Understanding the Temperature Effect on the Rheology of Water-Bentonite Suspensions

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ABSTRACT

A successful drilling operation is heavily dependent on the effectiveness of the drilling fluid in use. Exploration of new hydrocarbon fields in complex subsurface environments under high pressure and high temperature (HPHT) conditions, requires the development and use of exceptional drilling fluids, which maintain their rheological properties even at such hostile environments. Drilling fluids are complex, non-Newtonian systems and bentonite is a key component for their formulation. The understanding of its physico-chemical properties that is related to different clay particle linking processes, can lead to the development of "smarter" and more effective drilling fluid systems. This work examines the effect of temperature on the rheological behavior of aqueous bentonite suspensions by performing extensive rheological analysis which can contribute to the understanding of the interfacial and surface phenomena that take place, as well as the modes of interaction between bentonite particles in an aqueous environment.

INTRODUCTION

Clay materials are widely used in several industries such as oil and gas, pharmaceutical and cosmetics, food, agriculture and ceramics. Bentonite is an aluminium phyllosilicate clay consisting mostly of montmorillonite and is a key component for drilling applications. It is mainly used to control the rheological and filtration properties in water-based fluid systems. Due to its high swelling capacity, it provides exceptional flow capabilities by forming a gel-like structure, which is responsible for the yield stress of the suspension giving superior cuttings suspension when circulation of the drilling fluid is stopped. However, montmorillonite clay begins to chemically break down at temperatures higher than 121°C[1], thus restricting its application for HPHT wells without the use of high temperature additives.

In drilling a well, it is essential to know the effect of temperature on the rheological properties of the drilling fluid at operational conditions[2]. The successful prediction of frictional pressure drops is dependent on an accurate knowledge of the drilling fluid rheology[3]. As the fluids travel around the wellbore, their rheological profile is undergoing significant alterations. This can be attributed to the HPHT downhole conditions encountered, which can cause the degradation of the drilling fluid additives as well as to the chemical modification of the fluid when it comes in contact with other formations on its way to the surface[4].

The combination of temperature, pressure, time- and shear- history dependence of the rheological properties makes the characterization and forecasting of drilling fluids rheological profile more complicated. Good knowledge of the synergistic interaction of different drilling

fluid additives, can lead to the development of "smarter" drilling fluid systems with optimal and made-to-order rheological properties[5]. In our preceding studies[6,7], we used water-bentonite suspensions as the base fluid for the formulation of complex drilling fluid systems, giving superior rheological and filtration characteristics. The different additives used each time necessitate a deep understanding of their strengths and limitations in order to control the rheology of the fluid and subsequently the drilling operations performance.

Yet, despite some studies that were carried out over the previous years[2,8,9], which have tried to understand the temperature effect on the rheological properties of aqueous bentonite suspensions, there is still a lot of room for a deeper understanding of the temperature dependence of the flow properties and especially of the contribution of microstructure mechanisms.

This paper presents data showing the effect of temperature (up to 70°C) at atmospheric pressure on the rheological properties of water-bentonite suspensions. The experimental results point out that there is a complex particle to particle interaction at ambient temperature which is enhanced at higher temperatures and that the produced suspensions have reversible thermal/shear history characteristics. Numerous physico-chemical analysis techniques were employed to reveal this phenomenon in order to examine such complex inter-particle structures.

EXPERIMENTAL

Materials and Sample Preparation

The bentonite (Aquagel-Gold Seal) was supplied by Halliburton in powder form with specific gravity 2.6 and without any polymer additives, according to vendor specifications. It is tan in colour with a pH range 8-10.

X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) analysis were employed to reveal its mineralogical and chemical composition, respectively. XRD analysis was carried out using a Rigaku Ultima IV multipurpose X-ray diffractometer. XRD pattern was collected at 2theta (2θ) angle from 3 to 80 degrees with a sampling width of 0.01 degree and scanning speed of 0.5 degree/minute, and was analysed using the Rigaku PDXL2 analysis software. The elemental analysis of the Bentonite powder was carried out using a Rigaku ZSX Primuss II wavelength dispersive X-ray Fluorescence (XRF) spectrometer (WD-XRD). The powder sample was loaded on an aluminium cup and a pellet is prepared using 20T power press without adding any binder.

A Beckman Coulter Laser Scattering Particle Size Analyzer with dry-powder module was used to study particle size distribution of the bentonite powder.

Finally, a FEI QUANTA 400 Environmental Scanning Electron Microscope (SEM) equipped with EDAX Apollo Energy Dispersive X-ray Spectroscopy (EDS) system, was used for surface structure and chemical analysis, respectively. For SEM analysis, the samples were coated with gold using a Leica EM SCD050 coating machine.

Bentonite (45.16 g) was added to 600 ml of de-ionized water to give us 7.0 wt.% suspension with pH range 7.8-8.2, and mixed at 11000 rpm in a Hamilton Beach mixer for 20 min in order to create the samples. The samples were prepared according to American Petroleum Institute (API) procedures[10,11]. The suspension was left to hydrate for 16 h in plastic containers. All rheological measurements for all tested samples were taken one day after the initial preparation of the samples. Before making the rheological measurements the samples were stirred for five minutes in the Hamilton Beach mixer in order to achieve the same shear history for each sample[10]. The preparation and measurement protocols for each sample was followed strictly, in order to ensure consistency and to minimize any biases of our results.

Rheological Measurements

The impact of temperature on the rheological profiles of the water-bentonite suspensions (7 wt.%) was examined at various temperatures (25-70°C) and ambient pressure using a Couette type viscometer (Grace M3600). Viscometric data were obtained at fixed speeds of 600, 300, 200, 100, 60, 30, 6, 3 rpm, which give Newtonian shear rates of 1021.38, 510.67, 340.46, 170.23, 102.14, 51.069, 10.21 and 5.11 s^{-1}, respectively[12]. The yield stress is estimated from the obtained rheograms after extrapolating the shear stress – shear rate curve to zero shear rate and fitting an appropriate rheological model. The readings were taken from high to low speeds, while rotation lasted for 60s at each rotational speed, with readings being recorded every 10s, thus giving six measurements for each rotational speed with a total duration of 8 min per cycle. These six values were averaged and recorded. The rheological parameter estimation was done according to the Herschel-Bulkley (HB) model, given by Eq. 1:

$$\tau = \tau_{HB} + K(\dot{\gamma})^n \qquad (1)$$

which uses three rheological parameters, the Herschel-Bulkley yield stress (τ_{HB}), the flow consistency index (K), which is an indication of viscosity, and the flow behaviour index (n). The Herschel-Bulkley rheological model has proven to give the most accurate fitting results for water-bentonite suspensions used in these experiments.

Methodology

The rheological measurements of the water-bentonite suspensions were performed in the rotational viscometer, which was connected to a circulating water bath being able to maintain temperature with an accuracy of ±0.5°C. The water bath allowed the water to circulate around the viscometer cup, while the viscometer would run the experiment. The range of the tested temperatures was 25°C-70°C. Preceding each test, we started the circulating water bath and waited until the desired temperature was reached. The gradual increase of temperature, was performed with a rate of 1°C/min. Once the desired temperature was achieved, the sample was stirred for 5 min using a mechanical stirrer (Hamilton Beach) prior to each measurement, in order to achieve the same shear history. Then, the sample was placed into the measuring cup and the experiment started immediately, with an initial step of 200s at 600rpm, before any values to be recorded. This step was added in the experimental procedure in order to achieve a temperature equilibration of the sample. The temperature of the experiments was monitored by a temperature sensor embedded into the viscometer cup. Before starting the experiment the exact temperature of the sample inside the viscometer cup was measured with an external thermometer in order to double check temperature accuracy. When a test was done, the tested sample was transferred to the closed container and the measurements with the same procedures were repeated for other temperatures.

Three sets of experiments were carried out with 5 samples in total. In particular:
a) 2 samples (S1 and S2) were measured at a continuous temperature cycle (25°C→40 °C→60 °C→70 °C), referred as continuous samples.
b) 2 samples (S3 and S4) were measured directly at 40°C and 60°C, those being referred as direct samples.
c) 1 sample (S5) was measured at 25°C after natural aging for 1, 30 and 60 days.

RESULTS AND DISCUSSION

Physico-Chemical Analysis of Bentonite

XRD analysis of the raw bentonite powder is shown in Figure 1. The major mineralogical component of the bentonite is montmorillonite, an absorbent aluminium

phyllosilicate clay. Other bentonite clay species such as illite and a small amount of Quartz are also present as minor phases.
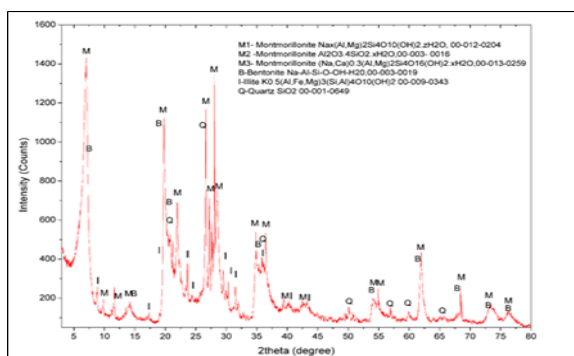

Figure 1. X-Ray Diffraction (XRD) analysis of bentonite.

XRF elemental analysis revealed that the main elements in the powder are Si, Al, Fe, Na, Mg and Ca, which are in accordance with the chemical composition of bentonite clays and quartz, identified by the XRD analysis (Fig. 1). The weight percentage of the major elements are reported in Table 1.

Table 1. X-Ray Fluorescence (XRF) elemental analysis (%) of bentonite.

SiO_2	Al_2O_3	Fe_2O_3	Na_2O	MgO	CaO
65.30	20.30	5.75	2.38	2.24	1.30

Particle Size Analysis (PSA), showed that the mean particle size of the bentonite is 36μm (Fig. 2). This is in agreement with the observed particle size from the SEM analysis (Fig. 3).
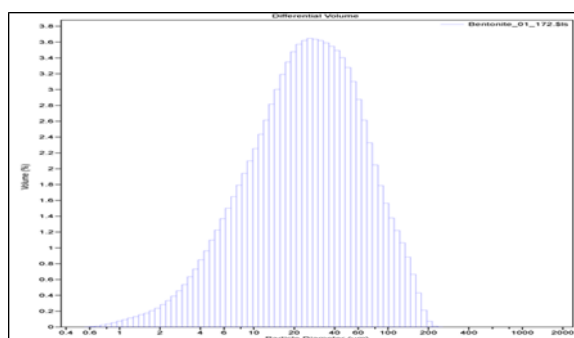

Figure 2. Particle Size Analysis of bentonite powder.

We compare SEM images at 100μm, while insets are taken at 40μm of the same sample, from suspensions at 25˚C (Fig. 3a), then directly to 40˚C (Fig. 3b) and 60˚C (Fig. 3c) and raw bentonite powder at 20μm (Fig. 3d). Similarities and differences for their size and morphology are evident when comparing the suspensions with SEM. The main conclusion that can be drawn from Fig. 3, is that the suspensions have a smoother uniform surface and better dispersion compared to other samples. At higher temperatures (40˚C and 60˚C), the surfaces of samples became rougher with higher concentrations of porous muffin-shaped particles on their surfaces. This morphology can probably affect their rheological characteristics, which requires further investigation in order to gain a deeper understanding. Higher magnification (Fig. 3d), reveals the particle size of the bentonite, probably being composed of single platelets with an average length of 20μm. The EDS elemental analysis of the bentonite powder (Fig. 4) shows the presence of major elements such as Si, Al, Na, Mg, K, Ca, and confirms the results obtained from XRF (Table 1).
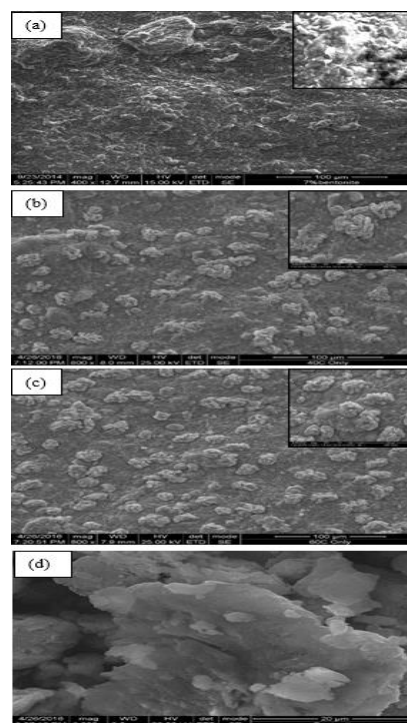
Figure 3. SEM images at 100μm and insets at 40μm, from top to bottom: a) water-bentonite suspension at 25˚C, b) water-bentonite suspension tested directly at 40˚C, c) water-bentonite suspension tested directly at 60˚C and d) bentonite powder at 20μm.
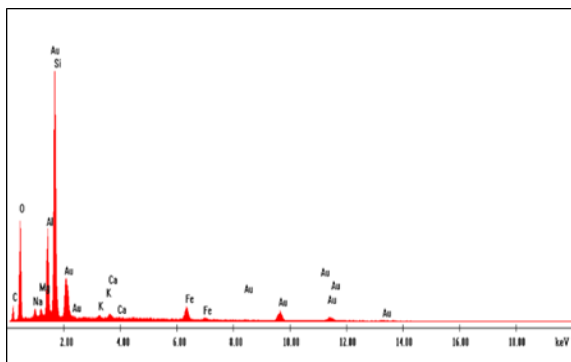

Figure 4. Energy Dispersive X-Ray Spectroscopy (EDS) analysis of raw bentonite powder.

Rheological Analysis

It is apparent from the rheograms in Fig. 5 and 6, that the samples of water-bentonite suspensions which were tested continuously (S1 and S2), are highly sensitive at all tested temperatures. The two samples display similar rheological behaviour with maximum shear stress differences ±5%. The fluids exhibit a yield stress, followed by a shear thinning behaviour with higher shear stress values for increased temperatures. Furthermore, there are larger differences of the stress values at ambient temperature at lower shear rates compared to higher shear rates. More specifically, at low shear rates (5.1-170 s^{-1}) both S1 and S2 samples, have almost doubled their shear stress values at all tested temperatures, while at high shear rates (510.69 and 1021.38 s^{-1}) the maximum difference in the obtained stress values is ±10%. Fig.6 shows the rheogram of S2 sample, which tested back to 25˚C after a continuous testing at 25˚C, 40˚C and 60˚C. One can observe an interesting trend here. At

high shear rates, stress values increased by an average of 40% compared to the initial values obtained at 25˚C, while at 6 and 3 rpm the stress values are similar to those obtained at 25˚C, giving a similar yield stress value as shown later. This can be plausibly attributed to the microstructural network and gel-like structure of bentonite suspensions, which is broken at higher shear rates, while becomes stronger at lower shear rates, giving rise to the build-up of an interconnected network structure in the aqueous suspension. Van Olphen[13], reported that gelation of bentonite particles is mainly governed by electrical forces and as shear rate is decreased these electrical interactions play a more prominent role and affect the rheological properties to a greater extent.
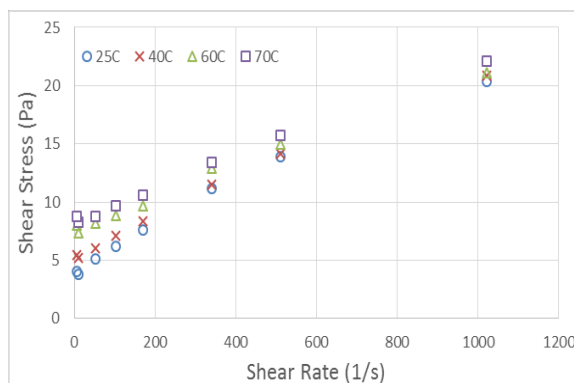

Figure 5. Rheograms of 7 wt% water-bentonite suspensions at different temperatures (S1).
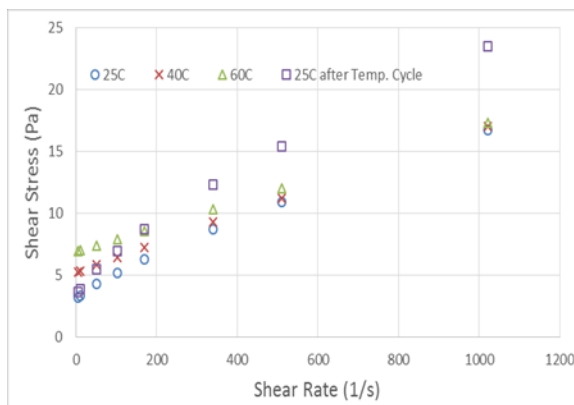

Figure 6. Rheograms of 7 wt% water-bentonite suspensions at different temperatures (S2).

Fig. 7 and 8 compare the apparent viscosity of the suspensions (S1 and S2) at the different tested temperatures (25˚C-70˚C). It can be seen that higher temperatures cause an increase of the viscosity at all shear rates, for both S1 and S2 with shear thinning characteristics. This is in contrast to the base fluid (water) behaviour, where high temperatures cause a decrease in viscosity values. A possible explanation for this behaviour is that exposure of the suspensions at higher temperatures has caused a better dispersion of the bentonite, therefore increasing the number of individual platelets in suspension. Our results are in good agreement with these presented by Annis[2], who observed a significant increase in the viscosity for higher temperatures and argued that high shear rate viscosities are mainly due to mechanical interaction of the solids and the liquid. The low shear rate viscosities are greater than the viscosity at higher shear rates and this difference becomes greater as temperature increases[14]. This can be possibly attributed to the fact that particle aggregates were broken down into smaller flow units by the applied forces, leading to lower viscosity values at higher shear rates. Under high shear rates the fluid is not able to build a strong inter-particle network which arises from the gelation of water-bentonite suspensions upon exposure at high temperatures. The S2 (Fig. 8) was tested back to 25˚C, after a continuous testing from 25˚C to 60˚C, showing that apparent viscosity was not significantly affected when exposed to a higher temperature (60˚C), with a maximum of 5% changes at higher shear rates and 15% at lower rates.
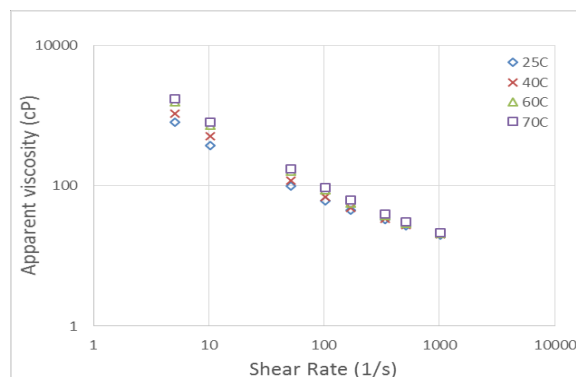

Figure 7. Apparent viscosity of 7 wt% water-bentonite suspensions as a function of shear rate at different temperatures (S1).
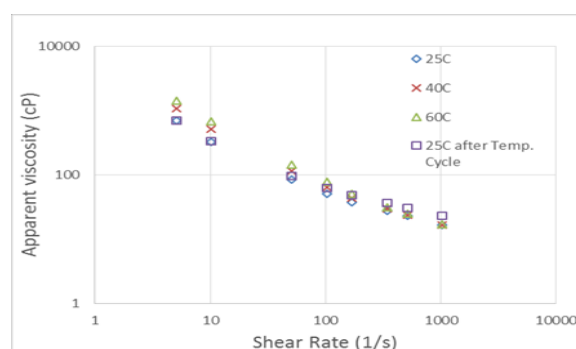

Figure 8. Apparent viscosity of 7 wt% water-bentonite suspensions as a function of shear rate at different temperatures (S2).

Tables 2 and 3, give the rheological Herschel-Bulkley (HB) parameters at different temperatures for the S1 and S2 samples. It can be clearly seen that there is an excellent fit of the HB model because of the very high regression coefficient (R^2) values and the very small variation of the sum of square errors (ΣQ^2) achieved, with R^2 to be higher than 0.99 in all cases and the range of ΣQ^2 between 0.35–1.43 Pa^2.

Table 2. Herschel-Bulkley Model parameters fitted at different temperatures for 7 wt% water-bentonite suspensions (S1).

Temperature (ºC)	Herschel-Bulkley Model				
	τ_o	K	n	R^2	ΣQ^2
	(Pa)	(Pa·s^n)			(Pa)^2
25	3.38	0.097	0.747	0.9990	0.45

40	4.92	0.050	0.833	0.9992	0.35
60	7.36	0.026	0.907	0.9972	0.88
70	8.19	0.022	0.931	0.9985	0.47

Table 3. Herschel-Bulkley (HB) Model parameters fitted at different temperatures for 7 wt% water-bentonite suspensions (S2).

| Temperature (°C) | Herschel-Bulkley Model | | | | |
	τ_o (Pa)	K (Pa·s^n)	n	R^2	$\sum Q^2$ (Pa)^2
25	3.04	0.053	0.802	0.9973	1.43
40	5.18	0.015	0.963	0.9967	1.43
60	6.92	0.009	1.017	0.9973	0.82
25*	3.19	0.130	0.728	0.9993	1.14

*Rheological analysis at 25°C after a full temperature cycle (25°C-60°C).

Fig. 9 presents a comparison of the HB yield stress values over a range of temperatures (25°C – 70°C) for S1 and S2 samples. Determining a trend of the yield stress development across elevated temperatures is of great importance, especially in drilling operations, in order to understand the complex fluid flow properties and optimize cuttings transport efficiency. The existence of yield stress is related to the Van der Waals forces, which promote the formation of flocs that provoke a resistance to flow. In water-bentonite suspensions higher temperatures cause the flocculation and dispersion of the bentonite platelets. Yield stress values increase with temperature for both samples. The first sample (S1) showed an almost linear increase with 3.38 Pa at 25°C, 7.36 Pa at 60°C and 8.19 Pa at 70°C. This represents a change of 118% and 142%, respectively. The second sample (S2) presented an increase in the yield stress values at the tested temperatures from 3.04 Pa at 25°C to 6.92 Pa at 60°C (127% change). The values of the yield stress for the two samples are very close with a maximum deviation of ± 5% until 60°C. As the temperature increases, the bentonite flocculates giving rise to the formation of edge-to-edge or edge-to-face associations, thus giving higher yield stress and viscosity values[2]. It can also be seen that the change in yield stress after the end of the continuous temperature cycle is small, with values of 3.04 Pa and 3.19 Pa before and after temperature cycle, respectively. This proves the reversibility of the produced suspension (S2), which regains its original yield stress value after an exposure at 60°C with small variations of ±10%, in its viscosity values (Fig. 8).
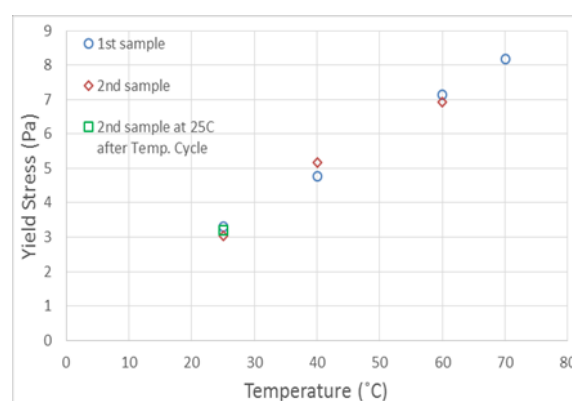

Figure 9. Comparison of yield stress for the tested samples (S1 and S2) at different temperatures.

Fig. 10 presents the variation of flow consistency (K) and flow behaviour (n) index across a temperature range of 25°C - 70°C, for the S1 sample. Analysis for the S2 sample is not presented graphically for clarity purposes, however the detailed values can be seen in Table 3. One can observe the decrease in K as the temperature increases, which probably represents the decrease of water viscosity. The flow behaviour index (n) showed an increase which dictates that the fluids tend to the Newtonian behaviour at high shear rates, which can also be observed when looking at the slope of the rheograms at high shear rates (Fig. 5 and Fig. 6).
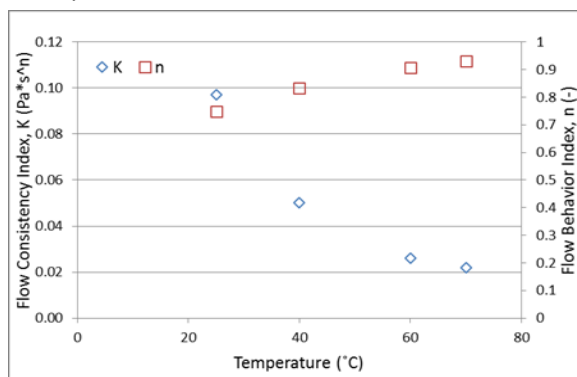
Figure 10. Variation of Herschel-Bulkley flow consistency (K) and flow behaviour (n) index with temperature for the S1 sample.

Another interesting issue is the effect of temperature in the produced suspensions under varying conditions (time, temperature) of exposure. For this reason, two new samples (S3 and S4) were prepared, and tested directly to 40˚C and 60˚C. From Fig. 11 and Table 4, it can be observed that the samples which were tested directly at 40˚C and 60˚C showed lower yield stress values than these of the continuous cycle (25˚C-60˚C), with an average decrease of 30%. This difference is larger as the temperature increases, which reveals the great impact of temperature history profile on their rheological characteristics. Alderman et al.[9], reported that the rheological properties of clay suspensions are extremely time, temperature and shear-history dependent.
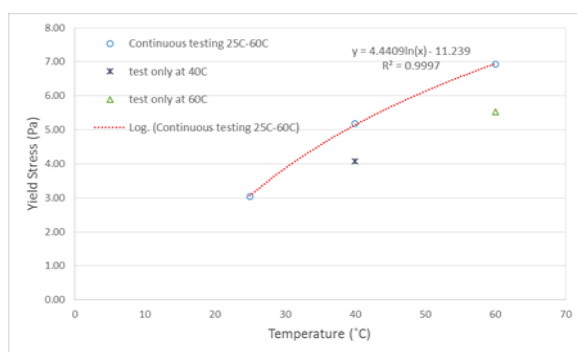

Figure 11. Comparison of yield stress values of the S2 with samples that tested directly to 40˚C and 60˚C.

Table 4. Herschel-Bulkley (HB) Model parameters fitted for samples directly measured at 40˚C and 60˚C (S3 and S4).

| Temperature (ºC) | Herschel-Bulkley Model | | | | |
	τ_o (Pa)	K (Pa·s^n)	n	R^2	$\sum Q^2$ (Pa)^2
Only 40˚C	4.07	0.024	0.884	0.9963	1.29
Only 60˚C	5.54	0.007	1.037	0.9949	1.44

The rheological stability of the produced suspensions under different aging time was evaluated by testing a new sample (S5) at fresh conditions (1 day), after 30 days and after 60 days at 25˚C. Table 5 and Fig. 12 present the variation of the HB parameters and the rheogram, respectively. It is observed that there is a small increase in the yield stress after 30 and 60 days with a value of 3.69 Pa and 3.76 Pa, respectively, compared to its initial value of 3.41 Pa. This can be attributed to the formation of a stronger particle network due to an enhanced clay platelet dispersion over time. The variations in K and n are small, while R^2 is higher than 0.99 in all cases. Our results indicate that the prepared suspensions were rheologically stable with minor rheological changes after 60 days of natural aging.

Table 5. Herschel-Bulkley (HB) Model parameters fitted for the S5 sample at 25˚C after a) 1 day b) 30 days and c) 60 days.

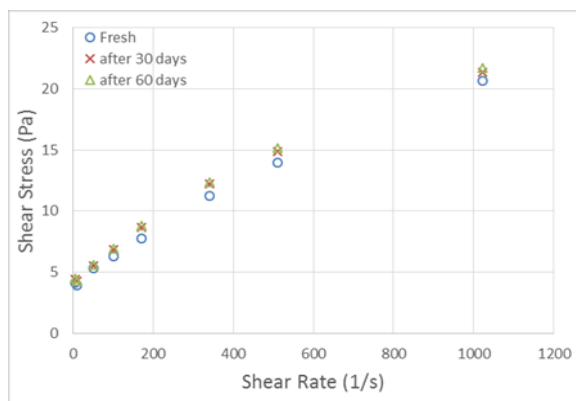| 25˚C Aging (days) | Herschel-Bulkley Model | | | | |
	τ_o (Pa)	K (Pa·s^n)	n	R^2	$\sum Q^2$ (Pa)^2
1	3.41	0.083	0.770	0.9992	0.74
30	3.69	0.095	0.754	0.9985	1.42
60	3.76	0.093	0.759	0.9983	1.73

Figure 12. Rheograms of the S5 sample at 25˚C for a) fresh conditions, b) after 30 days and c) after 60 days.

CONCLUSIONS

In the present study, we investigated the impact of temperature on the rheological profile of the water-bentonite suspensions (7 wt.%) at various temperatures (25-70°C) and ambient pressure. A comprehensive physico-chemical characterization of the bentonite was presented using XRD, XRF and SEM analysis and coupled with rheological data in order to reveal microstructural qualities affecting the suspensions rheological properties. SEM images of the suspensions after different exposure temperatures, revealed that the association of the particles in different configurations plays a critical role in their rheological profile. The prepared water-bentonite suspensions were examined for their rheological characteristics over a shear-rate range of 5 to 1021 s^{-1} and exhibited a yield stress followed by a shear thinning behaviour, which tends to become Newtonian at higher temperatures. The three parameter Herschel-Bulkley model was proved to have an excellent fit of the experimentally derived data. Yield stress and viscosity become increasingly sensitive to temperature, as temperature increases. Higher yield stress and viscosity values were obtained for higher temperatures, which can be attributed to the flocculation of bentonite particles. High-shear viscosities are less sensitive to temperature variations, which

can be due to the gel-like structure of water-bentonite suspensions, which breaks at higher shear-rates, while they form a strong microstructural network at lower shear rates. The temperature history profile has a great impact on rheological characteristics of the suspensions, which proved to be rheologically stable after an aging period of 30 and 60 days with minor changes in their rheological properties measured at 25˚C. It has been shown that by using standard sample preparation and measuring procedures, it is possible to achieve reproducible data for the temperature dependence shear rheology behaviour of water-bentonite suspensions. Further investigations are already under way in order to elucidate the complex inter-particle interactions which govern the rheological behaviour of water-bentonite suspensions at higher temperatures[15].

ACKNOWLEDGMENTS

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