Effects of poly-sal polymer and barite addition on rheological properties of Algerian bentonite

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**Abstract**

In this paper, we investigate the effect of Poly-Sal polymer and barite on the rheological properties of bentonite of Maghnia (western Algeria). The modified Cross model is used to fit the stationary flow curves of bentonite at different concentrations of Poly-Sal add in base bentonite (4%) and the generalized model of Kelvin-Voigt is successfully applied to fit the creep and recovery data and to analyze the viscoelastic properties of the mixture Bentonite-Barite. Finally, the thixotropic behavior studied of the mixture Bentonite-Barite at constant temperature is analyzed by using a structural kinetic model (SKM) in order to account for the time dependent effect. It is demonstrated that the increase in quantity of barite in base bentonite induces a restructuring and reorganization of the particles of the bentonite at the microstructural level.

Keywords: bentonite, barite, Poly-Sal, structural parameter, thixotropy, viscoelasticity

1. Introduction

The Bentonite represents an important clay material for a multitude of processes and industrial applications due to the exceptional properties of its dispersion in water [1] and their significant influences on the drilling process of oil and gas wells [2-3]. They are found, in particular, as a texturing agent, in cosmetics, as drilling muds in the petroleum industry [4-5-6] or as a sealant in civil engineering [7-8]. The bentonite is also employed as a thickener in waterproofing of hydraulic structures (dams, large reservoirs, etc...). They are also used for stabilization of the oil-water emulsions [9-10-11].

Despite their potential usefulness, applications of bentonite have been limited because of some reasons, namely their swelling [12] and evolution with time. In order to widen the use of bentonite and improve their sorption properties many additives have been added in bentonite such the electrolytes, polymers [13-14] and barite [15-16].

In addition, the knowledge of the rheological properties of bentonite suspension and bentonite additives is important in industry applications in order to provide information for design and process evaluation, control, storage stability and the degree of bentonite-additive interactions. It is noted that the rheological behavior of bentonite dispersions depends on different factors such as the type and concentration of bentonite, the size of bentonite particles, the pH and the concentration of the additives in dispersions.

The effect of sodium carboxymethylcellulose, xanthan gum and sodium dodecyl sulfate on rheological proprieties of bentonite was studied [17]. It was shown; for the three additives; that the apparent viscosities of the solutions increase with increasing concentrations. Other authors [18], has investigated the effect of polyethylene Oxide (PEO) and shear rate on rheological properties of bentonite suspensions. The authors demonstrated that when polyethylene oxide (PEO) was added to bentonite clay, the yield stress and fluid consistency index of the mixture increased. The effect of the temperature on the rheological properties of a complex bentonite-sodium carboxymethylcellulose was investigated [19]. They observed that in the liquid like regime the viscosity of the fluids decreased as the temperature increased, and in the solid-like regime, they observed; at low shear stresses; the Brownian effect dominates the hydrodynamic one. An increase of temperature generates an increase of the Brownian motion. Recently, the effect of Hydroxyethyl cellulose on rheological proprieties of Algerian bentonite was studied [20]. A significant increase in the rheological properties of the mixture bentonite–HEC with the increase in HEC concentration has been shown. The impact of barite on structural recovery behavior of bentonite was studied [15]. It has been clearly demonstrated that the structural recovery of mixture bentonite-barite is time-dependent and their yield stress increases with time of rest and quantity of barite add in bentonite. The authors also used the Leong and Nguyen–Boger models in order to model the structural recovery behavior of barite-loaded bentonite suspensions. The impact of barite and ilmenite mixture on enhancing the drilling muds has been investigated [21]. The study showed that the rheological properties of barite/ilmenite mixture give comparable results as barite and has the potential to be used as alternative weighting material especially in a heavier drilling mud.

From the literature different rheological properties of the mixtures bentonite-sodium carboxymethylcellulose, bentonite-xanthan gum, bentonite- polyethylene Oxide and bentonite- Hydroxyethyl cellulose have been investigated and analyzed by various models [18, 20, 22-25]. However, as far as
we know only a few studies focused on the rheological behavior of bentonite-barite but no study done on rheological behavior of the mixture bentonite-Poly-sal. Although this polymer is designed to reduce the fluid losses and can be used in drilling fluids to increase the viscosity. For this reason the knowledge of the rheological characteristics of the mixtures bentonite-Poly-sal polymer and bentonite-barite plays a fundamental role in flows and performance of transport technologies such as losses of linear and singular energy, non-flow zones, recirculation time, and operation of drilling fluids.

The objective of this paper is, mainly, to study the effect of Poly-sal polymer on the rheological properties of a bentonite in a steady state and on the other hand to study the effect of barite on the viscoelastic and thixotropic properties of bentonite. In order to provide useful information for the proper design of pipes and the selection of pumps during use of bentonite-Poly-sal and bentonite-barite in drilling fluids or in others application.

2. Theoretical time dependent modeling

In order to model the structural evaluation of the bentonite-barite, we applied the structural kinetic model (SKM) [26], which has been successfully employed for starch pastes and concentrated suspensions of minerals. In this study, the kinetic structural approach assumes that the change in the rheological behavior is associated with shear-induced breakdown of the internal structure in the bentonite-barite system.

The structured state of the thixotropic structure at any time \( t \) and under an applied shear rate can be represented by the structural parameter \( \lambda \):

\[
\lambda = \lambda(t, \gamma)
\]

Which \( \lambda(t, \gamma) \) is defined as:

\[
\lambda(t, \gamma) = \frac{\eta - \eta_e}{\eta_0 - \eta_e}
\]

Where \( \eta_0 \) is the initial apparent viscosity at \( t=0 \) (structured state), and \( \eta_e \) is the equilibrium apparent viscosity as \( t \to \infty \) (non-structured state). Note that, both \( \eta_0 \) and \( \eta_e \) are functions of the applied shear rate only [27]. The structural parameter \( \lambda \) ranged from an initial value of unity for zero shear time to an equilibrium \( \lambda \) value lower than the unity. The rate of structural breakdown can be expressed as:

\[
-\frac{d\lambda}{dt} = k(\lambda - \lambda_e)^n
\]

Where \( k = k(\gamma) \) is the rate constant and \( n \) is the order of the structure breakdown reaction. At a constant applied shear rate, integration of (3) from \( t=0 \) to \( t \) yields:

\[
(\lambda - \lambda_e)^{1-n} = (n - 1)kt + (\lambda_0 - \lambda_e)^{1-n}
\]

Substituting (2) into (4) yields for a constant shear rate:

\[
(\frac{\eta - \eta_e}{\eta_0 - \eta_e})^{1-n} = (n - 1)kt + 1
\]

3. Materials and methods

3.1 Materials and sample preparation

3.1.1 Materials

The polymer used in this work is the Poly-sal, it’s designed to provide filtration control in all types of water-based drilling fluids. This non-ionic, natural polymer is effective in all make-up waters, including high salinity and high hardness brines such as NaCl, KCl, MgCl₂, CaCl₂ and complex brines. The Poly-sal polymer used in this work was supplied from Company Algeria. The Table 1 presented the physical properties of the Poly-sal used in this study.

<table>
<thead>
<tr>
<th>Physical appearance</th>
<th>Tan granular powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.5</td>
</tr>
<tr>
<td>pH</td>
<td>7.0</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Soluble</td>
</tr>
<tr>
<td>Bulk density</td>
<td>561 kg/m³</td>
</tr>
</tbody>
</table>

Table 1 Typical physical properties of the Poly-sal used in this study

The clay used in this study is the bentonite of Maghnia (west of Algeria). The main components of this bentonite sample are: \( \text{SiO}_2 \) (61.78%), \( \text{Al}_2\text{O}_3 \) (17.15%), \( \text{Fe}_2\text{O}_3 \) (3.82%), \( \text{MgO} \) (3.56%), \( \text{CaO} \) (0.26%). The specific surface of bentonite and barite used in this study are 1.05 m²/g and 2.84 m²/g respectively. Fig. 1 shows the particle size distribution of bentonite and barite suspensions measured by the light scattering technique with a Malvern Instruments Mastersizer 2000 system. In order to avoid the formation of aggregates during the measurements, the sample was submitted to ultrasound excitation. We observed in Fig. 1 the particle sizes of bentonite ranging between 1 and 138 µm were found with a symmetric distribution centered at about 46 µm and particle sizes of barite ranging between 1 and 138 µm were found with a symmetric distribution centered at about 25 µm. We also observed that the maximum volume of bentonite is greater than the maximum volume of barite which means that the bentonite is more swelling compared to barite.

Fig. 1 Particle size distribution of bentonite and barite

1. ábra A bentonit és barit szemcseméret eloszlása
3.1.2 Sample preparation

Given that the way of preparation has a great influence on the final state of suspensions, thus on the rheological behavior, all tests were carefully carried out under equal conditions to allow for comparison of the results.

3.1.2.1 Effect of Poly-sal

For each mixture, the base bentonite suspension has the same mass concentration (4 wt%). The bentonite powder was dispersed in the required amount of distilled water without any chemical additives. The homogenization was performed under continuous magnetic agitation for 24 hours. The additives at different concentrations (0.2; 0.4; 0.6; 0.8 and 1 wt%) were then added to the base suspensions, afterwards, the mixtures obtained were subjected to a continuous agitation for 24 hours. An average pH ranging between 9.6 and 11.5 was measured.

3.1.2.2 The effect of barite

The mixture bentonite-barite used in this study contain in proportion by weight 0, 1, 2, 3 and 4 g barite to bentonite. The based bentonite mixture consists of 4% wt solid (i.e. 4 g bentonite and 96 g water). In the preparation of the mixture with 1 ratio of barite to bentonite, the mixture compositions consist of 96 g water, 4 g bentonite and 4 g barite. For the 0.75 barite to bentonite ratio the composition is 96 g water, 4 g bentonite and 3 g barite. For the 0.5 ratio, the composition is 4 g bentonite, 2 g barite and 96 g water. For the 0.25 ratio, the composition is 4 g bentonite, 1 g barite and 96 g water. For the 0 ratio the composition is 4 g bentonite, 0 g barite and 96 g water.

3.2 Experimental set up

The rheological measurements were performed by using a torque controlled Rheometer (RS600 from Thermo-Fischer), equipped with a cone-plate geometry (diameter: 60mm; angle: 2°; gap: 105 μm). It has a Peltier temperature control system that allows having a very quick response to any change in temperature. In order to prevent changes in composition during measurements due to water evaporation, a solvent trap was placed around the measuring device.

3.1.2 Experimental methods

3.1.2.1 Steady shear measurements

For study the effect of Poly-sal on the flow properties of bentonite, the sample was pre-sheared at a frequency of 500s⁻¹ for 60 seconds in the measuring device in order to avoid any memory effect. After pre-shearing the sample has kept at rest for 600 seconds prior to measurements in order to permit the material recovering its initial structure partially at least. After kept rest of 600 seconds a continuous ramp of shear stress has been applied. The imposed shear stress range depends on the mass concentration of Poly-sal added in base bentonite (4%). In this study for the concentration of Poly-sal less than 1%, a continuous ramp of shear stress, which is ranging from 0 to 3.5 Pa applied during 600 seconds. For the concentrations greater or equal to 1% a continuous ramp of shear stress, which is ranging from 0 to 4 Pa applied during 600 seconds.

3.1.2.2 Creep-recovery measurements

Creep and recovery tests are carried out as follows: After a rest time of 600 seconds prior to the measurements, a constant shear stress τ=0.5 was applied to the simples and the compliance (J) was recorded as a function of creep time; at t = 180 seconds the stress τ was set to zero and the recoverable part of compliance was measured as a function of the recovery time equal at 180 seconds.

4. Results and discussion

4.1 Effect of Poly-sal on the flow properties of bentonite

The bentonite dispersions were prepared with 4% solid content in desalted water and the Poly-sal concentrations ranging between 0 and 1%. Fig. 2 shows the flow curves of mixtures bentonite 4% at different concentrations of Poly-sal. Experimental data were fitted to the modified Cross model (Eq. (6)) [28], which has been successfully employed for weak gel systems.

$$\tau = \tau_0 + \eta_\infty \dot{\gamma} + \frac{(\eta_0 - \eta_\infty)\dot{\gamma}}{1+(\lambda_\gamma)^m}$$

(6)

It is clear that the shear stress of the bentonite-Poly-sal systems increased with the increase in the Poly-sal T content. Fig. 3 and 4 shows the variation of the parameters of the modified Cross model for bentonite-Poly-sal mixtures systems as a function of different concentration of Poly-sal added in base bentonite (4%) at 20 °C. We observe in Fig. 3 and 4, a rapid increase in the yield stress , zero shear rate viscosity and the infinite shear rate viscosity with the increase of Poly-sal concentration, this increase of yield stress, zero shear rate viscosity and the infinite shear rate viscosity is related to the adsorption of Poly-sal by the bentonite. This adsorption makes the specific surface higher and causes an increase of interaction between the bentonite particles. The increase in the yield stress causes an increase in the friction and an increase in the viscosity of the mixture due to the interaction between the solid particles and viscous effects [18]. In this case, the interactions between the clay particles and polymer intensify.
lead to difficult movements in the dispersing medium. In fact, the presence of Poly-sal in the mixture allows reinforcement of the rigidity and the consistency of the mixture because of the structural nature of the Poly-sal.

Fig. 3 Variation of yield stress and characteristic time of mixture bentonite base (4%)-Poly-sal at different concentration of Poly-sal (0, 0.4, 0.6, 0.8 and 1%)

3. ábra A folyású feszültség és a bentonite(4%)-Poly-sal keverék karakterisztikus idejének változása - a Poly-sal különböző koncentrációjában (0, 0.4, 0.6, 0.8 és 1%)

4.2 Effect of barite on the viscoelastic properties of bentonite

After a rest time (time during which the sample is left at rest in geometry) of 600 seconds, in the creep phase, the samples were subjected to constant stress at 0.5 Pa and at constant temperature (20±0.2 °C). In the recovery phase, the applied stress was suddenly removed and the sample recovery was registered for an additional period of 180 seconds.

Fig. 8 shows the values of compliance (τ) = \( \frac{F}{\eta} \), as a function of time, for the creep experiments corresponding to the bentonite–barite mixtures studied for ration barite to base bentonite (4%) range between 0 and 1, in a time interval between 0 and 180 seconds. For the interval of time between 180 seconds and 360 seconds, we have represented the corresponding recovery. An increase of the elastic compliance (\( G = \frac{F}{\eta} \)) with the increase of quantity of barite added in the based bentonite (4%), indicating an increase of the viscoelastic properties of mixtures barite-bentonite. In other word, the creep deformation decreases with increasing the barite in bentonite and the time necessary to reach a constant deformation during recovery, after removal of the shear stress decreases.

The elastic properties were defined by correlating the results with the well-known viscoelastic models of Burger model or Generalized Kelvin–Voigt model [29-30] based on the association in the series of the Maxwell model and the Kelvin–Voigt model.

The creep curves are described by:

\[
J_F = J_0 + \frac{\mu_0}{\mu} + \sum_{i=1}^{N} J_i \left[ \exp \left( -\frac{\tau}{\theta_i} \right) \right]
\] (7)

\[
\theta_i = \frac{\tau_i}{\eta_i}
\] (8)

Whereas the recovery strain is given by:

\[
J_R = \frac{\mu_0}{\mu} + \sum_{i=1}^{N} J_i \left[ \exp \left( \frac{\tau_i}{\eta_i} - 1 \right) \right] \exp \left( -\frac{\tau_i}{\eta_i} \right)
\] (9)

where \( J_0 \) is the purely elastic contribution (or the instantaneous elastic compliance), \( \mu_0 \) is the purely viscous contribution, represented by the despot of the Maxwell model, i.e., the uncoupled or residual steady-state viscosity obtained from the creep curve at long times when the compliance curve is linear, \( J \) is the contribution to retarded elastic compliance, \( \theta \) is the retarded time, \( \eta \) is the retarded viscosity and \( \tau_i \) is the time where the stress is applied for \( t < \tau_i \) and removed at \( t = \tau_i \). The fitting parameters are detailed in Table 2. The column \( G_0 \) represents the instantaneous elastic modulus of the Maxwell unit at \( t = 0 \); that is the instantaneous elastic response of the system and the column \( G_1 = \frac{\mu_0}{\mu} J_i \) is the elastic modulus of Kelvin–Voigt. The latter represents the contributions of the retarded elastic region to the total compliance. The strong increase is observed in \( G_0 \) and \( G_1 \) when the quantity of barite is changed between 0 and 4 g cause the manifestation of the shift from viscous to elastic behavior and an increase of the viscoelastic properties in that range of barite.
It has the meaning of viscosity of the system in the Newtonian regime, whereas it also shows a clear increasing trend as the quantity of barite in the based bentonite (4%) increases. This increasing of viscosity could be the interactions between bentonite-barite mixture particles and the enhancement of Brownian motion. At high quantity of barite added in based bentonite, the applied stress of 0.5 Pa is not sufficient to break particle-to-particle bonds, and the mixtures (Bentonite-Barite) do not flow. For lower quantity of barite values such resistance to flow is not so large, and this explains the values of and in this case the retarded deformation, related to the breaking and reconstruction of weak links between the particles. The characteristic relaxation time associated with these breaking/reconstruction processes is. Although this time does not show a definite trend when estimated from creep data.

4.3. Apparent viscosity evolution under constant shear rate and determination of the structural parameter of mixtures barite-bentonite

Figs. 6 and 7 show the time dependence of apparent viscosity for constant shear rates (0.5 s⁻¹ and 0.8 s⁻¹) at different quantities of barite (0, 1, 2, 3 and 4 g) added in base bentonite (4%) fitted with the second-order SKM (see Eq. (5)).

For all studied quantities of barite added in base bentonite and for both shear rates, the viscosity decreases significantly with shearing time, particularly in the initial stages of shearing. After approximately 140 seconds shearing periods for shear rate of 0.5 s⁻¹ applied on the mixtures and after approximately 100 seconds of shearing periods for shear rate of 0.8 s⁻¹ applied in the mixtures, the viscosity tends to an equilibrium value. Therefore the equilibrium state of mixtures barite-bentonite depends on the shear rate applied to the system. Fig. 8 shows the variation of the rate constant k and the equilibrium structural parameter λ as a function of the quantity of barite added in base bentonite (4%) and for both shear rates applied.

The rate k constant k can be considered as a measure of the rate of the structural breakdown, i.e. the degree of thixotropy. On the other hand, the ratio of equilibrium to initial viscosity can be considered as an equilibrium structural parameter $\lambda_e$. We observed in Fig. 6 an increase of the degree of thixotropy with increase of the quantity of barite in bentonite. This increase in the degree of thixotropy leads to an increase in the yield stress and the apparent viscosity of the mixtures bentonite-barite.

As it is shown in Fig. 9 structural parameter changes are most significant during the initial shear period after which nearly constant values are reached.
The effect of Poly-sal polymer on the stationary behavior of bentonite and the effect of barite on the viscoelastic and thixotropic behavior of bentonite were studied. The stationary flow curves of bentonite at different concentration of Poly-sal add in base bentonite (4%) was successfully modeled using the Modified Cross model. The generalized model of Kelvin-Voigt and the Cross model parameters causes an increase in the friction and an increase in the viscosity of the mixture.

The increase of quantity of barite in bentonite suspensions was found to increase the viscosity of the mixture. The effect of barite on the break-down behavior of the bentonite suspension was examined. The time dependent viscosity decreased rapidly with shearing time and reached a steady state. The structural parameter of mixture suspension (bentonite-barite) increases with increasing the quantity of barite added in bentonite. This behavior could be explained by the defloculating of mixtures particles in the water at high quantity of barite added (4 g). The applied stress of 0.8 s\(^{-1}\) is not sufficient to break particle-to-particle bonds. The mixture in this case developed a network structure which leads to enhance the organization of particles in the mixtures at the microstructural level [31].

5. Conclusions

The effect of Poly-sal polymer on the stationary behavior of bentonite and the effect of barite on the viscoelastic and thixotropic properties of mixture bentonite-barite. The addition of Poly-sal in a concentration range between 0 and 1% to 4% of bentonite leads to an increase in the yield stress \(\tau_y\), zero shear rate viscosity \(\eta_0\) and the infinite shear rate viscosity \(\eta_{\infty}\) with dose of Poly-sal. The increase of these parameters is related to the interaction between the solid particles and the viscous effects. The increase of the modified Cross model parameters causes an increase in the friction and an increase in the viscosity of the mixture.

The increase of quantity of barite in bentonite suspensions causes an increase of the viscoelastic behavior of the system and the structure of particle-to-particle bonds. In order to avoid the problems related to the structure of particle-to-particle bonds of bentonite, caused by high concentration of barite, during the process of pumping, we propose the addition of an electrolyte as a third additive i.e., bentonite-barite- electrolyte. The effect of barite on the break-down behavior of the bentonite suspension was examined. The time dependent viscosity decreased rapidly with shearing time and reached a steady state. The structural kinetic model (SKM) for viscosity decay with time at the constant shear rate was applied successfully to analyze the time-dependent behavior of bentonite-barite mixtures. The rate of structure breakdown (degree of thixotropy) increases with increasing quantity of barite added to based bentonite.

References


The 23rd International Conference on Composites Materials (ICCM 23) will be held in Belfast, Northern Ireland, from the 1st to 6th of August 2021. ICCM is the premier international conference in the field of composite materials and was first held in 1975 in the cities of Geneva and Boston. Since that time the conference has been held biennially in North American, European, Asian, Oceanic, and African cities. ICCM 23 will attract the leading researchers and practitioners, to report and exchange ideas on the latest developments in the advancement and exploitation of a wide range of composites materials and structures. The general themes of material development, testing, modelling, manufacturing and design will encompass a breadth of topics which will provide a comprehensive global snapshot of the state-of-the-art. Plenary and keynote lectures from pre-eminent leaders in the field are planned, along with oral and poster presentations from an expected large delegation coming together in Belfast from all corners of the world. A number of site visits and an entertaining social programme are also planned.