EFFECTS OF THE NATURE OF THE EXCHANGEABLE CATION AND CLAY CONCENTRATION ON THE RHEOLOGICAL PROPERTIES OF SMECTITE SUSPENSIONS

C. Malfoy[1,*], A. Pantet[1,†], P. Monnet[2,†] and D. Righi[1]

[1] Université de Poitiers, HydrASA, UMR 6532, 40 avenue du recteur Pineau, 86022 Poitiers, France
[2] Université de Poitiers, LEA, UMR 6609, Boulevard Marie et Pierre Curie, 86962 Futuroscope cedex, France

Abstract—The rheological characteristics of purified bentonite suspensions as a function of exchangeable cation (Ca^{2+}, NH_4^+, Li^+) are studied at three different clay concentrations (40 gL^{-1}, 60 gL^{-1}, 80 gL^{-1}). A Herschel-Bulkley model is used to determine rheological parameters such as yield value, consistency and fluidification index. The flow curves are typical for shear thinning fluids but differ on two points; presence of yield stress and/or thixotropy. The Li suspensions are not yield stress fluid, and the thixotropy is weakly expressed only for the 80 gL^{-1} suspension. On the contrary, Ca-clay suspension flow curves always present yield stress and a large thixotropic area. The NH_4-clay suspensions exhibit an intermediate behavior as there is no thixotropy, but a yield stress appears for the most concentrated suspension. These differences in macroscopic mechanical properties are discussed with reference to the suggested microscopic clay organization in suspension.

Key Words—Bentonite, Clay Suspensions, Exchangeable Cation, Mechanical Properties, Montmorillonite, Rheology.

INTRODUCTION

Bentonites are natural clay materials with specific properties such as swelling, adsorption, large surface area, fine-sized particles which are used in various industries such as cosmetics, paint, pharmaceutical, oenology, *etc*. Mixed with water (usually in concentrations of 20 to 80 gL^{-1}), they form drilling muds which are employed in the oil industry and civil engineering activities such as tunnelling, horizontal directional drilling, *etc*. The mechanical characteristics of these complex clay-water systems enable this work to be done in safety and at lower cost.

Bentonite suspensions develop colloidal properties arising from a three-dimensional organization of the clay-water system which behaves as a viscoelastic fluid. The mechanism involves hydration of clay and then associations and interactions between particles exhibiting various morphologies. Previous studies on water-saturated montmorillonite pastes (Tessier, 1984, 1990; Touret, 1988) suggested that three structural scales of organization could be considered: (1) parallel stacking of layers creating more or less thick particles with more or less expanded interlayers; (2) mutual ordering of particles forming aggregates; and (3) mutual ordering of aggregates forming a 3D network. The sizes of particles and aggregates are essentially conditioned by the type of exchangeable cation and the amount and location of layer charge. Transmission electron microscopy (TEM) images of these materials showed that the mode of association of clay particles is strongly related to the nature of the interlayer cation. Textural analysis of these water-saturated samples (size and compaction of components, distribution of the pore space, *etc*.) helps to explain the various types of mechanical behavior.

Interactions and organization between colloidal particles are governed by two types of force; attractive (Van Der Waals forces) and repulsive (Born forces, osmotic stress due to the double diffuse layer, solvation). The DLVO (Derjaguin-Landau-Verwey-Overbeek) theory (Coussot and Ancey, 1999) estimates the conditions of stability of clay suspensions by calculating the balance between the repulsive and attractive forces, according to the inter-particle distance, and by taking into account Brownian motion and particle diffusion. The mechanical properties of bentonite suspensions characterize – at a macroscopic scale – the relationship existing between these forces, the spatial ordering and dynamics of clay particles in suspension.

Only a few studies include both mineralogical characterization and rheological investigations of bentonite suspensions (Keren, 1988, 1989; Güven and Pollastro, 1992; Heller and Keren, 2001; Penner and Lagaly, 2001). Most of these works deal with dilute suspensions (<25 gL^{-1}) and compare mechanical behavior of Ca- and Na-bentonite suspensions. This is because Ca-bentonites are of common occurrence in the geological environment while Na-bentonites are industrial materials obtained by 'activation' of the Ca-forms in order to enhance their performances when used

* E-mail address of corresponding author:
christine.malfoy@hydr asa.univ-poitiers.fr
† Groupe Géomécanique et Génie Civil de Poitiers

Table 1. Normalized chemical composition (oxides %); and CEC of initial raw bentonite Volclay (Ecoclay project final report, EUR 19609, 2000).

SiO_2	Al_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	Fe_2O_3	Total	CEC (meq/100 g)
67.25	21.25	0.00	2.74	1.63	2.44	0.68	0.23	4.06	100	63.21

as muds. Numerous works investigate the relationship between the stability of suspensions and electrolyte concentration, or pH variation. The colloidal organization of clay suspensions cannot be observed directly but can be deduced from their mechanical behavior. Rheology and rheophysics (simultaneous study of the rheological and structural properties of the material, at rest or under flow) may be useful in elucidating these structures.

Ramsay and Linder (1993) and Morvan *et al.* (1994) succeeded in measuring fractal objects by associating flow parameter measurements and ultrasmall- and small-angle X-ray scattering data on Na-smectite suspensions. The same investigations were determined with a synthetic clay (Laponite). However, such an approach was never tested on smectite clay saturated with various cations.

To understand the relationship between the micro-structure (or microtexture) of clays and their macroscopic mechanical behavior, it seems necessary to link knowledge acquired from mineralogical and mechanical studies. Here we perform a comprehensive physicochemical and rheological study on a commercial bentonite (Volclay) previously described as MX-80 (Ecoclay final report, 2000). Specifically, we investigate the impact of interlayer exchangeable cation and increasing clay content on the mechanical properties of smectite suspensions.
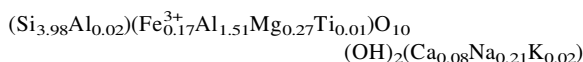
MATERIALS AND METHODS

Starting material and preliminary purification of samples

Preliminary treatments of the bentonite material may have a significant impact on the experimental results. Such treatments may modify or destroy some aspects of the original material. Moreover, commercial bentonites are heterogeneous and often 'activated' by additions of soluble salts, including calcite, which may be dissolved during suspension preparation. The expected electrolyte concentration and composition of exchangeable cations could be disturbed. Here, we 'purify' our material only by separating the <2 μm fraction. This is because decarbonation and dissolution of soluble salts are time consuming, and the determination of the mechanical measurements requires several hundred grams of powder for a complete study.

The material used is the clay fraction (<2 μm) of Volclay bentonite (Table 1, Figure 1) which consists mainly of montmorillonite with minor amounts of

quartz, K-feldspar, plagioclase and mica. The structural formula is (Ecoclay project final report, EUR 19609, 2000):

$$(Si_{3.98}Al_{0.02})(Fe^{3+}_{0.17}Al_{1.51}Mg_{0.27}Ti_{0.01})O_{10}$$
$$(OH)_2(Ca_{0.08}Na_{0.21}K_{0.02})$$

The <2 μm fraction was separated from the bulk sample by centrifugation and then Ca saturated using 1 N $CaCl_2$ solution. The Ca-clay obtained was washed with distilled water until the solution was free of chloride (negative test with $AgNO_3$). Finally, the purified product was air dried at 60ºC and pulverized mechanically. Since Besq (2000) showed that the rheological properties of bentonite suspensions can be affected by storage conditions, the bulk clay sample was stored as small individual 5 g subsamples in hermetically sealed boxes at 20ºC.

The clay samples were saturated with three cations: Ca^{2+}, NH_4^+ or Li^+. Li- and NH_4-clays were prepared from the initial Ca-saturated material by two contacts of 1 h each and one contact of 48 h with 1 M LiCl and 1 M NH_4Cl solutions and then washed until Cl-free as indicated previously.

The choice of cations was motivated by the following reasons: (1) to investigate the effect of cation valency; and (2) to investigate two types of monovalent cations having different hydration energy. It is well known that the nature of the interlayer cation has a significant influence on the interlayer expansion of smectites in water, as it does on the association of clay layers (Sposito, 1984; McBride, 1994).
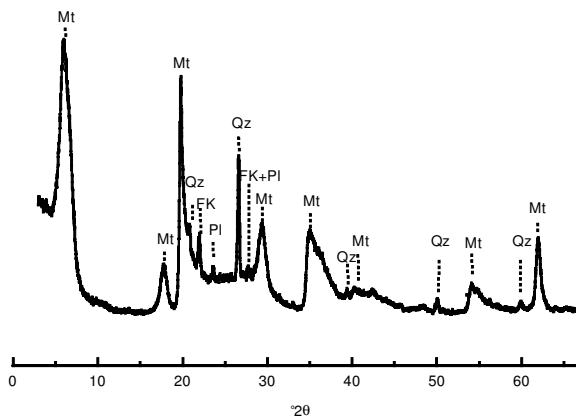

Figure 1. XRD pattern of randomly oriented powder of the <2 μm Volclay bentonite. (Mt: montmorillonite; Mi: micas; Pl: plagioclase; Qz: quartz; Fk: K-feldspar.)

Preparation of the suspensions

The mixing procedure of clay powder with water was strictly controlled as it influences the rheological behavior of the resulting suspension (Viseras *et al.*, 1999; Malfoy *et al.*, 2001). The solvent was distilled water and, as we wish to work at very low electrolyte concentration, the equilibrium pH was not modified by addition of any acid or base. The clay powder was hand-shaken with 45 mL of distilled water and the resulting suspension treated with an ultrasonic probe for 7 min 30 s, at half maximum intensity and using a pulse mode of 5 s sonification followed by 5 s relaxation (Fisher Bioblock Scientific 750 W sonicator). Three concentrations were prepared: $40~\mathrm{gL}^{-1}$, $60~\mathrm{gL}^{-1}$, $80~\mathrm{gL}^{-1}$ (4%, 6%, 8% w/w, respectively). The suspensions were left at rest for 24 h to ensure total hydration of the material. An important requirement when performing a rheological study is that the suspensions must be stable with time, which requires a sufficient mixing energy.

Methods of analysis

A Reologica-Stresstech HR control stress rheometer was used with coaxial cylinders geometry. To avoid water evaporation, a film of weakly viscous silicon oil (Rhodia 47 V5) was spread on the upper free surface of the suspension ($T = 20^{\circ}\mathrm{C}$).

The experimental flow curves were obtained using the 'quick flow curve' procedure of Besq (2000). In order that the samples would be in the same initial structural state, the procedure started with a shearing stage at a shear rate of $500~\mathrm{s}^{-1}$ for 240 s, followed by a rest period of 600 s. The resulting particle associations are assumed to be the initial structural state. Then, the material was subjected to increasing and decreasing shear stress gradients for 30 min. For a given shear stress value the difference (if any) between the shear rate values obtained with the increase and decrease modes reveals the thixotropic properties of the fluid. The area between the increasing and decreasing curves defines the thixotropic area.

Flow curves from clay-water suspensions exhibit yield stress and thixotropic behavior (Pignon *et al.*, 1996; Ramsay and Linder, 1993). The suspensions are viscoelastic fluids which behave either as solids or liquids according to the applied shear stress. The critical value of stress for shifting from solid to liquid behavior defines the yield value τ_0.

In many studies the yield value is extrapolated by fitting the flow curves at low shear rate with the Bingham law:

$$\tau = \tau_0 + \mu\dot{\gamma} \qquad (1)$$

τ is the shear stress, τ_0 is the yield stress value, μ is the Bingham viscosity and $\dot{\gamma}$ the shear rate. The ratio $\tau/\dot{\gamma}$ defines the apparent viscosity of the suspension. However, in agreement with Pignon *et al.* (1996) and

Coussot (1997) who reported that the behavior of clay-water suspensions are best described by the Herschel-Bulkley (HB) law, we chose to apply the HB model for our rheological data processing. This choice was supported by the goodness of fit and the simplicity and efficiency of this model.

$\tau = \tau_0 + k\dot{\gamma}^n$ is the Herschel-Bulkley model expression   (2)

k (consistency) and n (fluidification index) are characteristic values of the fluid ($n < 1$ for shear thinning fluids; *i.e.* the viscosity of the fluid decreases as shear rate increases for stable flow. The parameters of the HB model are given in two stages from the experimental data: (1) yield stress values (τ_0) are obtained by extrapolation of the linear part of the flow curve, at low shear rate, in the semi-logarithmic representation; (2) k (consistency) and n (fluidification index) are obtained by quadratic minimization using the yield stress value obtained in stage 1.

RESULTS

The preparation procedure allows us to obtain clay suspensions that are stable for at least 1 week in the case of Li- and NH_4-clay suspensions but only for 3 days for Ca-clay suspensions. Moreover, the macroscopic aspect and behavior appear to be different according to the exchangeable cation and clay concentration.

The Ca- and NH_4-clay suspensions are weakly viscous fluids while Li-clay adheres to the sample box. The $80~\mathrm{gL}^{-1}$ Li suspension does not flow even when the sample box is inverted.

Flow curves are displayed with both an arithmetic as well as a semi-logarithmic scale. Such representation allows us to display flow phases and yield stress values more precisely (Figures 2, 3, 4).

All suspensions produced flow curves typical of shear thinning fluids (non-Newtonian fluid) but the curves differ in two important ways: presence of a yield stress and/or thixotropy. Except for the 8% NH_4-clay suspension that exhibits an apparent yield stress not present at lower concentrations, increasing the clay concentration does not change the general pattern of the curve but emphasizes the observed behavior.

An apparent yield stress is noticed for Ca-clay suspensions at all concentrations while it never appears for Li-clay suspensions. The major difference observed between the various curves is the presence of a thixotropic area for Ca-clay suspensions, at all concentrations, which does not exist for other suspensions except, and weakly expressed, for the 8% suspension of Li-clay.

For Ca-clay suspensions the flow curve (Figure 5), in increasing shear stress mode, presents three sections which are more developed as the clay particles content increases. At low shear rate, the first section (Figure 5, section 1) could be attributed to the destruction of a
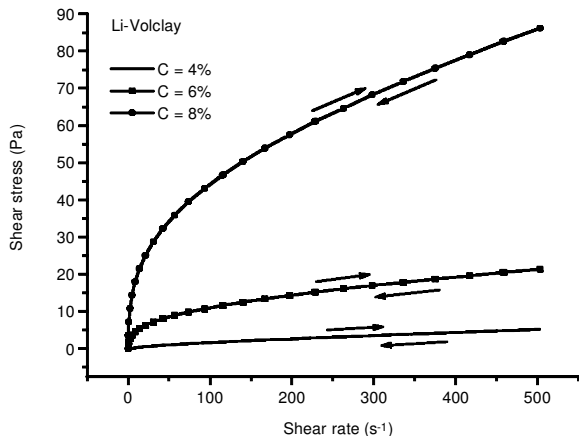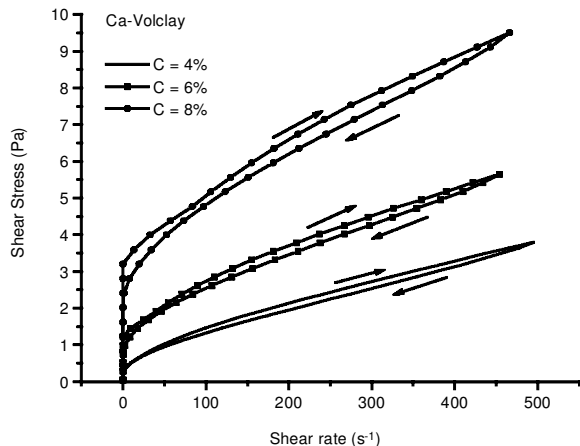
Figure 2. Flow curves of Ca-clay suspensions at 4%, 6%, 8%.

Figure 3. Flow curves of Li-clay suspensions at 4%, 6%, 8%.

poorly resistant structure or to measurement artefacts (slip at the wall or fracturing) as previously observed by Magnin and Piau (1990).

After the overstep of the yield value, section 2 (Figure 5) indicates a fast fluidification of the material. It is then possible to define the extrapolated yield value, T_0, by extrapolation of the linear part of the curve. Finally, we observe a Herschel-Bulkley type (section 3) indicating a slow fluidification. Flow curves in decreasing shear stress are regular. Thixotropic areas increase with clay concentration.

Table 2 presents the values of the parameters calculated with the Herschel-Bulkley model. As expected, the yield value, the consistency and the viscosity of the suspensions increase with concentration. The fluidification index n remains constant which indicates that even if the concentration increases, the suspension keeps the same degree of fluidity.

For Li- and NH_4-clay suspensions at 4 and 6% concentration (Figures 3 and 4, Table 2) the flow curves in increasing shear rate mode show a very progressive fluidification. However, the stress required to obtain
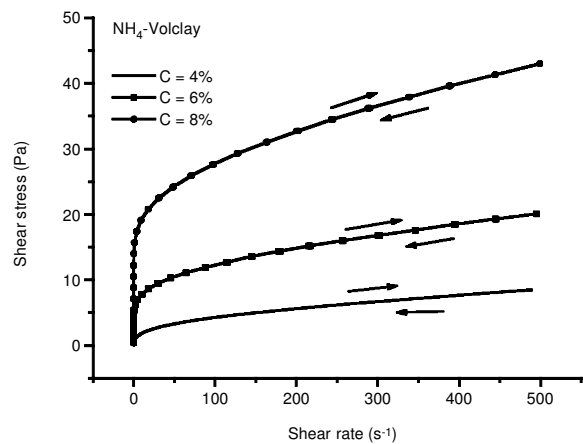
equivalent shear rates is slightly weaker for the NH_4-clay suspensions. At 8% concentration, the NH_4-clay suspension presents a yield stress but no thixotropy, whereas Li-clay suspension is slightly thixotropic but without any yield stress (Figure 6). The consistency increases with concentration while fluidification index decreases for Li- and NH_4-clay suspensions (Table 2).

Figure 7 and Table 2 show the change in the apparent viscosity of suspensions, measured at $500 \ s^{-1}$, according to the exchangeable cation and clay concentration.

At 4% concentration, all suspensions show very similar viscosities. The viscosities increase with clay concentration, but the increase pattern differs with the exchangeable cation.

In the 4–8% range of concentration, the increase of viscosity is almost linear for Ca- and NH_4-clay suspensions. However, the increase of viscosity remains very moderate for the Ca-clay suspensions (the suspension at 8% is only three times more viscous than the suspension

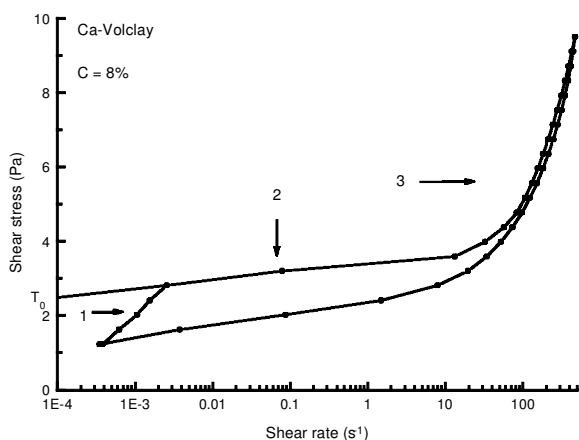Figure 4. Flow curves of NH_4-clay suspensions at 4%, 6%, 8%.

Figure 5. Semi-logarithmic representation of the flow curves of Ca-clay suspensions which allow us to detail the three phases of flow: (1) slip at the wall and overstep of the yield stress; (2) fast fluidification; (3) slow fluidification. T_0 is the extrapolated value of the yield stress.

Table 2. Herschel Bulkley parameters and viscosity of the suspensions for increasing shear stress curve.

		τ_0 (Pa)	k	n	Apparent viscosity at $500 s^{-1}$ (Pa s)
Ca-Volclay	4%	0.4	3.9×10^{-2}	0.72	7.7×10^{-3}
	6%	1.2	5.4×10^{-2}	0.72	1.0×10^{-2}
	8%	3.2	7.4×10^{-2}	0.72	2.0×10^{-2}
NH_4-Volclay	4%	0	6.8×10^{-1}	0.40	1.0×10^{-2}
	6%	0	4.4	0.24	4.0×10^{-2}
	8%	6	9.4	0.23	8.6×10^{-2}
Li-Volclay	4%	0	6.0×10^{-2}	0.71	1.0×10^{-2}
	6%	0	1.9	0.39	4.3×10^{-2}
	8%	0	1.9	0.23	1.7×10^{-1}

at 4%) whereas the 8% NH_4-clay suspension is nine times more viscous than the 4% one. The Li-clay suspension differs mainly by the exponential increase of the viscosity with clay concentration (the 8% Li-clay suspension is 17 times more viscous than the 4% one).

Thus, at high shear rate and high concentration, the viscosity increases with exchangeable cation in the following order: $Ca^{2+} < NH_4^+ < Li^+$.

DISCUSSION

The macroscopic rheological properties of clay suspensions may be elucidated through the microscopic shearing mechanisms in the clay fraction. Smectites, which have expandable interlayers between their basic unit layers, display different organizations depending on their clay concentration, type of exchangeable cation, and ionic strength of the solution. In this study, only solutions with very small ionic force were used but exchangeable sites of the clays were saturated with three different cations: Ca^{2+}, NH_4^+ and Li^+.

In smectite containing Ca^{2+} as the exchangeable cation, the unit layers are closely spaced due to strong electrostatic attraction between the cations and the negatively charged clay surfaces. As a result, interlayer hydration is limited to 2 or 3 molecular layers of water. The close fitting of the water molecules in the interlayer space results in relatively stable structure seen as a particle-associating 6–7 unit layers (Edwards *et al.*, 1965). Most of the water is located in the space between these particles (or aggregates of particles) rather than in the interlayer space. In Li-smectites the exchangeable Li^+ ions have large hydration radii and form a wide, diffuse double layer. Thus the electrostatic attractions between clay layers are weak, forming a loose and dispersed structure of particles. The interlayer spaces are very expansive and accommodate a large proportion of the total water contained in the system. Smectites with NH_4^+ as exchangeable cations exhibit particles with a smaller number of layers (association of only three unit layers, Edwards *et al.*, 1965) as compared to Ca-clay. The observed rheological behaviors are consistent with the clay organizations as described above. We can distinguish the geometrical entities according to their size (represented by the number of layers in particles, degree of association of particles in aggregates) and their capacity to deform until break up (entities with fixed geometry and those in variable but reversible geometry), from mechanical connections being able to exist
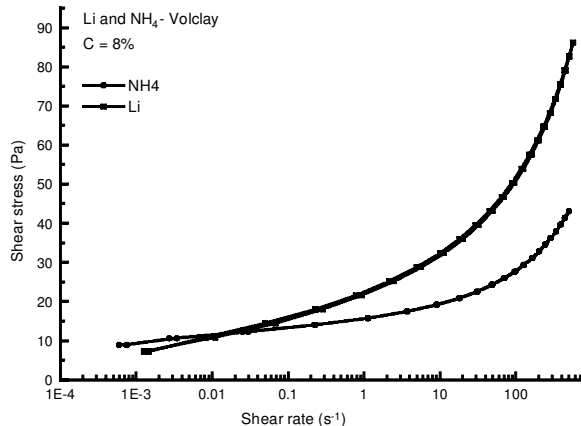
Figure 6. Semi-logarithmic representation of Li- and NH_4-clay flow curves showing a very progressive fluidification. The 8% NH_4-clay suspension presents a yield stress.
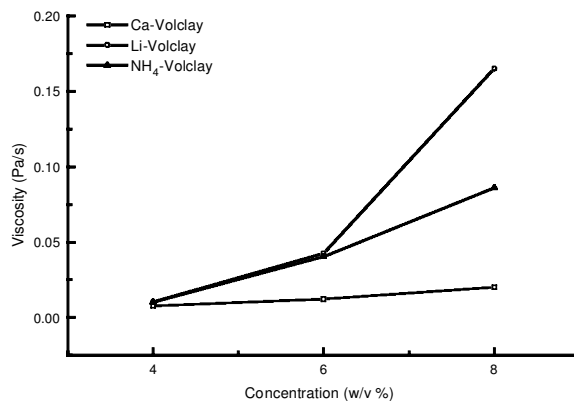
Figure 7. Apparent viscosity of the suspensions at $500 \ s^{-1}$ according to the clay concentration.

Table 3. Synthesis of results and interpretations.

	Ca-volclay		Li-Volclay		NH$_4$-Volclay	
	Data and observations	Interpretations	Data and observations	Interpretations	Data and observat	Interpretations
Criterion 1	Stable for a short period of time	Structuring cation forming turbostratic particles. Poorly deformable entities 6 times less numerous than in a Li-suspension at the same concentration. Weak quantity of bounded water.	Stable	Numerous entities constituted of one unit layer surrounded with a wide diffuse double layer of water. Important quantity of bounded water.	Stable	Strongly structuring cation forming particles. Undeformable entities three times less numerous than in a Li-suspension at the same concentration. Intermediate quantity of bounded water.
Criterion 2	Yield stress Solid-liquid suspensions at every concentration Three phases of flow: 1 – yield stress, 2 – fast fluidification, 3 – Herschel Bulkley behavior	1 – At rest and at low shear stress until critical shear stress cohesive contacts between entities, trapped water. 2 – break down of the structure and releasing of trapped water. 3 – orientation.	No yield stress. Liquid suspension at every concentration. One phase: low fluidification	Dense medium orientation of numerous little entities.	No yield stress. Liquid suspension at 4 or 6%. One phase: low fluidification. Yield stress. Solid-liquid suspension at 8%	Little dense medium at weak concentration poor contacts between the entities liquid suspension. 8% is a critic concentration. Solid-liquid suspension.
	Moderate viscosity	Cohesive repulsive contacts.	High viscosity from 4 to 8%	Repulsive forces.	Intermediate viscosity.	Cohesive contact which leads to yield stress after a critical concentration.
Criterion 3	Important thixotropy	Structurated entities with deformable geometry under flow. Return to initial state after a long time.	No thixotropy	Entities with fixed geometry not affected by the shearing. Immediate return to the initial state.	No thixotropy.	Entities with fixed geometry not affected by the shearing. Immediate return to the initial state.

between these units. It is then possible to build textural schemas of the suspensions on reports with rheological results by basing itself on three criteria (Table 3): (1) at rest; visual observation of the suspensions; (2) under flow; rheograms show that the colloidal structure could behave as a solid or a liquid; (3) thixotropy; observation of thixotropy which reports molecular attractions and reversible variation of the geometry of entities with time.

In Li-clay suspensions, particles present a very large lateral extension and much deformability. One unit layer could be part of two particles, which induces a large cohesion of the bulk suspension. As the ionic force of suspensions is very small, the diffuse double layer around particles is wide and offers a large area for contacts between entities. Thus, suspensions present a significant apparent viscosity. Charged colloidal particles resist shear flow in two ways, referred to as primary and secondary electroviscous effects (Güven and Pollastro, 1992). The first effect is the distortion of diffuse double layers under flow, and the second is due to the overlap of these double layers. As the concentration increases, diffuse double layers repel them apart. At low concentration, particles are randomly oriented at low shear rate but align at high shear rate. In concentrated suspensions, particle orientation under flow is more difficult to achieve as the available space for gyration is smaller. The structure then remains randomly oriented even at high shear rate which induces a higher resistance to flow. As the structure is formed with a large number of small entities, which are randomly oriented, the viscosity is very high.

In the case of NH_4-clay, the flow curves are of two types depending on clay concentration. The flow units apparently consist of compact, undeformable particles which do not share layers and probably do not form larger aggregates. At low concentration there is poor cohesion between these units which behave as isolated grains. Most of the water is free water. The regular shape of the flow curve suggests that there is a single type of structure. At 8% concentration, the increased number of clay particles seems to reduce the volume available for brownian motion and for particle gyration under flow. This could be a reason for the weak yield stress observed. With increasing shear stress, entities are oriented in the direction of flow, decreasing the viscosity. The absence of thixotropy for all of the investigated concentrations confirms that these suspensions could be compared to a granular medium which restores its initial state after flowing.

In the case of Ca-Volclay, there is a yield stress for every concentration. The supposed structure is composed of poorly deformable particles probably associated in aggregates at maximum swelling state. Because of turbostratic arrangement, one layer of a given particle can be part of another particle. This involves local cohesion to which we attribute the presence of a yield stress (cohesive contact). But the network may be biphasic with dense domains of associated clay particles (or aggregates) enclosing a large area containing trapped water. The whole system remains very porous. When the yield stress value is reached, this first type of structure breaks down rapidly and the quantity of trapped water decreases leading to rapid fluidification and loss of viscosity. Entities break up and orient in the direction of flow when there is no more trapped water. This new structure takes over and entities still ordered probably break into smaller entities which explains the continuous loss of viscosity when shear stress increases. The presence of the strong thixotropy is probably due to time-dependent reorganization of the initial network when shear rate decreases.

The viscosities of Ca- and NH_4-clay suspensions are always lower than those of Li-clay suspensions for the same concentrations. This might be because the thin and flexible monolayers of Li-clay orient with more difficulty under flow than the rigid platelets of Ca- or NH_4-clay and hence are more resistant to flow.

The fluidification index is the same for each concentration which suggests that suspensions have the same fluidity whatever the concentration is. Further work is required to clarify this point.

CONCLUSION

Rheological data reveal important behavioral variations that correlate with the micro-organization of clay particles.

The nature of the exchangeable cation has a significant influence on the textural properties of clay suspensions. The flow curves for Li- and NH_4-clay are very similar, but at a concentration of 8%, Li-suspension is weakly thixotropic, while NH_4-suspension presents a yield value. The Ca-clay suspensions differ by the presence of yield value and thixotropic behavior.

In general, an increase in clay concentration enhances the observed behavior (except for NH_4-suspension at 8% as explained above). Nevertheless, it seems that there is a critical concentration beyond which there is a strong evolution of yield value, thixotropy (if they exist) and viscosity.

These differences are related to very fine disparities in the microstruture of the particles. This study reveals that macroscopic mechanical measurements are sensitive enough to quantify these micro-variations.

ACKNOWLEDGMENTS

REFERENCES

Besq, A. (2000) Ecoulements laminaires de suspensions de bentonites industrielles. Caractérisation rhéométrique – Ecoulements en conduites axisymétriques. Applications

aux activités du Génie Civil. PhD thesis, Université Poitiers, Poitiers, France, 224 pp.

Coussot, Ph. (1997) *Mudflow, Mudflow Rheology and Dynamics*. Balkema editions, Dordrecht, The Netherlands, 255 pp.

Coussot, Ph. and Ancey, Ch. (1999) *Rheophysique des Pâtes et des Suspensions*, Edition Diffusion Press Sciences, Les Ulis, France, 257 pp.

Ecoclay Final report (2000) *Effect of Cement on Clay Barrier Performance*. Ecoclay project. European Commission Community Research, EUR 19609, 140 pp.

Edwards, D.G., Posner, A.M. and Quirk, J.P. (1965) Repulsion of chloride ions between negatively charged clay surfaces. Part 2 and Part 3. *Transactions of the Faraday Society*, **61**, 2816–2819.

Güven, N. and Pollastro, R.M., editors (1992) *Clay-Water Interface and its Rheological Implications*. CMS Workshop Lectures **4**. Clay Mineral Society, Bloomington, Indiana, 245 pp.

Heller, H. and Keren, R. (2001) Rheology of Na-rich montmorillonite suspension as affected by electrolyte concentration and shear rate. *Clays and Clay Minerals*, **49**, 286–291.

Keren, R. (1988) Rheology of aqueous suspensions of sodium/calcium montmorillonite. *Soil Science Society of America Journal*, **52**, 924–928.

Keren, R. (1989) Effect of clay charge density and adsorbed ions on the rheology of montmorillonite suspensions. *Soil Science Society of America Journal*, **53**, 25–29.

Magnin, A. and Piau, J.M. (1990) Cone-and-plate rheometry of yield stress fluids. Study of an aqueous gel. *Journal of Non-Newtonian Fluids Mechanics*, **36**, 85–108.

Malfoy, C., Pantet, A. and Monnet, P. (2001) Impact du mode de malaxage et de la minéralogie sur le comportement mécanique des boues de bentonite. *Acte du 36 ème colloque du Groupe Français de Rhéologie*.

McBride, M.B. (1994) *Environmental Chemistry of Soils*. Oxford University Press, UK, pp. 63–120.

Morvan, M., Espinat, D., Lambard, J. and Zemb, Th. (1994) Ultrasmall- and small-angle X-ray scattering of smectite clay suspensions. *Colloids and Surfaces*, **A82**, 193–203.

Penner, D. and Lagaly, G. (2001) Influence of anions on the rheological properties of clay mineral dispersions. *Applied Clay Science*, **19**, 131–142.

Pignon, F., Magnin, A. and Piau, J.M. (1996) Processus de désagrégation dans des gels d'argiles thixotropes sous écoulement de cisaillement. *Les Cahiers de Rhéologie*. **XV**, 294–300.

Ramsay, J.D.F. and Linder, P. (1993) Small-angle neutron scattering investigations of the structure of thixotropic dispersions of smectite clay colloids. *Journal of the Chemical Society. Faraday Transactions*, **89**(23), 4207–4214.

Sposito, G. (1984) *The Surface Chemistry of Soils*. Oxford University Press, New York, 234 pp.

Tessier, D. (1984) Etude expérimentale de l'organisation des matériaux argileux. Hydratation, gonflement et structuration au cours de la dessication et de la réhumectation. INRA PhD thesis, Université Paris VII, France, 361 pp.

Tessier, D. (1990) Behaviour and microstructure of clay minerals. Pp. 387–414 in: *Soil Colloids and their Associations in Aggregates* (M. De Boodt, M. Hayes and A. Herbillon, editors). Plenum Press, New York.

Touret, O. (1988) Structure des argiles hydratées thermodynamique de la déshydratation et de la compaction des smectites. PhD thesis, Université Strasbourg, France, 312 pp.

Viseras, C., Meeten, G.H. and Lopez-Galindo, A. (1999) Pharmaceutical grade phyllosilicate dispersions: the influence of shear history on floc structure. *International Journal of Pharmaceutics*, **182**, 7–20.