index of 2.5 with different salinities, the experimental data was fitted with the Herschel-Bulkley model (Figure 3b) over a shear-rate range of 0 to $1200 \text{ (s}^{-1}\text{)}$. The Herschel-Bulkley model fitted the experimental data much better than the other models, such as the Bingham model, the power-law, and the Carreau function. In general, the Bingham model is well fitted at very low concentrations of solid (or high water content) and low salinity. For the power law, the rheological behavior is well defined wherever the yield stress is negligible, which occurs when the viscous characteristics primarily govern the rheological behavior of fine-particle suspensions. At high shear rates, the power-law model may deviate slightly from the experimental data.

Under the assumption that the material behaves as a Herschel-Bulkley fluid, the relationship between the rheological properties and the solid concentration (Figure 4) revealed that the rheological properties (*i.e.* yield stress, τ_y , and consistency, K) of bentonite clays varied linearly in a semi-log plot with the volumetric solid concentration (C_{vs}), which ranged from 3 to 6% for BF and from 10 to 16% for BS. The determination of the yield stress and the viscosity of the selected materials (Table 3) revealed similar trends, but a difference was observed in terms of the clay minerals. The rheological properties with respect to the changes in salinity were compared. The lowest values of the rheological parameters were obtained at $\sim 3.5\%$ ($w = 994\%$) for BF and 10% ($w = 340\%$) for BS. The difference in the yield stress (τ_y) was significant at the same concentration of solid (*e.g.* at $C_{vs} = 10\%$). In each case, the bentonite clays presented a trend that is similar to previously

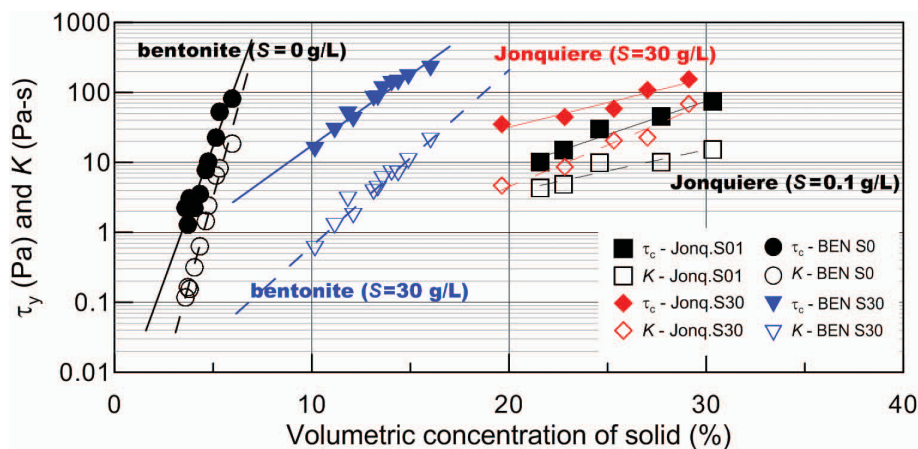


Figure 4. Rheological properties (yield stress and consistency, K , obtained from the Herschel-Bulkley function) as a function of the volumetric concentration of solid (%) and salinity (g/L). BEN.S0 = bentonite hydrated with 0 g/L salinity, BEN.S30 = bentonite hydrated with 30 g/L salinity, Jonq.S01 = Jonquiere clays with 0.1 g/L salinity, and Jonq.S30 = Jonquiere clays with 30 g/L salinity. Volumetric concentration of solid is C_{vs} (%). Data from Jeong (2006).

reported results (O'Brien and Julien, 1988), whereas the rheological properties of BF increased more rapidly with C_{vs} than those of BS. This behavior occurred because, in salt water, the interactions between particle–particle associations in montmorillonite may be large flocculated units that lead to large flow channels and high permeability. At the same rheological properties, the C_{vs} of BF can be up to three times lower than that of BS. In the case of highly dispersed bentonite, the rheological properties must be determined carefully and compared to select the best model. Bentonite in fresh water exhibited shear-thinning behavior at high shear rates but an ideal plastic behavior at low shear rates. Similarly, for the materials with large particle sizes, the rheological models could show a wide gap between the theoretical fits and the experimental data at low shear rates (Jeong, 2006). The behavior of bentonite in salt water was very similar to that of non-swelling soft clays, and this may be due to sufficiently strong particle–particle interac-

tions (*i.e.* edge and/or face mode of particle association) caused by salinity.

Effect of salinity on the liquid limit and yield strength

The rheological behavior of fine-grained suspensions, such as clays and silts, is rate- and time-dependent and could be influenced by physico-chemical properties (Jeong *et al.*, 2009, 2010). A schematic view of the geotechnical and rheological characterizations (Figures 5, 6) of the two types of clay minerals is presented for illite and montmorillonite clays. The influence of the physico-chemical characteristics of the low-activity and high-activity clays (*i.e.* swelling and non-swelling clays, respectively) may be explained by the relationship between the liquidity index (I_L) and the remolded shear strength (C_{ur} , kPa). This relationship can be determined by simple geotechnical instruments, such as a fall cone or an unconfined compression tester. The values of the remolded shear strength of clays are expected to be very close to the yield stress (Locat and

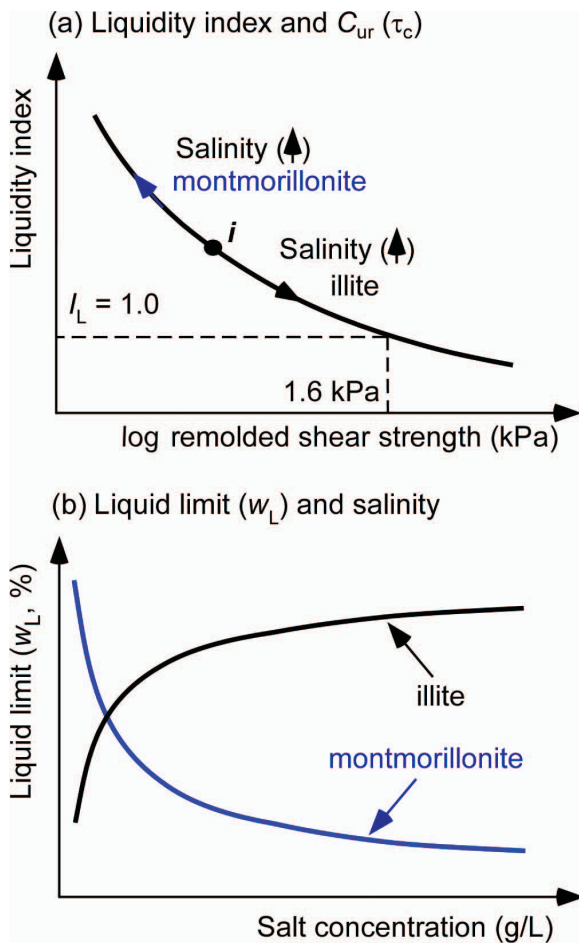


Figure 5. Geotechnical and rheological characterization of two different types of clay minerals: (1) illite; and (2) montmorillonite. *i* is an initial starting point. The arrow indicates an increase in the physical quantities.

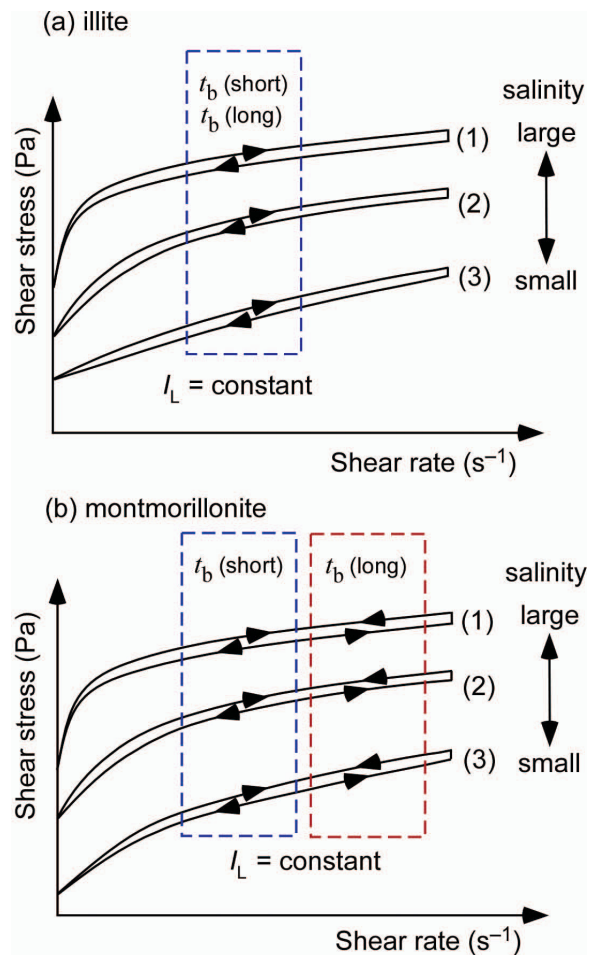


Figure 6. Shear rate dependency of the flow behavior: yield stress, thixotropy, and rheology of clays.

Demers, 1988). The typical relationship between the liquidity index and the remolded undrained shear strength can be measured using a Swedish fall cone (Figure 5a). For illitic clays, an increase in salinity generally results in an increase in the remolded shear strength at a given liquidity index (e.g. Leroueil *et al.*, 1983; Locat and Demers, 1988; Jeong, 2006). Given that the liquidity index (I_L) is equal to unity, the remolded shear strength is 1.6 kPa (Leroueil *et al.*, 1983). Depending on whether the liquidity index is greater or less than 1, the shear strength may depend strongly on the soil mineralogy, mainly because of the structural difference of the clay minerals. According to Terzaghi *et al.* (1996), bentonite in fresh water exhibits small flow channels and a low permeability. The bentonite swelling properties are highly degraded by concentrated salt solutions, with higher electrolyte concentrations producing lower void ratios and a more flocculated clay fabric (Petrov and Rowe, 1997).

The effect of salinity (Figure 5b) on the index properties was compared. Illite and montmorillonite are known to have opposite responses to salinity. For illitic soils (Locat, 1982), the liquid limits of the Québec clays increased slightly with increasing salinity. For the Drammen plastic clay, similar test results were presented by Torrance (1974). However, the salinity exhibits a significant effect on the liquid limit of the swelling bentonite clay. For montmorillonitic soils, the NaCl concentration is generally inversely proportional to the liquid limit (Petrov and Rowe, 1997; Schmitz and van Paassen, 2003; Jeong, 2006). Consequently, a reduction in the remolded shear strength may occur because of the increase in salinity. Due to double-layer compression and *c*-axis contraction (van Olphen, 1963; Luckham and Rossi, 1999), the addition of salt causes a significant decrease in the liquid limits. Thus, the liquid limit decreased ~2.5-fold when the salinity is varied from 0 to 30 g/L. According to van Olphen (1963), a small change in the NaCl concentration can influence the index properties (e.g. liquidity index) and the rheological properties (e.g. yield stress and viscosity) of bentonite clay. The author demonstrated that the Bingham yield stress decreases sharply with the addition of a few milliequivalents per liter of NaCl, which indicates some degree of deflocculation. With a further increase in the salt concentration, the viscosity and yield stress increase gradually. The apparent viscosity of clay or sand alone decrease after the initial stress-induced liquefaction, unlike quicksand, in which salt is an essential ingredient for the destabilization of the granular network (Khaldoun *et al.*, 2005).

Using the hysteresis loop, the time-dependent rheological behavior should be taken into account for the materials that are strongly dependent on the type of clay mineral. The results revealed (Figure 6) that the rheological response was related significantly to the hysteresis loop of the natural clays. The cycle of upward

and downward flow curves can be shown at the same physicochemical boundary. The arrows indicate the directions of the upward and downward shear rates in the flow curves. Based on the three flow curves with different salinities, the difference in the shear stress ($\Delta\tau$) can be expressed as a function of the time factor (t_b). The time factor is defined here as the shearing time (min) at the highest shear rate (i.e. 512 rpm). For illitic soils, similar results were presented by Perret *et al.* (1996), who defined the thixotropic behavior observed for the Jonquiere clay slurry (Figure 6a). The steady-state condition apparently was reached in a relatively short period of time (<60 min of shearing at a high speed). Salinity can also be affected by the hysteresis loop areas, which may relate to the thixotropy and gelation at very low shear rates (Perret *et al.*, 1996; Locat, 1997). In general, an increase in salinity provides a larger apparent yield stress and smaller viscosity with a smaller hysteresis loop area. The flow curve observed for the illitic soils was similar to that observed for the material with large particles (e.g. larger than clay, but much smaller than gravel) over a long period of shearing. Because the fine-particle suspensions contained a large amount of clay minerals, the materials favor thixotropic effects (Schatzmann *et al.*, 2003). However, some fluids are known to be anti-thixotropic (i.e. rheopectic, viscosity increases with time), such as the shear-thickening properties of colloidal suspensions.

The time-dependent, thixotropic behavior of bentonite clay was investigated further. For the soils sheared at the highest shear rate (512 rpm), a significant change in the shear stress ($\Delta\tau$) occurred for the short and long shearing times, t_b (Figure 6b). For very short periods of shearing (t_b short), bentonite clay behaves as a thixotrope, like the Jonquiere clay. For relatively long periods of shearing (t_b long), bentonite clay behaves quite differently.

Prior to the test of the time-dependent behavior, steady-state measurements of both clays were performed (Figures 7, 8) at a strain rate of 512 rpm. A steady-state condition in illite-rich Jonquiere clay was reached within 30 min, and was reached in <10 min when the salinity was decreased. Similar results were observed for low-activity clays when the solid concentration was decreased (Jeong, 2006). In increasing shear mode, the soil structure broke down with application of increasing shear stress (Figure 6). Therefore, as the applied stress increased, more of the soil structure was broken down. Consequently, lower yield stress and viscosity were obtained. The soil exhibited thixotropic behavior. Most of the illitic soils belong to this category. Interestingly, the steady-state measurements that were obtained from bentonite clay exhibited different results (Figure 8). The viscosity increased with an increase in the shearing time. However, the variation in the viscosity (or shear stress) is less sensitive when the clays have a low solid concentration and low salinity (Figure 8). These findings

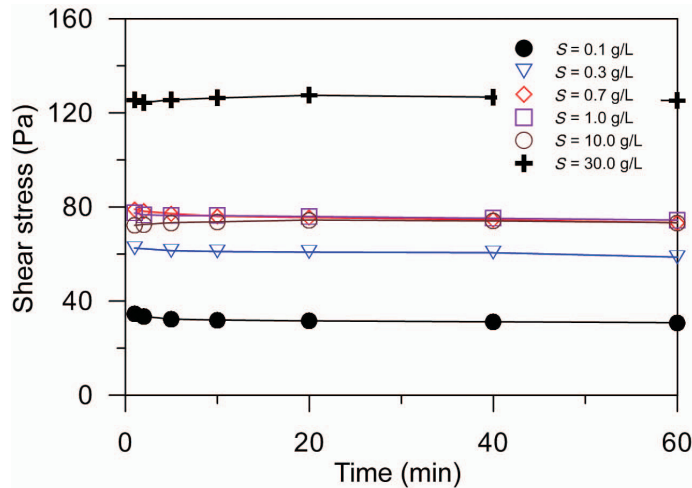


Figure 7. Steady-state measurements of illite-rich Jonquiere clay ($t_b = 15$ s).

agree with those of Legrand and Da Costa (1990), who also reported that the viscous characteristics of bentonite muds were affected strongly by shear velocity. The structural breakdown caused by shearing provided an important decrease in the viscosity for different solid concentrations. Montmorillonite-rich clay also revealed a strong thixotropic behavior for a relatively short period of shearing (*e.g.* before 1 h of shearing). As noted by Jeong (2006), a steady state seems to be reached after 6 h.

The hysteresis of illite-rich and montmorillonite-rich clays was examined. For the hysteresis curves of the illite-rich clay (Figure 9) and the montmorillonite-rich clay (Figure 10), the maximum shear time was given by $t_b = 15$ s. For both samples, the paths of the upward (solid line) and downward (dashed line) curves were nearly identical. The clay suspension presented a yield stress but no thixotropy, which indicates that the fluids

were less sensitive to the shearing time. The Wyoming bentonite clays were compared as a function of salinity and the time factor t_b (Figures 11 and 12, respectively). The thixotropic behavior was very similar to the illite-rich clays, irrespective of salinity, when the sample was sheared for a relatively short period of time, such as $t_b = 15$ s. However, for $t_b = 300$ s, a hysteresis loop occurred for the highest shear rate, which means the thixotropic areas increased with shearing time. As illustrated in the figure, the sample exhibited rheopectic behavior, irrespective of salinity. The viscous nature of the montmorillonite-rich clays increased progressively over a similar range of initial and final water contents. For the rare cases of long periods of pre-shearing, a high shear rate was required to reach a steady-state condition, and this may be one of the sources of uncertainty in the determination of the yield stress. Thus, the time factor

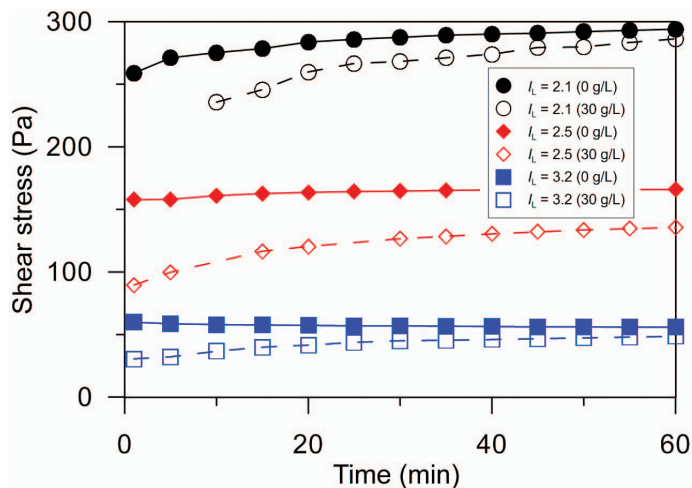


Figure 8. Steady-state measurements of montmorillonite-rich clay ($t_b = 15$ s).

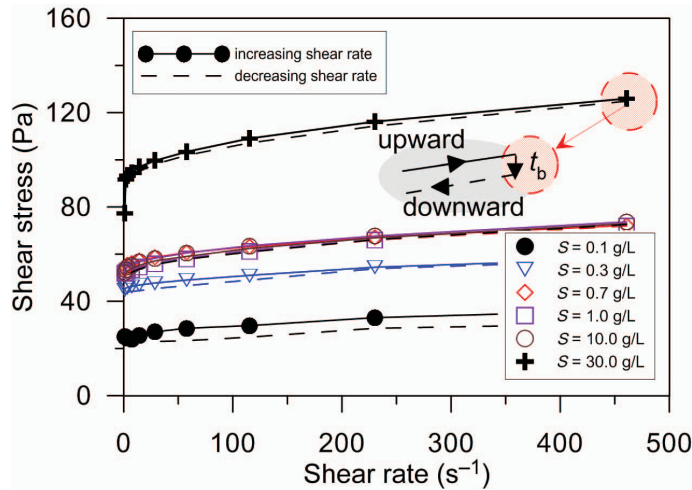


Figure 9. Time-dependent behavior of illite-rich Jonquiere clay ($t_b = 15$ s).

may be an important parameter of low-activity and high-activity clays for describing specific soil behavior.

These results may also be related to the difficulty of measuring yield stress in practice. Most of the difficulties could be removed when taking the thixotropy of yield stress fluids into account (Møller *et al.*, 2006; Bonn and Denn, 2009). Many advances have been made in rheophysics, but measuring and modeling the time-dependent flow behavior of colloidal suspensions to describe the physical phenomena of the structure remain challenging (Mewis and Wagner, 2009). Yield stress fluids react as a solid at low stress levels but behave like a liquid at high stress levels. The yield stress indicates the stability of the network structure against shearing forces. Thus, the yielding state is associated with the intensity and number of bonds between bentonite particles (Legrand and Da Costa,

1990; Penner and Lagaly, 2000). To understand the structural buildup and breakdown as it develops during the flow history, the rheological properties should be defined. A general phenomenological characterization of illite-rich and montmorillonite-rich clays is reported in this paper with respect to variations in the salt concentration, shearing value, and duration. The structure builds on the attractive forces between particles, which are influenced by the salt concentration for a given solid concentration. In addition, the time-dependent thixotropic and rheopectic behavior can be affected by the experimental conditions. The fundamental issue about the flow properties of yield stress fluids remains a significant challenge, *e.g.* competition between aging and rejuvenation, shear banding, and time dependency (Coussot *et al.*, 2002; Møller *et al.*, 2008; Khaldoun *et al.*, 2009).

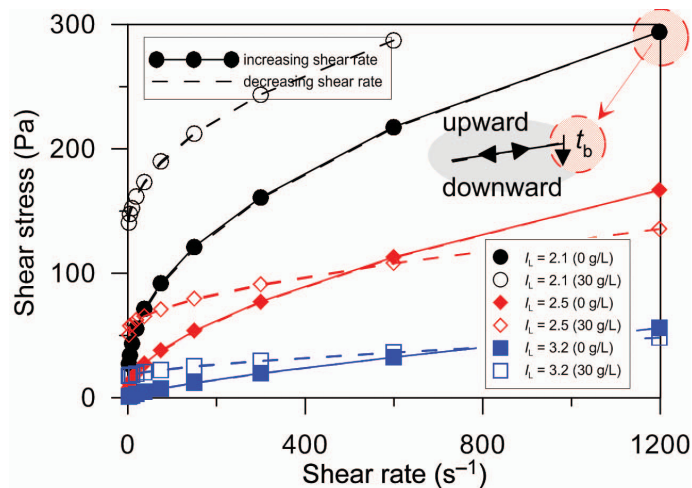


Figure 10. Time-dependent behavior of montmorillonite-rich clay ($t_b = 15$ s).

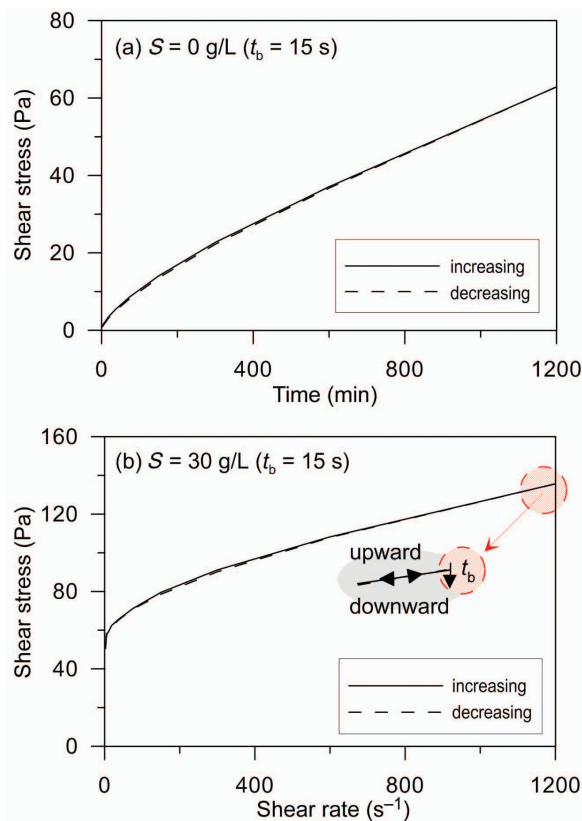


Figure 11. Time-dependent behavior of montmorillonite-rich clay as a function of salinity ($t_b = 15$ s).

CONCLUSIONS

The rheological behavior of illite-rich (Jonquiere) and montmorillonite-rich (Wyoming bentonite) clays were studied in the presence of NaCl. The results revealed that the clays exhibit time-dependent, non-Newtonian behavior. The flow curves were better fitted by the Herschel-Bulkley model than by the perfect plastic Bingham model. Compared to the rheological behavior of illite-rich Jonquiere clay, a test program to ascertain the influence of montmorillonite-rich clay on the rheological behavior was conducted. The rheological properties varied because of the salinity and shearing time at the same solid concentration. For a given salinity, the clays were affected by the shear rate and the duration of shearing. For both clays, the residual shear strength in soil mechanics was very close to the yield strength in rheology. The structure can be explained by the rheological measurements. The illite-rich clays exhibited a viscoplastic-like behavior for low concentrations of solid and low salinity, and they showed a fundamental characteristic of a shear-thinning fluid at relatively high salinity, which is consistent with the Herschel-Bulkley model. However, the rheological behavior of the montmorillonite-rich clay was affected significantly by increased salinity, most notably at high shear rates. Thus, the montmorillonite-rich clays showed

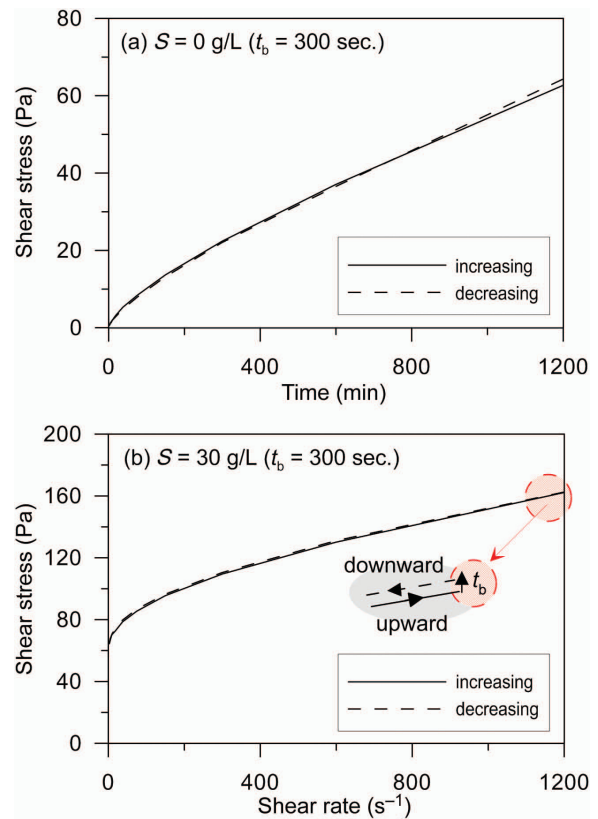


Figure 12. Time-dependent behavior of montmorillonite-rich clay as a function of salinity ($t_b = 300$ s).

significant changes in the apparent yield stress and plastic viscosity with increasing salinity. The clays differed in their thixotropic behavior. At the highest shear rates, the viscosity of the illite-rich clays decreased with an increase in the elapsed time, but the viscosity of the montmorillonite-rich clays increased with an increase in the elapsed time, which may be due to the change in the particle–particle associations.

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