Rheological Characteristics of Aqueous Ca-Bentonite Dispersions*

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The rheological properties of Ca-bentonite suspensions in different volume concentrations have been studied as a function of pH and the concentration of added electrolytes. In addition, the conductance of suspensions was determined. The flow behaviour of suspensions with and without containing electrolytes fitted the Bingham plastic flow. The yield stress of suspensions, showed that the transition process from viscous flow to plastic flow required relatively high shear stress for the given volume concentrations. The suspension exhibited a shear-thinning behaviour in their native pH conditions. Below the pH value of 3, the stability of edge to face contact decreased. Apparent viscosity (n_p) values of suspensions were strongly pH dependent as plastic viscosity (n_p) values were nearly constant in the selected pH conditions. Apparent viscosity of suspensions exhibited different behaviour depending on the type of electrolytes. Although the highest increase in the specific conductivity was obtained with large amount of KCl addition, in case of NaCl addition, specific conductivity was increased largely more than in the KCl addition with increasing volume concentrations.

Introduction

Rheological characteristics of bentonite dispersions in water may change ranging from a laminar flow to plastic flow, thus the suspensions can be paste and slurry. These rheological characteristics play an important role in industrial applications.1-3

Rheological properties of various bentonites differ so widely depending on morphological and chemical characteristics of the smectites which are clay minerals with three layers. Smectite minerals4 in Ca-bentonite can form quasicrystals due to the interlayer hydration complexes of divalent interlayer cations such as Mg^{2+} and Ca^{2+}. The thickness of the smectite quasicrystallites in a suspension varies closely with the experimental conditions, such as pH4-7, exchangeable cations8-9 and hydrodynamic forces10. Besides, the basal faces of smectite particles carry permanent negative charges due to the ionic substitution within the layers while the electrical charges at edges of smectite platelets vary with pH, the type, the concentration of added electrolytes11 and the presence of organic additives12. The pH conditions of smectite dispersion in water may modify the charge sign on the edges of a smectite platelet. On the other hand, the electrolyte addition to a smectite suspension compresses the electrical double layers on the particle surface and different exchangeable cations induce particle association. Due to these effects the structure of flow network may change from true viscous flow to plastic flow. Russel and Israelachvili13 14 explained that the modes of particle interaction that govern the flow network can be either by long-range interaction or association phenomenon.

The aim of the present study is to review the factors such as pH, electrolytes and concentration which greatly affect the viscosity and flow behaviour of Ca-bentonite suspensions.

Materials and Methods

A minerologically purified Ca-bentonite sample was obtained from the north-west part of Turkey. Minerological and chemical analysis of samples were carried out by X-ray diffraction (Philips PW 1140/90 instrument) and wet chemistry and atomic absorption spectroscopy. X-ray diffraction data and the result of chemical analysis are shown in Figure 1 and Table 1. Silicon and calcium content of the sample were carried out by gravimetry and EDTA titrations respectively. The rest of the elements were determined by an atomic absorption spectrophotometer (Perkin-Elmer, model 3030). In addition, percentage of...
exchangeable cations was determined for 100 g Ca-bentonite after the removal of soluble salts (NaCl, NaNO₃, Na₂SO₄, KCl) as well as the free carbonates (calcite, dolomite) found in the bentonite (Table 1) before the addition of electrolytes.

The electrolytes (NaCl, KCl, KOH) and all the other chemicals used were Merck. The weighted amounts of Ca-bentonite were dispersed in the proper amount of distilled water by mechanical stirring in order to prepare suspensions in different volume concentration; then all suspensions were allowed to stand for a 24 h period. Conductance measurements of suspensions were also carried out with Extech, pH-conductivity + TDS meter.

### Rheological Measurements

Apparent and plastic viscosity of suspensions were determined with a Fann type viscometer (Baroid, model 35 SA). Figure 2 show the variations in the $\eta_p$ apparent and plastic $\eta_p$ viscosities as a function of concentrations (v/v, %).

The shear stress ($\tau$) - shear rate (γ) rheograms of suspensions for various concentrations ($\phi_1$=5.6, $\phi_2$=8.4, $\phi_3$=10.9, per cent) are shown in Figure 3. The yield values of suspensions are obtained by extrapolation of linear curves of $\tau = f(\gamma)$. The experimental ($\tau_p$) and the theoretical ($\tau$) results of yield values for different volume frac-

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**Table 1** — Chemical Analysis of Ca-bentonite

<table>
<thead>
<tr>
<th>Oxides</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>TiO₂</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>IL</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/w,%</td>
<td>62.80</td>
<td>9.00</td>
<td>2.2</td>
<td>0.5</td>
<td>1.8</td>
<td>4.6</td>
<td>1.0</td>
<td>0.8</td>
<td>16.1</td>
</tr>
</tbody>
</table>

w/w,% of exchangeable cations after removal of
IL: Ignition Loss, Relative Precision: 0.09-1.4 ppt soluble salts
To evaluate the effects of pH on the rheological properties of Ca-bentonite 0.1 M HCl was slowly added into the suspensions, and then pH was measured. The results are given in Figures 4–7.

The effects of different electrolytes on the apparent viscosities of suspensions were studied by adding weighted amount of solid electrolyte to suspensions. The given per centage of solid electrolytes relative to the amount of dry Ca-bentonite in suspension of \( \phi_1 \) to \( \phi_7 \) varied between 1 to 7 per cent. The rheogram \( \tau=\gamma(\phi) \) of \( \phi_1, \phi_2, \phi_3 \) carrying different electrolytes and variations of apparent viscosity with electrolytes are illustrated in Figures 8–11 respectively. Variation of conductance with the added electrolytes is shown in Figure 12.

**Results and Discussion**

As shown from the result of X-ray diffraction analysis (Figure 1), Ca-smectite and illite are the major minerals of the sample with feldspar, quartz, calcite and dolomite being minor minerals.

The flow curves of Ca-bentonite suspensions of different volume concentration, as shown in Figure 3, are linear between the relatively low and high rates of shear. All the suspensions exhibit Bingham plastic flow with a par-
ticular network. However, Ca-bentonite which contains Ca-smectite as a major mineral, in general, gives face to face network (band-like structure). It can be changed by a small variation in the composition of the medium drastically.

In Figure 2, apparent viscosity and plastic viscosity were plotted as a function of various volume fractions. The values of apparent viscosity exhibit a linear increase until the volume fraction of \( \phi_4 \) (10.9 per cent), but a deviation from linearity occurs at the volume concentration of \( \phi_3 \) (13.2 per cent) due to particle characteristics such as morphology, size, surface area, etc., and particle interactions as well as the structure of suspension. Also, the admixed materials certainly exerts an influence, but the factors given above are found to be predominant.

As shown in Table 2 the yield stresses of suspensions increase with increasing volume concentrations. Experimental yield values are the extrapolated shear stress of \( \tau=f(\gamma) \) curve. The calculated values of yield stress were found with the equations of \( \eta_p = \theta_{N_i} - \theta_{N_s} \) and \( \tau_s = \theta_{N_i} - \eta_p \) is where \( N_i \) and \( N_s \) are 600 and 300 cycle \( \text{min}^{-1} \) respectively, and \( \eta_p \) is the plastic viscosity. The extrapolated and the calculated yield stress show a good
Table 2 – Variation of yield stress with different volume concentration

<table>
<thead>
<tr>
<th>φₙ, volume concentration (v/v)</th>
<th>τₛ, yield stress, mPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.9</td>
<td>Calculated, τₛ</td>
</tr>
<tr>
<td>5.6</td>
<td>480</td>
</tr>
<tr>
<td>8.4</td>
<td>1920</td>
</tr>
<tr>
<td>10.9</td>
<td>2880</td>
</tr>
<tr>
<td>13.2</td>
<td>3840</td>
</tr>
<tr>
<td>15.5</td>
<td>6240</td>
</tr>
<tr>
<td>18.4</td>
<td>13920</td>
</tr>
<tr>
<td>20.9</td>
<td>470</td>
</tr>
<tr>
<td>23.6</td>
<td>1880</td>
</tr>
<tr>
<td>28.4</td>
<td>2860</td>
</tr>
<tr>
<td>33.2</td>
<td>3220</td>
</tr>
<tr>
<td>38.9</td>
<td>6220</td>
</tr>
<tr>
<td>43.6</td>
<td>13900</td>
</tr>
</tbody>
</table>

agreement. The yield stress values imply that in the transition process, from viscous flow to plastic flow, relatively high shear stress is required for the given volume concentrations.

The apparent viscosity values of suspensions show a large decrease for the volume concentration of φ₂, φ₃, and φ₄ between the shear rate values of 10.2 and 170.3 s⁻¹ (Table 3) indicating that suspensions have shear thinning. Thus, increasing shear stress causes some deformation, and therefore the viscosity of system decreases. The suspensions exhibit a shear thinning behaviour in slightly alkaline region which is the native pH conditions of suspensions.

Rheogram of suspensions of φ₂, φ₃, and φ₄ (Figure 4) show that in the given pH conditions, between pH values of 3 and 7, no changes occur in the behaviour of Bingham plastic flow. The lowest values of shear stress obtained at pH 3 reflects the decreasing stability of edge to face contacts. The suspension of φ₁ at pH 7 and the suspension of φ₃ at pH 3 show the same behaviour at the shear rate of 680 s⁻¹, and also the φ₂ at pH 7 and the φ₃ at pH 5 behave similarly at the shear rate of 340 s⁻¹.

The variation of shear stress with pH at constant shear rate (600 cycle min⁻¹) show that the shear stress of suspensions of φ₂ and φ₃ changes with pH with a rather small rate compared to the shear stress of φ₁ (Figure 5). That is because, when pH increases, a rapid repulsion between the particles occurs, and then particles move independently under the shear stress applied.

The viscosity of bentonite-water system is strongly pH dependent. For the bentonite dispersion in water, Lagaly explained that due to the irregular shape of particles and lamellae, low pH value, that is high concentration of hydrogen ions, increase the charge density at the particle edges. In the case of an increase in pH values, a repulsion between the particles is promoted since the charge density at the particle edges become negative due to OH⁻ ions, and therefore the apparent viscosity values (ηₛ) increase as shown in Figure 6. In the present study, apparent viscosity (ηₛ) increases with pH linearly between the pH value of 3 and 8 for the φ₂, φ₃, and φ₄ suspensions. Also τₛ values show linear increase in the certain pH range for φ₂, and φ₃ (Figure 7). This result suggests that the stability range of edge to face contact begins to decrease at pH < 3, and face to face contact based on band like structure begins to increase. Ca-bentonite particles can
associate in different ways such as face to face or edge to edge, but in general face to face association is predominant. These approaches are proved by the observation of considerable plasticity with increasing pH in the system. At pH<3 values, edge to face contact based on card-house network is fragmented, and thus the geometrical constraint is weakened, and yield stress of the system decreases. Studies on the detailed knowledge of structure by X-ray techniques are continuing. For the highest and the lowest pH values of the given suspensions, yield stress ($\tau_y$) values do not fit the observed trend (Figure 7). The plastic viscosity ($\eta_p$) values of suspensions differ slightly from each other, but they may be accepted nearly constant in the selected pH conditions.

The results of different electrolyte addition to suspensions are shown in Figures 8 to 11. It is seen from the rheogram of suspensions (Figure 8) that all suspensions with the added electrolytes still exhibit Bingham plastic behaviour. In some cases, lines have cross-sections which indicate that certain suspensions show similar behaviour at the given shear rate. Besides, with the added electrolytes yield stresses of suspensions increase when the solid content of suspension increases.

In Figures 9 to 11, it is generally observed that the apparent viscosity of suspensions decreases with the initial addition of any kind of electrolyte, and that it increases with increasing amount of electrolytes. This phenomena can be explained by a screening effect on the electrical charges of faces and edges of particles that arises with small amount of electrolyte addition. This makes electrostatic interactions between particles decrease, and thus the apparent viscosity diminishes. In the case of $\varphi_4$ suspension (Figure 9), the minimum values of apparent viscosity increases with increasing salt concentration in different ways depending on the type of added electrolytes. Although KOH addition provides alkali medium in suspension, and thus aggregate formation, the increment of apparent viscosity with KOH addition in $\varphi_4$ suspension is relatively high compared to other suspensions. On the contrary, NaCl addition causes small changes on the apparent viscosity. This is, probably, due to Na$^+$ ions excluding Ca$^{2+}$ ions found in the contact region of particles, and thus diffuse ionic layer is compressed, face to face contact of particles predominate, and hard-like structure is formed because of the predominance of van der Waals forces over the repulsion between face to face clay surfaces. As a result, the tendency of gel formation increases. KCl and NaCl addition to $\varphi_4$ suspension (Figure 10) show similar changes in the apparent viscosity which has a minimum value at electrolyte of 1 per cent as the different concentration of KOH exhibits slight differences in the apparent viscosity and cause aggregate formation for the same reason as NaCl in $\varphi_4$ suspension. In suspension of $\varphi_4$, KOH and NaCl addition give nearly similar effect on the apparent viscosity as explained above. The KCl addition of 1 per cent to $\varphi_4$ gives a minimum for the apparent viscosity (Figure 11).

KCl addition to $\varphi_4$, $\varphi_3$ and $\varphi_4$ suspensions increased the apparent viscosity more than other electrolytes. The increasing amount of KCl causes K$^+$ ions to diffuse between the layers of particles and displaces the exchangeable cations such as Na$^+$, Li$^+$. Ionic radius of K$^+$ ions is smaller than Ca$^{2+}$ ions, thus its mobility and zeta potential higher than Ca$^{2+}$ ions$^{4,17}$. If the concentration of K$^+$ ions is sufficiently high, it can displace Ca$^{2+}$ ions also$^{18}$ as Na$^+$ ions displace Ca$^{2+}$ ions$^{19}$. Due to the mobility of K$^+$ ions, repulsion between layers of particles increases. Water can penetrate between layers causing van der Waals attraction to diminish, thus particles dissociate into small platelets. As a result the surface area of particle increases, more water can be held by particles, thus free water in suspensions decreases, and therefore the apparent viscosity increases$^{20,21}$. Besides, large surface area, hence small
Table 3 – Thixotropy conditions of suspensions

<table>
<thead>
<tr>
<th>Shear rate, ( \gamma ) S(^{-1} )</th>
<th>( \Phi_1^* ) (5.6)</th>
<th>( \Phi_2^* ) (8.4)</th>
<th>( \Phi_3^* ) (10.9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Phi_n )</td>
<td>( \eta_n ), mPas</td>
<td>( \Phi_n )</td>
<td>( \eta_n ), mPas</td>
</tr>
<tr>
<td>5.10</td>
<td>1.5</td>
<td>150.0</td>
<td>5.0</td>
</tr>
<tr>
<td>10.2</td>
<td>2.0</td>
<td>100.0</td>
<td>6.0</td>
</tr>
<tr>
<td>170.3</td>
<td>3.0</td>
<td>9.0</td>
<td>7.0</td>
</tr>
<tr>
<td>340.6</td>
<td>3.5</td>
<td>5.3</td>
<td>8.0</td>
</tr>
<tr>
<td>510.9</td>
<td>6.0</td>
<td>6.0</td>
<td>8.5</td>
</tr>
<tr>
<td>1021.8</td>
<td>8.0</td>
<td>4.0</td>
<td>11.0</td>
</tr>
</tbody>
</table>

*\( \Phi_n \), Dial reading, \( \eta_n \): Apparent viscosity.

**Figure** 10 - \( \eta_n = f \) (electrolyte, \%) curve of \( \Phi_1 \) suspensions (\( \Phi_1^* \), 8.4, %)

**Figure** 11 - \( \eta_n = f \) (electrolyte, \%) curve of \( \Phi_3 \) suspensions (\( \Phi_3^* \), 10.9, %)

The difference between the effect of KCl and KOH electrolytes on the apparent viscosity arises from the different characters of their anions. Due to the higher mobility of Cl\(^-\) ions than OH\(^-\) ions, dissociation of particles into small platelets increases with above explained reason, and the tendency of gelation increases with Cl\(^-\) ions.

The acid addition to the system during pH adjustment also exhibits the same effect as electrolytes do due to the adsorption of protons and anions on the particle surface and edge respectively. The adsorbed ions cause screening effect on the electrostatic forces, diminishing the charge, and thus the decreasing attraction between the particles and destroying card-house structure.
The variation of specific conductivity with the clay volume concentration in the presence of electrolytes (Figure 12) differs depending on the electrolyte type and its concentration. In case of KOH at an addition of 5 to per cent, the specific conductivity decreases with increasing volume concentration. KOH at an addition of 1 to 2 per cent increases the specific conductivity with increasing clay volume concentration. KCl addition of 2 to 7 per cent decreases the specific conductivity as the volume concentration increases. In the case of KCl addition of 1 per cent, conductivity varies with volume concentration irregularly. A decrease in specific conductivity with increasing volume concentration may arise from the enhanced interaction between particles, which reduces the charges responsible for the conductivity. The highest increase in the specific conductivity is obtained in $\phi_2$ susp.
pensions with KCl addition of 7 per cent. The increment in conductivity becomes 5.26 fold of the given suspension of without KCl.

The NaCl addition to suspensions in all concentrations increases the specific conductivity largely as the volume concentration increases. The reason is that Na\(^+\) ions exchange cations between the layers\(^9\) and thus the free exchangeable cations increase the conductivity. The presence of free cations in liquid medium causes the particle attraction, and therefore the card-house structure is maintained\(^6,17,22\). The increment of specific conductivity with increasing per centage of NaCl in suspension is not as much as KCl. The mobility of K\(^+\) ions is larger than Na\(^+\) ions. The stepwise hydration reaction of the both ions is exothermic and the ionic radius of K\(^+\) ions is larger than Na\(^+\) ions. Standard enhalpy changes for the hydration of K\(^+\) ions is higher than that of Na\(^+\) ions\(^4\). Therefore, K\(^+\) ions displace the exchangeable cations found between the layers more easily than Na\(^+\) ions, and finally increasing free cations enhance the conductivity of liquid medium.

Conclusions
Hoffman\(^22\) attributed the plasticity of clay particles dispersed in water medium to a card-house structure. The structural network between the particles of a suspension is always in question depending on the composition of the medium so that even small alteration in the composition, the flow behaviour, and hence the particle network of a suspension, can change drastically\(^5\).

In the present study, the flow behaviour of suspensions exhibits Bingham features and their network structure depends greatly on the pH conditions of the system as well as the volume concentration of solid particles. In the concentrated suspensions, increasing pH decreases the edge to face contact, and thus the stability of card-house network diminishes.

The viscosity of the studied system is strongly pH dependent. The linear increase of apparent viscosity and yield stress values between the certain pH values suggests that the stability of edge to face contact decreases and possibly band-like structure begins to increase with increasing pH values. The increase in pH seems to fragment the card-house network. Particularly for Ca-smectite particles, aggregation begins to occur with more face to face association than edge to face association of particles.

The Bingham body of suspensions is maintained with the electrolyte addition and also the size and number of aggregates are enhanced. The most pronounced increase in the apparent viscosity is obtained by KCl addition because of the high mobility of Cl\(^-\) ions as well as K\(^+\) ions. With increasing particle concentration face to face aggregation progresses, and the gelation tendency of the system increases due to, mainly, the increased thickness of the face to face associated sheets of particles.

Specific conductivity of suspensions decreases with increasing particle concentration in liquid medium due to the charge interaction between the particles.

As a consequence, a stability is reached in the flow behaviour of the studied system. This stability occurs even though the network structure of flow changes with the addition of different electrolyte, and a considerable plasticity is encountered with increasing pH. An easy flow is obtained in the deflocculated condition so that in oil well drilling, easy flow is required for the proper circulation with the available pumping equipment at relatively high clay concentration.

References