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Research Letter

Rheological Behavior of Smectite Dispersions: The Influence of Suspension Concentration and Exchangeable Cation

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The mechanical behaviors of smectite materials in water are very sensitive to many parameters, such as concentration, particle size and morphology, exchangeable cation nature, and chemical environment (pH, ionic strength). The literature usually provides general rules for sodium and calcium bentonites. However, it appears that the quantitative results present a large range of values. This study has established the relationships between the smectite nature (mineralogy, morphology, reactivity) and its rheological behavior according to the exchangeable cation. To develop a complete rheological study, we need 800 g of montmorillonite purified and saturated with Na^+ or Ca^{2+}. Huge production necessitates optimized process with accurate control of the powder quality and the chemical environment. Smectite particles have been extracted from a natural bentonite and then saturated with sodium or calcium. Then, each sample was characterized with classical methods like X-ray diffractometry (XRD), and laser granulometry but also cutting-edge technologies like scanning transmission electron microscopy on wet samples (Wet STEM). The Na-smectite dispersion contains a lot of small units whereas the Ca-smectite dispersion contains a few large units. Rheological study consists in flow curves obtained with a high-resolution rheometer. Logarithmic representation of the rheograms permits detecting a yield stress, it separates solid and fluid behavior. The rheological datas (viscosity, consistency, and yield stress) allow defining the limits depending on the concentration and on the saturation state. A Newtonian law could be applied to around 4% for Na- and Ca-smectites. Seaward of these concentrations, the dispersions are shear thinning and modelled by Ostwald law. Finally a yield stress appears at 6% for Na-smectite and 11% for Ca-smectite, the flow curves could be modelled by Hershel-Bukley law. Results are in accordance with the bibliography.

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1. INTRODUCTION

The specific properties of bentonite (hydration, swelling, water adsorption, viscosity, and thixotropy) make it a valuable material in the form of mineral powder for a wide range of uses; agronomy, cosmetics, civil engineering, as a geoliner in landfills, sewage lagoons, or as a compacted barrier for nuclear waste repositories [1]. Bentonite contains primarily smectite clays (mainly montmorillonite) and other secondary minerals, like feldspar, quartz, calcite, and iron oxides. Bentonite suspensions exhibit strong colloidal properties with yield stress and viscoelastic behavior, because of three-dimensional organization of the smectite clay crystallites in water. They display varying rheological properties that are highly dependent on the nature of the smectite (layer charge, localization of the layer charge, nature of exchangeable cations, particle size, etc.), suspension preparation, concentration, pH, ionic strength, and so forth [2].

Sodium-saturated smectite dispersions have a more pronounced yield stress than calcium-smectite dispersions. The exchangeable cation effect results in contrasted modes of layer linkage. Smectite layers, that have negative charge, are surrounded by a double diffuse layer (DDL), containing cations to balance the negative charge. The calcium smectite platelets are aggregated into quasicrystals with a thin DDL, in contrast sodium saturated smectites often are isolated platelets with large DDL [2–11].

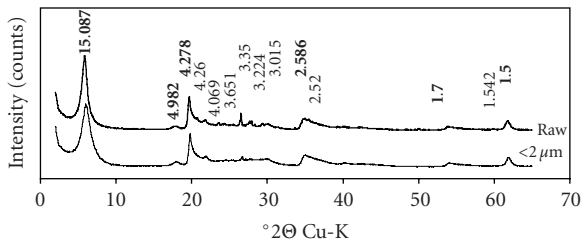


Figure 1: Powder patterns of the raw bentonite (upper diffractogram) and the fine fraction (lower diffractogram)-smectite (bold values), quartz (4.260 Å, 3.350 Å), anorthite (3.224 Å, 1.542 Å), opal CT (4.069 Å), mica (3.651 Å), and magnetite (2.520 Å).

Despite this knowledge, the comparison of rheological parameters, even for similar materials like sodium bentonite, as determined by different authors is difficult because experimental conditions are slightly different and also because the cation exchange is not a simple answer. Experimental conditions are different to the extent that it is difficult to correlate data measured by various authors. This divergence originates from differences in pretreatment and preparation as well as from different modes of quantification [12, 13]. In this study, we focused on the unit characterization of homoionic smectite dispersions (Na- and Ca-smectites) and many mixtures (Na-Ca), Coupling rheological techniques, which allows exploring how the structures or the networks of particles inside smectite suspensions are affected by modifications of the clay properties.

2. MATERIAL AND METHODS

2.1. Extraction process development

First, the raw bentonite from the BENTOFRANCE (200 g) was dispersed in distilled water (500 mL) using a strainer and sieved at 80 μm. Then, the fine fraction is extracted from the infra 80 μm fraction by controlled centrifugation according to the usual stokes relationship. In order to optimize the extraction process of the fine fraction (named currently infra 2 μm fraction), we stopped the process at the seventh step. This process was repeated many times and the resulting materials were mixed, dried, and crushed in order to obtain 800 g of homogenized smectite in five weeks. The mineralogy [14] was determined by X-ray diffraction (XRD) with Philips X'Pert PRO PW3050/6x goniometer (using Fe-filtered CuKα radiation, 40 kV, 40 mA) over randomly oriented powders, analyzed in 2–65°2θ range with astep of 0.05°2θ, counting the time of 3 second per step. The clay mineralogy of the fine fraction was analyzed by XRD on randow powders and compared with the raw bentonite (Figure 1). The part of secondary minerals has slightly decreased with the extraction process by controlled centrifugation.

2.2. Preparation of calcium and sodium exchanged smectite

The usual exchange process consists in contacting the clay with a saturating solution, like NaCl or $CaCl_2$, according to the expected saturation, during five periods of one hour. However, its efficiency may vary according to the clay properties [9, 15]. The saturation rates were deduced from the exchangeable cations, by comparing the content of the saturating cation with the sum of all cations. The cationic exchange capacity (CEC) and exchangeable cations (Σ) were measured using the ammonium method (AFNOR standard X 31,130 November 1985) and Flame Atomic Absorption Spectrometry (FAAS). The optimized saturating process, by increasing the concentration of sodium ions in the saturating solution and the contact period, allows to increase the ratio Na/Σcations near 1, indicating a satisfied saturation.

2.3. Characterization methods to compare the two saturated materials

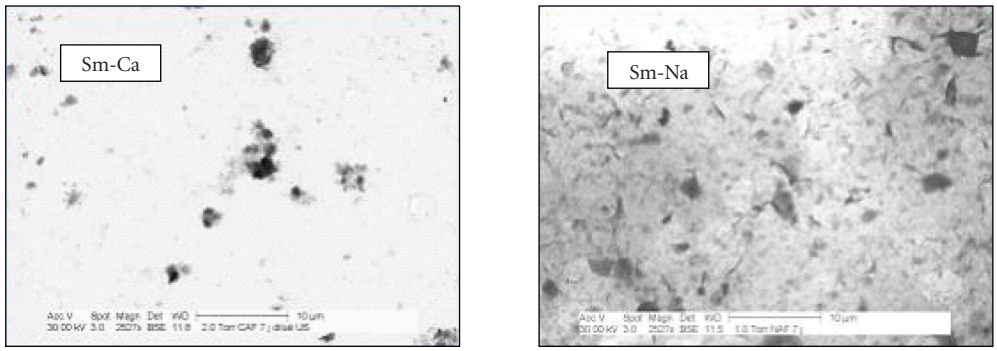
In order to investigate the impact of saturation on dispersions, we have characterized Na-smectite and Ca-smectite. Unit sizes were measured with laser diffraction in dilute dispersions (almost 0.05%). This method was used to evaluate the size of the suspended unit after aging without disintegration treatment (hexametaphosphate sodium adding). The distribution of Na-smectite powders is bimodal with the first mode at 0.6 μm and the second at 2.1 μm. The index curves are d_{10} = 0.3 μm, d_{90} = 3 μm, and d_{50} is 1 μm. The Ca-smectite dispersion seems to be bidispersed (5.3 μm mode—not determined with the focal lense) with a broad distribution: d_{10} is 1.9 μm, d_{50} is 7.1 μm, and d_{90} is 51.8 μm.

The Wet STEM observation method was developed on an environmental scanning electron microscopy (ESEM) that enables wet samples to be observed without potential damage through the use of partial water vapor pressure in the microscope specimen chamber. The special device was developed by Bogner et al. [16]. The Na-smectite dispersion needed higher dilution to meet clarity requirements.

2.4. Rheological behavior of the homoionic and mixed suspensions

Dispersions were prepared by adding 0.2%–12% (w/w) of fine fraction to distilled water (10 mL). The flasks were briefly hand-shaken, and dispersions were performed for 3 minutes at 16 000 rpm with a homogenizer (IKA Ultra-Turrax T25). Then, the resulting dispersions were slowly homogenized in a rotating shaker (50 rpm, Prolabo) for 9 hours on average, and were let at rest for 15 hours at 20°C. The equilibrium pH 8.4 ± 0.1 was not modified. Shaking time and shaking energy were cautiously checked during the dispersion preparation in order to ensure reproducibility and to allow comparisons of the rheological tests. According to Peysson [17], "the dispersion is stable if the mean unit size distribution is stationary in time and space over a rest period longer than the testing period."

The rheological measurements were performed with a Gemini HR stress-controlled rheometer (Malvern instrument). The rheological methods are sensitive enough to quantify accurately variations in the microstructuring of the smectite suspensions [18]. Experimental flow curves were obtained with rough parallel-plate geometry (40 mm) spaced



(a) (b)

Figure 2: (a), (b) Microscopic view (wet STEM) for diluted suspensions: Sm-Ca (0,1 g/l) and Sm-Na (0,01 g/l) (photo: A. Bogner and G. Thollet, INSA Lyon).

500 μm apart. The mechanical stability of dispersions was verified by agreement of successive tests. Then, the dispersions were subjected to increasing and decreasing shear rates for 7 minutes by 20 steps from 0.1 s^{-1} to 150 s^{-1}. A preshear at 100 s^{-1} was imposed for 60 seconds, followed by a rest period of 5 s before each test, in order to place the dispersion in an initial structural state.

Three models were used to characterize the following behavior:

(1) Newton: $\tau = \eta \times \dot{\gamma}$;
(2) Ostwald: $\tau = k\dot{\gamma}^n$;
(3) Herschel-Bulkley: $\tau = \tau_0 + k\dot{\gamma}^n$,

where τ (Pa) is the shear stress, η (Pa·s) is the Newtonian viscosity, and $\dot{\gamma}$ (s^{-1}) is the shear rate. τ_0 (Pa) is the yield stress (empirical yield stress), k is the consistency, and n is the phenomenological coefficient.

3. RESULTS

3.1. Observations by wet STEM

Each sample was observed by wet STEM, and 10 photographs of each sample were analyzed with the NIS software. Each unit was approximatively defined and assimilated to an elliptical measurable area. Ca-smectite particle sizes vary from 0.07 μm^2 (d_{10}) to 0.77 μm^2 (d_{90}), the particles are dispersed (Figure 2(a)). Particles are dense and seem to be composed of linked entities. Small units could result from the aggregate break-up. Large spaces are occupied only by water. Na-smectite units seem to fill all the available space (Figure 2(b)). This observation could result from the three-dimensional superimposition or from the particles settling down in the droplet. Particles sizes are quite homogeneous with a mean area of 0.13 μm^2. Particles distribution ranges from 0.035 μm^2 (d_{10}) to 0.3 μm^2 (d_{90}), although a few large particles were observed. The surface areas of the Ca-sm units are approximatively 2.5 times larger than those of the Na-sm units.

3.2. Rheological comparison tests

The mechanical behavior of the clay dispersions varies with concentration and Na-content.

(1) At suspension concentrations lower than 4%, dispersions display Newtonian behavior. Rheograms of Na-smectite, and Ca-smectite dispersions are shown on Figure 3. Newtonian viscosity values of each sample were calculated for each concentration. The Newtonian behavior implies that units flow in water without contact.
(2) At higher concentration, dispersions display shear-thinning behavior which would indicate brittle organization through three-dimensional clay particle association. The flow curves are modelled with Ostwald equation. The increasing concentrations cause structure strengthening, finally resulting in a yield value.
(3) At highest concentrations and sodium contents, the rheograms are complex. At lower stress values, a linear relation (A-B) can be seen in a log-lin plot of stress versus strain (Figure 4). Viscoelastic deformations of the gel, although the yield stress is not reached, have been studied by creep and oscillatory tests. The part (B-C) distinguishes these two regions, it represents the transition from elastic solid to viscous liquid, which is associated with the yielding process.

The fluid is not completely sheared, so the shear rate values indicated by the rheometer are smaller than the real ones. Two yield stresses, "static" and "dynamic," can be defined, respectively, at the points B and C [19]. The parts C-D and D-E-F describe the shear-shinning behavior by increasing and decreasing the shear rate. The Herschel-Bulkley parameters are defined from the down curve (D-E-F).

Figure 5 shows the mechanical behavior of the dispersions according to their concentration and smectite composition. Over the X-axis, the suspension concentration varies from very dilute dispersions (2 g/l) to concentrated pastes (120 g/l). Over the Y-axis, the Na-content varies from 0% (Ca-smectite) to 100% (Na-smectite). The rheological data

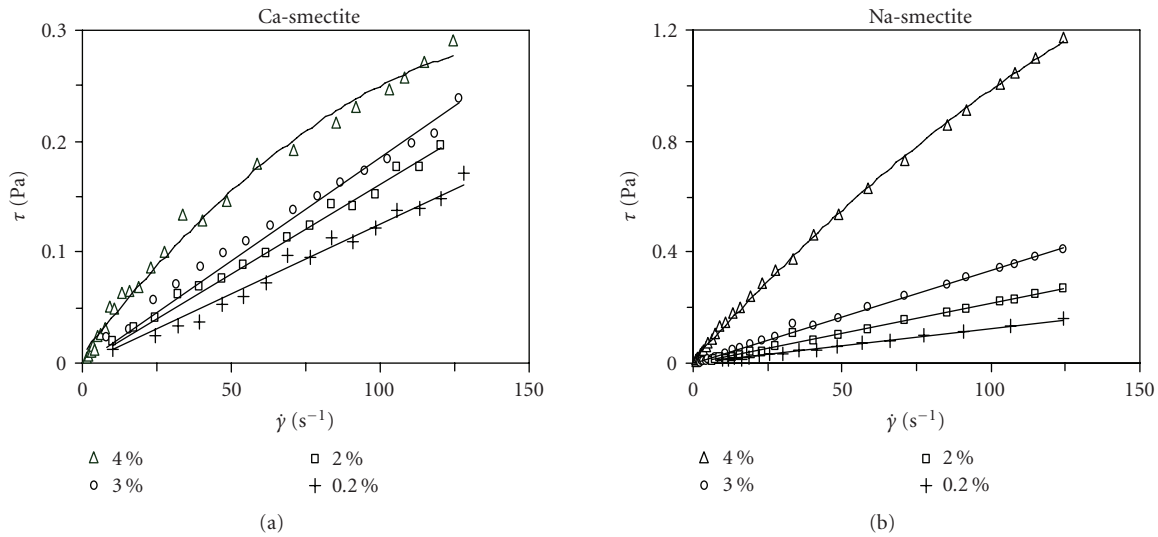


Figure 3: Flow curves for Ca-sm (a) and Na-sm (b) at four concentrations (0.2%, 2%, 3%, and 4%).

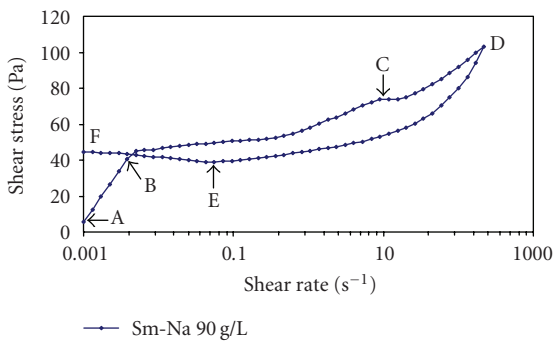


Figure 4: Shear stress-shear rate curve for Na-smectite suspension at 90 g·L^{-1}.

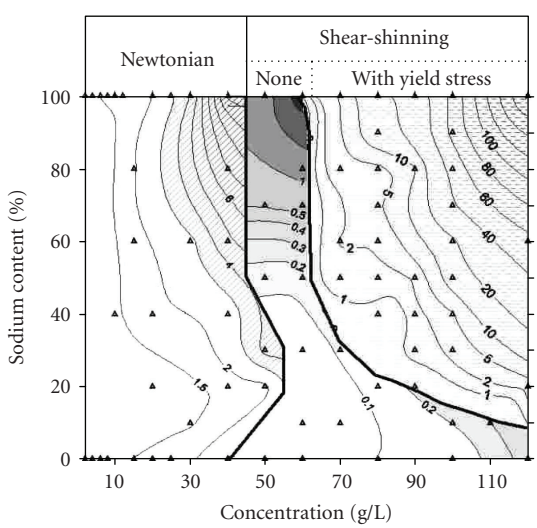


Figure 5: Isovalues lines giving the parameters of flow tests on homionic and mixed suspensions at different concentrations (isolines for each domains: μ, Newtonian viscosity-k, consistency, and τ_0, yield stress).

are defined for each suspension and allow to give the limits depending on the concentration and on the saturation state. Krigging method from Surfer software allowed this representation with isovalues lines for characteristic parameters (μ, newtonian viscosity-k, consistency and τ_0, yield stress) of the corresponding model.

The Newtonian area terminates approximately at the same concentration for Ca and Na but viscosity evolution is quite different. We could consider first a sodium influence area, where viscosity increase with increasing concentration and sodium content and second a calcium influence area, where viscosity increases with increasing concentration but decreases with the sodium content. This observation could be partially explained by the polydisperse effect between Na- and Ca-platelets, which have different sizes. In granular or colloïdal media, it is known, that adding fine particles between coarse particles allows a better compactness, but also increases fludity [20, 21].

At higher concentrations, sodium hydration capacity could develop and viscosity increases continuously. The yield stress evolution is consistent and gradual with increasing sodium percent but sharp with the dispersion concentration of the sodium clay.

4. CONCLUSION

This study has shown that the rheological behavior of smectite suspensions, prepared from a bentonite, is complex, depending on the smectite concentration and Na-content. Smectite was extracted from a natural bentonite, saturated with sodium or calcium, and its mineralogy was determined with XRD. The samples were dispersed in water at low concentration and studied with laser granulometry and wet STEM. The results showed that the suspended Na-smectite particles are smaller and more dispersed than the Ca-smectite units. At higher concentration, the suspensions develop yield stress when the Na-content is 20%. It appears

that the rheological measurements are very sensitive to the platelets organization in a complex network, depending on many parameters. When comparing rheological data of bentonite, attention is drawn to the necessity of describing accurately the pretreatment processes, especially when procedures for exchanging interlayer cations are used, as they significantly influence the structural properties of the clay and hence its technical properties. Associating fine mineralogical techniques with rheological measurements is probably a way to understand the organization clay suspensions.

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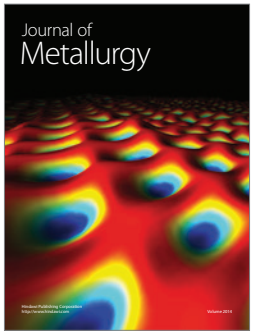

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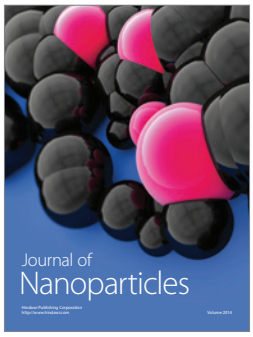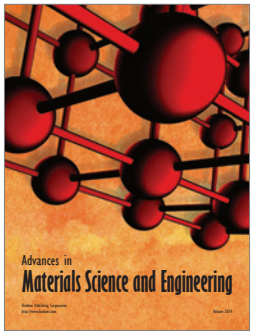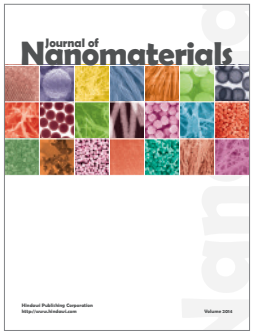
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