

Changes in suspension properties of structural modified montmorillonites

(Mudanças em propriedades de suspensões de montmorilonitas modificadas estruturalmente)

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Abstract

Rheological changes were found in smectite (Wyoming- and Cheto-type montmorillonites) suspensions after structural modifications. The effect of the particle size and Na⁺ exchange on the flow curves of 6% wt/wt suspensions of smectites with and without Na₂CO₃ were examined. Mineralogical, structural and physicochemical characteristics were studied by X-ray diffraction (XRD), infrared spectroscopy (IR), cationic exchange capacity (CEC), Mg²⁺, Al³⁺ determinations, particle size distribution and swelling index (SI). Grinding in an oscillating mill modified the particle sizes. The montmorillonite grain size and the structural disorder increased after larger grinding times. The grinding treatment modified the apparent viscosity and the yield stress of the montmorillonite suspensions. The homoionic Na Cheto-type montmorillonite with fine particle size (obtained by grinding) increased the flow properties. Nevertheless, rheological properties were lower than those of suspensions of the Wyoming-type montmorillonite. Montmorillonite-types reacted differently with Na₂CO₃ additions and this behavior may be related to their structural composition. The Na₂CO₃ activation improved the flow properties of the original Wyoming-type montmorillonite and after 30 s grinding.

Keywords: smectites, montmorillonite suspensions, rheology.

Resumo

Foram encontradas mudanças reológicas em suspensões de esmectitas (montmorillonitas tipos Wyoming e Cheto) após modificações estruturais. Foi examinado o efeito do tamanho de partícula e troca de Na⁺ nas curvas de escoamento de suspensões de esmectitas 6% peso com e sem Na₂CO₃. As características mineralógicas, estruturais e físico-químicas foram estudadas por difração de raios X (DRX), espectroscopia no infravermelho (IV), capacidade de troca catiônica (CTC), determinações de Mg²⁺ e Al³⁺, de distribuição de tamanho de partículas e de índice de expansão (swelling index - SI). Moagem em moinho oscilatório modificou o tamanho das partículas. O tamanho de grão da montmorillonita e a desordem estrutural aumentaram após maiores tempos de moagem. O tratamento por moagem modificou a viscosidade aparente e o limite de escoamento das suspensões de montmorillonita. A montmorillonita homoiônica de Na do tipo Cheto com pequeno tamanho de partícula (obtido por moagem) melhorou as propriedades de escoamento. Entretanto, as propriedades reológicas foram piores que as de suspensões de montmorillonita do tipo Wyoming. Os diferentes tipos de montmorillonitas reagiram de modo diferente com adições de Na₂CO₃ e este comportamento pode estar relacionado com suas composições estruturais. A ativação por Na₂CO₃ melhorou as propriedades de escoamento da montmorillonita tipo Wyoming original após moagem por 30 s.

Palavras-chave: esmectitas, suspensões de montmorillonita, reologia.

INTRODUCTION

Aqueous bentonite suspensions are widely used in industrial processes because they exhibit properties of thixotropic gels.

The bentonite is a rock essentially composed of smectite. The smectites are clays, which are classified, as 2:1 phyllosilicates constitute by an octahedral layer containing Al or Mg ions between two tetrahedral silica layers. The montmorillonite is one species of the dioctahedral smectites. Grim and Kulbicki [1] proposed that the montmorillonite may be subdivided into Cheto- and Wyoming-types according to the

Mg²⁺ content in octahedral layer with higher content in the Cheto-type. In previous papers it was observed that mineralogical composition, the percentage of fine particles and Na⁺ content of the raw materials are the principal factors to be considered in rheological properties [2]. The Wyoming-type montmorillonite suspensions with much fine particles content and high percentage of exchangeable Na⁺ show higher viscosity values, yield stress and thixotropy than the Cheto-type montmorillonite suspension. The last type has thickness particles and high Ca²⁺ content as exchangeable cation.

The aim of this paper is to modify the structural and physical

characteristics of two different type montmorillonites and to analyze the rheological properties of the aqueous suspensions with and without Na_2CO_3 previous treatment.

MATERIALS AND METHODS

The raw materials used in this study were: SA_{z-1} , Ca montmorillonite, USA; SW_{y-1} , Na montmorillonite, USA; and two commercially available smectitic materials (bentonites) CO and DG from Argentina. SA_{z-1} and CO are Cheto-type whereas SW_{y-1} and DG are Wyoming-type montmorillonites [2].

The homoionic SA_{z-1} -Na was prepared by saturation with 2N NaCl aqueous solutions and subsequent washings to eliminate residual Cl.

Mineralogical compositions of the montmorillonites were investigated by X-ray diffraction (XRD). A Phillips PW 1140 device at 40 kV and 20 mA with Cu radiation ($K\alpha=0.154$ nm) and Ni filter was used. The samples were analyzed by XRD powder in aggregate and oriented slides form.

Infrared spectrometry (IR) was obtained with a Perkin-Elmer 577 spectrometer. The samples were diluted in KBr and compacted to form thin pellets.

The cation exchange capacity (CEC) was determined using 2N ammonium acetate at pH=8. Exchangeable cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) were measured by atomic emission and absorption analysis.

The structural composition was derived from chemical analysis on the basis of anion charge of $\text{O}_{10}(\text{OH})_2$ per half-unit formula.

Particle size distribution was obtained using Sedigraph 5000D equipment.

The particle sizes were modified by grinding in an oscillating mill (Herzog HSM 100) with a rotative frequency of 12.5 sec^{-1} during measured times. The resulting materials were identified as B/T, where B was the SA_{z-1}Na , SW_{y-1} , CO or DG samples and T was the grinding time: 0, 30, 60 or 300 seconds.

The swelling index (SI) was measured by adding of 2.00 g of dry material to 100 cm^3 of distilled water.

Montmorillonites were saturated with Na_2CO_3 by adding the solution to dry materials ($\leq 74 \mu\text{m}$) at room temperature. This treatment was carried out using a saturated solution of Na_2CO_3 ($20 \text{ g}/100 \text{ cm}^3 \text{ H}_2\text{O}$) in a proportion of 100 meq/100 g sample. The mixture was homogenized and left standing for 24 hours. The wet Na_2CO_3 -treated material was dispersed in water for obtaining a suspension of 6 % wt/wt.

Rheological measurements were carried out using a Haake RV3 viscometer with a system of rotating concentric cylinder MVIP at 25°C . Flow curves were obtained from suspensions of original montmorillonites and after treatment with Na_2CO_3 .

RESULTS AND DISCUSSION

The process of grinding to modify particle size produced additional structural and physicochemical changes.

Fig. 1 shows the granulometry distribution of the montmorillonites after different grinding times. Particle size distributions of SW_{y-1} , $\text{SW}_{y-1}/30$, DG and DG/30 samples were not possible to obtain by using the same analyzer (the small particles were hydrated and produced the gelation of suspensions preventing the particle sedimentation). The percentage of fine particles of Cheto-type montmorillonites (SA_{z-1} and CO) increased after 30 s

grinding. All samples showed thickness size (D_{50} close to $10 \mu\text{m}$) after 300 s of grinding. Such behavior could be attributed to aggregate particles [3].

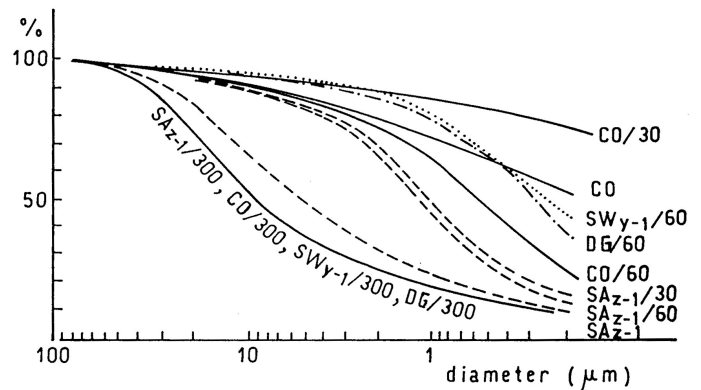


Figure 1: Particle size distribution of montmorillonite samples.

In smectites, the colloidal fraction of a distribution contributes to increase the specific surface area and to provide gel structure due to attractive/repulsive forces acting on colloid particles. Therefore, the submicron size content is related to swelling index. Wyoming-type montmorillonites (SW_{y-1} and DG) showed higher swelling index (SI) than the Cheto-type SA_{z-1} and CO as shown Fig. 2.

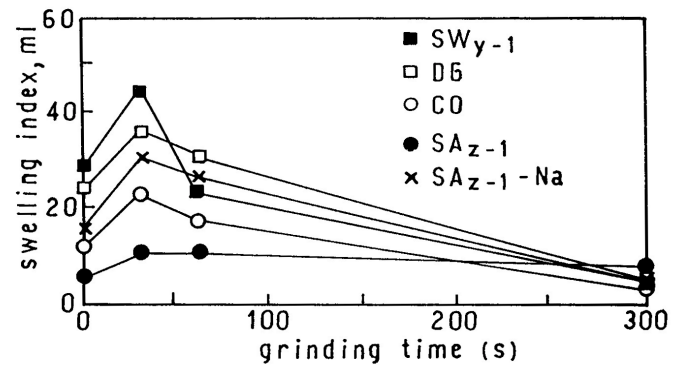


Figure 2: Swelling index vs. grinding time.

The exchange with NaCl in the SA_{z-1} ($\text{SA}_{z-1}\text{-Na}$) improved the degree of hydration of the clay and thereby increasing SI but the values were lower than Wyoming-types montmorillonites. SI of samples increased with grinding time (30 s), Fig. 2. Physical sorption of water occurs because the increase in colloidal content of smectites favors the adsorption phenomenon. The swelling index (SI) decreased when the samples were ground for larger times because produced a re-aggregation of material and then water retention was smaller.

Fig. 3 shows the $d(001)$ spacing after K-saturation and glycol treatment, in powder aggregate and oriented specimen of the CO and DG samples in original and after grinding conditions. SA_{z-1} and SW_{y-1} were analyzed in previous work [4]. The behavior of CO and DG samples was similar to that of the SA_{z-1} and the SW_{y-1} , respectively, which are characteristics of Cheto and Wyoming type montmorillonites. The Cheto-type montmorillonite expand about 1.5 nm whereas Wyoming-type expands about 1.7 nm after treatment with KCl-ethylene-glycol solvated [1]. Then, CO and DG samples

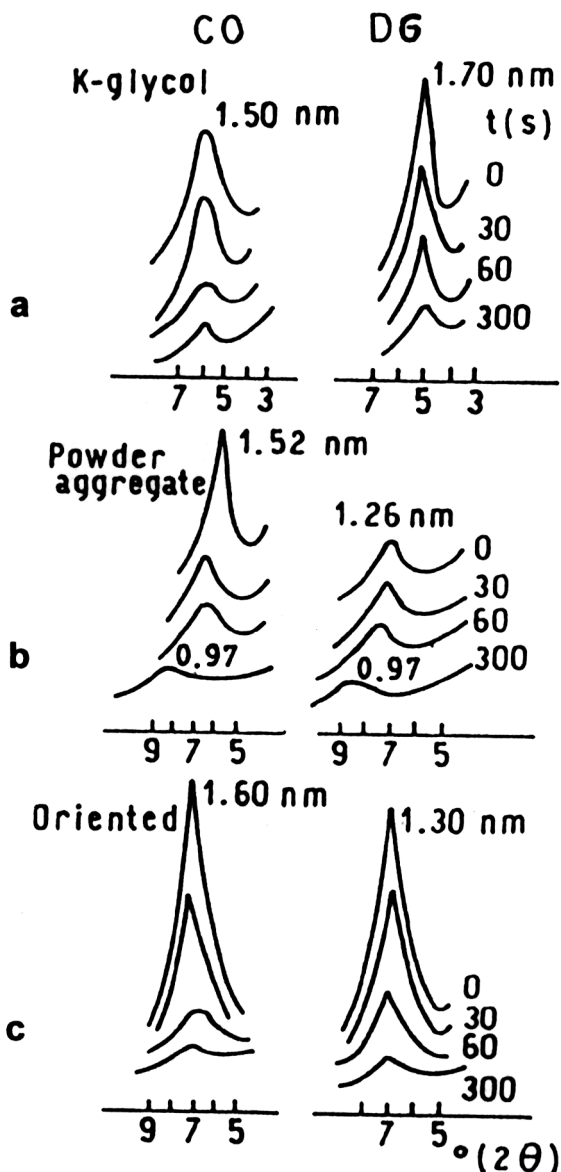


Figure 3: d(001) spacing of CO and DG samples after grinding. a: K-glycol treatment in oriented conditions; b: powder aggregate; c: in oriented conditions.

showed Cheto- and Wyoming-type montmorillonites, respectively (Fig. 3a) and such characteristics were maintained during all grinding times. The XRD peaks of the ground samples were lower in intensity and became broader than the original samples. Lattice strain and small crystallite size could contribute in broadening of the X-ray diffraction patterns [5]. The diffractograms in powder aggregate conditions (Fig. 3b) of the ground samples at 300 s, showed a decrease in the d(001) spacing, indicating a collapse of the structure (0.97 nm). This collapse was reversible because XRD of samples in oriented conditions (after rehydration) maintained the same value than original samples (1.30-1.60 nm for each montmorillonites type) but with lower intensity (Fig. 3c). This degree of reversibility evidenced that the samples exhibited a similar behavior than after thermal treatment at low temperature, 200 °C [4]

The total XRD diagram of samples in powder aggregates showed higher loss of crystallinity of the Wyoming-types (SW_{y-1} and DG) than the Cheto-types (SA_{z-1} and CO) when the samples were ground 300 s (not shown).

The crystalline alteration of the 2:1 phyllosilicates produced by mechanical treatment depends mainly of mill used. In previous studies of grinding with clay materials and using planetary ball mill, were shown that after a period of 30-60 minutes the *hkl* reflection had decreased [5-7] whereas using an oscillating mill [8, 9] such time is reduced.

Fig. 4 shows the infrared spectra of SW_{y-1} and SA_{z-1} (Wyoming- and Cheto-types, respectively) in original and ground 300 s conditions. The bands centered at 3640 cm^{-1} (OH), 915 cm^{-1} (Al_2OH) and 840 cm^{-1} (Mg-Al-OH) were more altered than the 1025 cm^{-1}

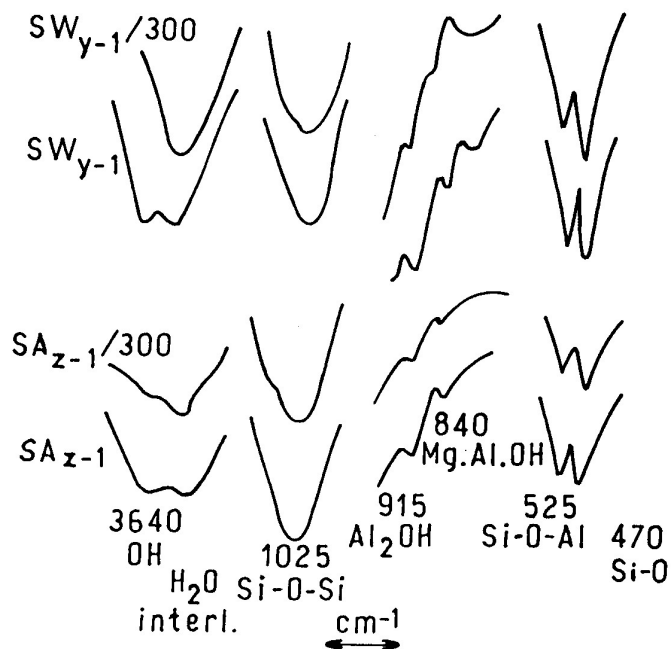


Figure 4: IR spectra of the original and modified SW_{y-1} and SA_{z-1} montmorillonites.

(Si-O), 525 cm^{-1} (Si-O-Al) and 470 cm^{-1} (Si-O) after 300 s of grinding time. These band modifications may be explained by Al-Mg migration to the surface. Smectite after a prolonged grinding (780 s) shows an IR spectrum similar to that of silica gel [9].

Breakdown of the layer increases of exposed functional group AlOH, SiOH, SiOAl and the cation exchange capacity could be

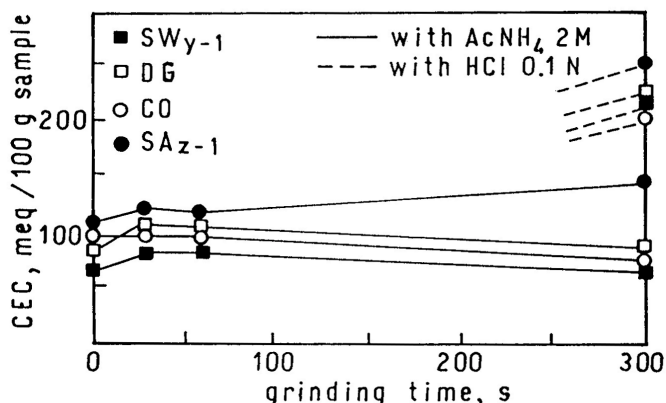


Figure 5: Cation exchange capacity of the different montmorillonites.

increased [3]. Fig. 5 shows the CEC of the samples determined with ammonium acetate. The aluminum migration from the structure was not detected in such solutions. Probably the aluminum was polymerized and strongly adsorbed on the clay surface. To confirm aluminum migration, the sample was washed with 0.1N HCl solution and Al release was colorimetrically determined by the Aluminon method. Fig. 5 also shows the CEC calculated by adding the amount of the aluminum extracted from the ground sample during 300 s.

Fig. 6 shows the amounts of Mg^{2+} and Al^{3+} removed from montmorillonite structure after grinding. The amount of cations removed may be indicative of the proportion structure damage by grinding. Higher amount of Mg^{2+} was extracted for Cheto-type montmorillonites (SA_{z-1} and CO) than Wyoming-types (SW_{y-1} and DG) after grinding. Whereas higher Al^{3+} was extracted from Wyoming-types. This observation was in according to the structural composition (Table I).

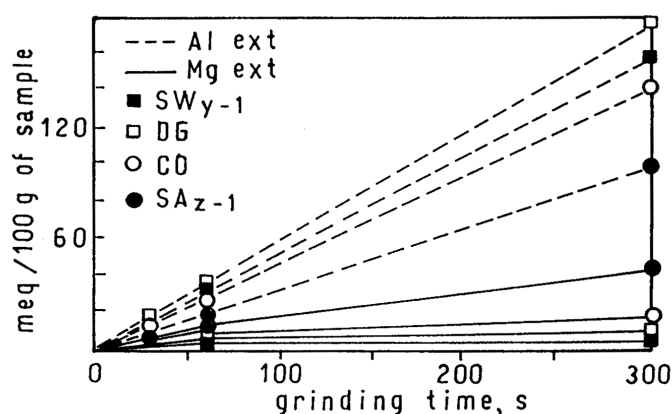


Figure 6: Mg^{2+} and Al^{3+} extracted from the structure after grinding.

The octahedral Mg^{2+} content in SA_{z-1} and CO samples correspond to the range of Cheto-type [1]. Table I shows that the octahedral sheet of the Cheto-type has greater Mg^{2+} content than that of the Wyoming-type, in which octahedral Al^{3+} content is higher. The sum of Mg and Al extracted from the structure after 300 s of grinding in all samples was around 30 % of the original content

Table I - Structural formulae of Cheto- and Wyoming-type montmorillonites.

	CHE TO-TYPE		WYOMING-TYPE	
	SA_{z-1}	CO	SW_{y-1}	DG
Si_{tet}	3.93	3.89	3.92	3.93
Al_{tet}	0.07	0.11	0.08	0.07
Al_{oct}	1.40	1.44	1.61	1.50
Fe_{oct}	0.10	0.09	0.13	0.19
Mg_{oct}	0.50	0.47	0.20	0.29
Mg+Al removed after 300 s of grinding(%)	28	29	29	32

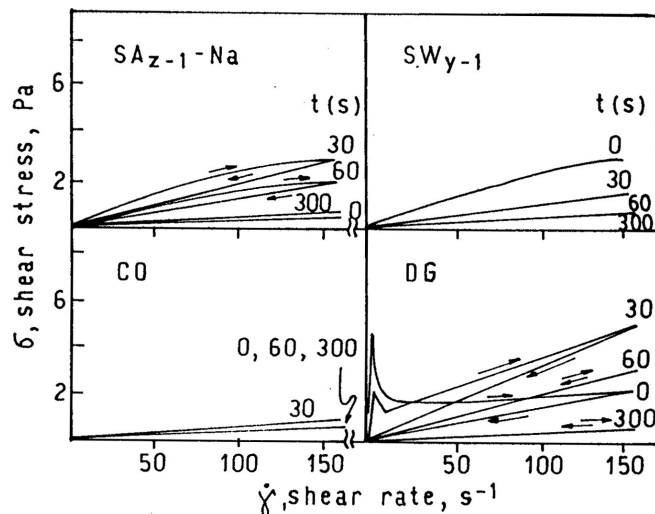


Figure 7: Flow curves of 6% wt/wt aqueous suspensions of the natural and modified Cheto-type (SA_{z-1} -Na and CO) and Wyoming-type (SW_{y-1} and DG) montmorillonites.

Fig. 7 shows flow curves of the original smectites after different grinding times. The curve of original SA_{z-1} sample was not shown because it was similar to that of CO suspension. Suspensions of the original CO and SA_{z-1} -Na samples had a low apparent viscosity, which is the shear stress to shear ratio at constant shear rate, and Newtonian behavior. The SW_{y-1} suspension is characterized by higher viscosity values and a slight shear thinning behavior (apparent viscosity slightly decreased with increasing shear rate). DG suspension showed a complex non-Newtonian behavior exhibiting high viscosity values, hysteresis loop and a high initial shear stress peak that may be associated with the existence of a gel network. This hysteresis loop is related to gel destruction in small aggregates due to the shear flow.

The exchange with Na^+ , and increase in fine particles obtained after short grinding time improved the rheological properties of the SA_{z-1} sample (Cheto-type) suspension. However, the values of the rheological properties obtained are lower than that of the original Wyoming-type. The SA_{z-1} -Na/30 and SA_{z-1} -Na/60 suspensions showed also a hysteresis loop. The grinding did not improve the flow behavior of SW_{y-1} suspension. The rheological properties of the DG/30 suspension were increased. The higher exchangeable Na^+ content in DG (66%) than the SW_{y-1} (52%) could be related with different behavior among Wyoming-types [2]. Large grinding times originated significant changes in rheological properties that may be attributed to thickness particles and the loss of crystallinity. Aggregation in thick particles reduced the viscosity.

Fig. 8 shows flow curves of the montmorillonite suspensions after sodium carbonate treatment. Na activation was not always effective.

The flow curve of the homoionic SA_{z-1} -Na/30 suspension treated with Na_2CO_3 (Fig. 8) was lower than that of the original suspension (Fig. 7). Probably the increase in sodium concentration produced flocculation of clay particles due to diffuse double layer compression and could be responsible of the reduction in rheological properties [10]. For the suspensions of SW_{y-1} and SW_{y-1} /30 the curves describe a complex non-Newtonian behavior showing high viscosity values, extrapolated yield stress and hysteresis loop. Therefore, these systems are characterized by a shear thinning and tixotropic

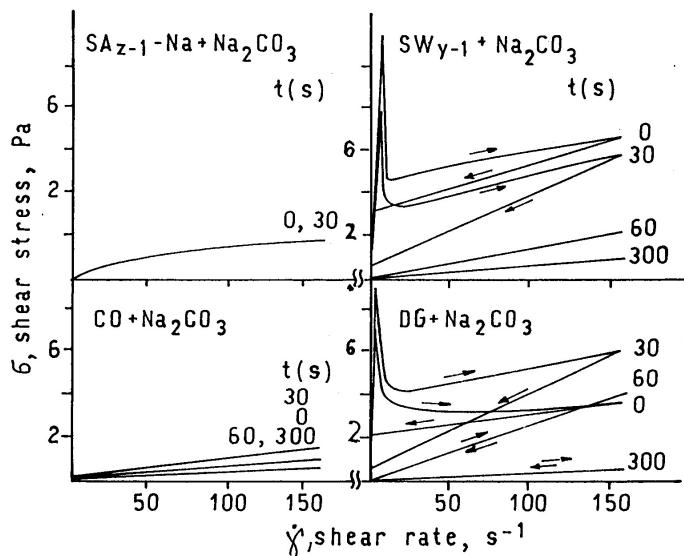


Figure 8: Flow curves of 6% wt/wt aqueous suspensions of Cheto- and Wyoming-type montmorillonites treated with Na_2CO_3 .

behavior. The increase in viscosity was mainly caused by the delamination of the particles due to Na^+ exchange in an alkaline medium. Moreover, according to Brandenburg and Lagaly [11], the presence of Ca^{2+} ions on the smectite surface promotes the formation of a band type structure among fine aggregates of sodic smectite. At high pH, the band-like structure produces an increase in viscosity.

CONCLUSIONS

The structural characteristics are important factors to be considered in suspension properties of the montmorillonites.

Homoionic Na Cheto-type montmorillonite having fine size of particles (obtained by grinding) increased the flow properties. Nevertheless, these flow properties were lower than that of suspensions of Wyoming-type montmorillonite. Both types of montmorillonites reacted differently with Na_2CO_3 . The high layer

charge of Cheto-type montmorillonite (Al^{3+} substituted by Mg^{2+} in octahedral sheet) and interlayer Ca^{2+} reduce osmotic swelling and delamination of particles in alkaline media.

Addition of Na_2CO_3 improved the flow properties of the Wyoming-type montmorillonite suspensions and it appears to be enhanced when the samples were ground for short times as the content of fine particles increases. In addition to aggregation of the particles, large grinding times originated damage of the structure on the bentonite, interlayer collapse and Al-Mg remotion from octahedral sheet of near 30%. Nevertheless, the characteristic type of montmorillonite remaining in the ground sample was preserved and the interlayer collapse was reversible after rehydration. Aggregation in thick particles reduced suspension viscosity.

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(Rec. 14/07/00, Rev. 24/10/00, Ac. 02/02/01)