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THE INFLUENCE OF STORAGE TIME ON THE RHEOLOGY AND PH OF BENTONITE SUSPENSIONS

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Abstract. *Bentonite clay particles swell due to adsorption of water, forming a colloidal suspension and exhibiting thixotropic and yield stress characteristics. The American Petroleum Institute* (API SPECIFICATION 13A 2007) *recommends storing formulated bentonite suspensions for at least 16 h before performing rheology experiments. However, the results shown suggest that this minimum time is not sufficient for complete stabilization of the material. The steady-state shear stress response when an imposed shear rate step ranging from 10^2 to 10^{-1} s^{-1} was evaluated for 7.42 and 9.11 wt% suspensions over 9 weeks after sample preparation. Different homogenization procedures were also evaluated. The steady-state shear stress considerably changed over the first week due to swelling of the particles. The results repeatability was compromised when the homogenization step was not performed. The full stabilization of the shear stresses of the homogenized samples was only observed after four weeks. This indicates that the ageing time suggested by the American Petroleum Institute is not sufficient to obtain stable samples. The pH of the samples decreased from 9.8 to approximately 8.7 over nine weeks. The most intense decrease was observed in the first week, indicating that the pH can be used as an indicator of sample stability.*

Keywords: bentonite suspensions, storage time, rheology, pH, preparation methodology.

1. INTRODUCTION

Bentonite is one of the main components of water based drilling fluids (Murray, 1991). It is a mineral clay, and its crystalline structure is formed by two tetrahedral layers of silica and an octahedral layer of alumina. When suspended in water, bentonite particles arrange in spaced layers, allowing the adsorption of cations and water molecules (Hofmann *et al.*, 1933; Luckham and Rossi, 1999), increasing the particles volume up to 20 times (Norrish, 1954). The final size of the particles varies according to the nature of the cations between the layers and the amount of water available (Brindley, 1955).

Bentonite colloidal suspensions are thixotropic yield stress materials (Coussot *et al.*, 2002; Ovarlez and Coussot, 2007; Ovarlez and Chateau, 2008; Ovarlez *et al.*, 2015). Particle swelling, yield stress and thixotropy are some of the characteristics that allow the use of clay in several industrial applications, such as absorbents, foundry sand bond, drilling mud, iron ore pelletizing, and others (U. S. Geological Survey, 2007). One methodology for the preparation of the bentonite suspension to perform rheological tests is given by the API Specification 13A (2007), which defines the

acceptable criteria for the formulation of drilling fluids. Kelessidis *et al.* (2007) claimed that strictly following API preparation procedures gives reproducible results in steady-state shear-rate controlled measurements. In spite of defining the main stages of the formulation, the proposed methodology is simple and does not explore relevant parameters for rheological tests, such as storage time and pH, which was also claimed to affect the rheology of bentonite suspensions (Laribi *et al.*, 2006; Kelessidis *et al.*, 2007; Choo and Bai, 2015). Fernandes *et al.* (2017) observed that sampling procedures, such as the intensity of the pre-shearing performed on samples of a synthetic drilling fluid, not only changed the measured value of the gel-liquid transition stress, but also affected the steady-state shear stress at a given shear rate.

The API Specification 13A (2007) recommends ageing the samples for at least 16 h after the preparation of the suspension. This shelf time influences the rheological properties of bentonite, as demonstrated by Abu-Jdayil (2011), Choo and Bai (2015) and Vryzas *et al.* (2016). Abu-Jdayil (2011) have studied suspensions with concentrations ranging from 0.5 to 10 wt% for 48 hours after the preparation and have concluded that the apparent viscosity of the bentonite suspensions increases with storage time. However, the author have concluded that the development of the suspension structure is found to be relatively limited after 24 h for most of the samples tested. Vryzas *et al.* (2016) have studied bentonite suspensions of 7 wt% concentration and found that the steady-state shear stresses under an imposed shear rates increase over time. The authors have assumed that the changes in viscosity halted after 30 days of storage. Choo and Bai (2015) have evaluated bentonite properties with 5, 7 and 9 wt% over up to 72 h after preparation. Flow curves were measured and the shear stresses increased over the course of 72 h after preparation. Similar behavior in laponite, a synthetic clay, was also observed by other authors (Shahin and Joshi, 2010; Abedi *et al.*, 2019).

The effect of storage time on the rheological properties of bentonite suspensions is still an open topic in literature, as there is no consensus on the ideal shelf times to achieve reproducible results. Therefore, the present work aims to investigate the effects of the storage time on the rheology of bentonite suspensions by determining the shear stresses under four shear rates over time after preparing the samples. The pH of the bentonite suspensions was also evaluated to verify if it is related to the stability of the samples. The influence of the homogenization stage prior to the rheological test was also evaluated. The sample mass concentration was measured weekly to identify particle sedimentation effects.

2. EXPERIMENTAL METHODOLOGY

Bentonite powder (Sigma Aldrich, id 285234), with mineral concentration of 90 to 100%, was used, and the samples were prepared following the American Petroleum Institute (API Specification 13A, 2007) recommendations. Tests were performed for two concentrations of clay in distilled water, 7.42 and 9.11 wt%. Two samples with each concentration were prepared so that the tests were carried out with and without the homogenization step, which consists on stirring the sample in a low-capacity industrial mixer (Hamilton Beach HMD200) for 5 minutes. The mass concentration, rheological and pH measurements were performed weekly over 9 weeks.

To check if gravity-induced phase separation is taking place on the samples, the mass concentration was verified. A suspension specimen (approximately 5 g) is taken from the container and weighed in an electronic scale (accuracy ± 0.01 g). This sample was then dried in an oven at 60 °C over 24 h to evaporate the water phase, and the residues weighed again. The bentonite concentration was calculated considering the residual mass as only dry bentonite powder.

The rheological tests were performed on the Haake Mars III rheometer at 25 °C. Temperature was controlled through a water-cooled Peltier system, and parallel cross-hatched plates (diameter 35 mm, gap 1 mm) were used to reduce wall-slip effects (Dimitriou *et al.*, 2011). In order to reduce the effects of evaporation, an atmosphere saturated in water vapor was created by placing water-soaked cotton around the bottom plate, which was then covered with a sample hood. Constant shear rates logarithmically distributed between 100 to 0.1 s^{-1} were imposed over of 300 s. The shear stress response of the material was measured at the end of each plateau, and each experimental condition was evaluated in triplicate. The pH was measured after the rheological test with a previously calibrated Quimis bench meter (model Q400AS).

3. RESULTS

3.1 Concentration

The concentrations were measured weekly for the four evaluated cases and are presented in Figure 1 (a) for 7.42 wt% and (b) for 9.11 wt%. The reduced concentration when compared to the reference is attributed to the moisture present in the bentonite powder used (90 to 100 % of the mineral), which evaporated over the drying procedure. Therefore, the corrected concentration is taken as the measured concentration on the day that the samples were prepared.

Results variability (6.44 to 7.82 % in Figure 1 (a) and 8.38 to 9.58 % in (b)) is attributed to the measurement error of the methodology used. The coefficients of variation indicate errors of 2.3, 5.3, 3.2 and 2.1% along the 10 weeks for samples 7.42 wt% with homogenization, without homogenization and 9.11 wt% with homogenization and without homogenization, respectively.
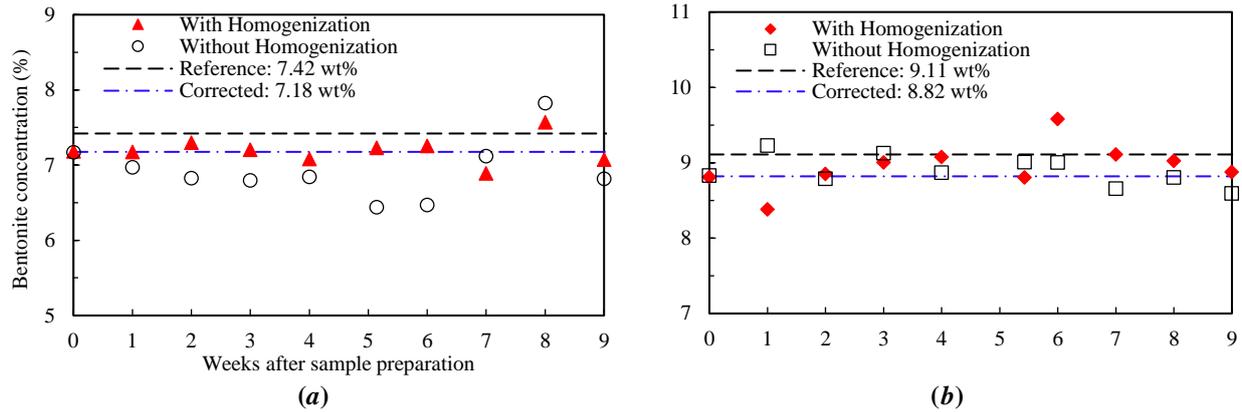
Figure 1. Weight concentration for samples with and without homogenization for (*a*) 7.42 wt% and (*b*) 9.11 wt%. Dashed black lines are the reference weight concentration values used for sample preparation. Dash-dotted blue lines represent the corrected sample concentration.

3.2 Rheological tests

The shear stresses measured at the end of each shear rate plateau are shown in Figure 2 for (*a*) 7.42 and (*b*) 9.11 wt% bentonite suspensions, with (*i*) and without (*ii*) homogenization. Error bars represent the standard deviation. As expected, the shear stresses measured at the more concentrated bentonite suspension are higher than those measured on the less concentrated one, as can be seen in the higher y-axis scale of the Figure 2 (*b*) when compared to Figure 2 (*a*).
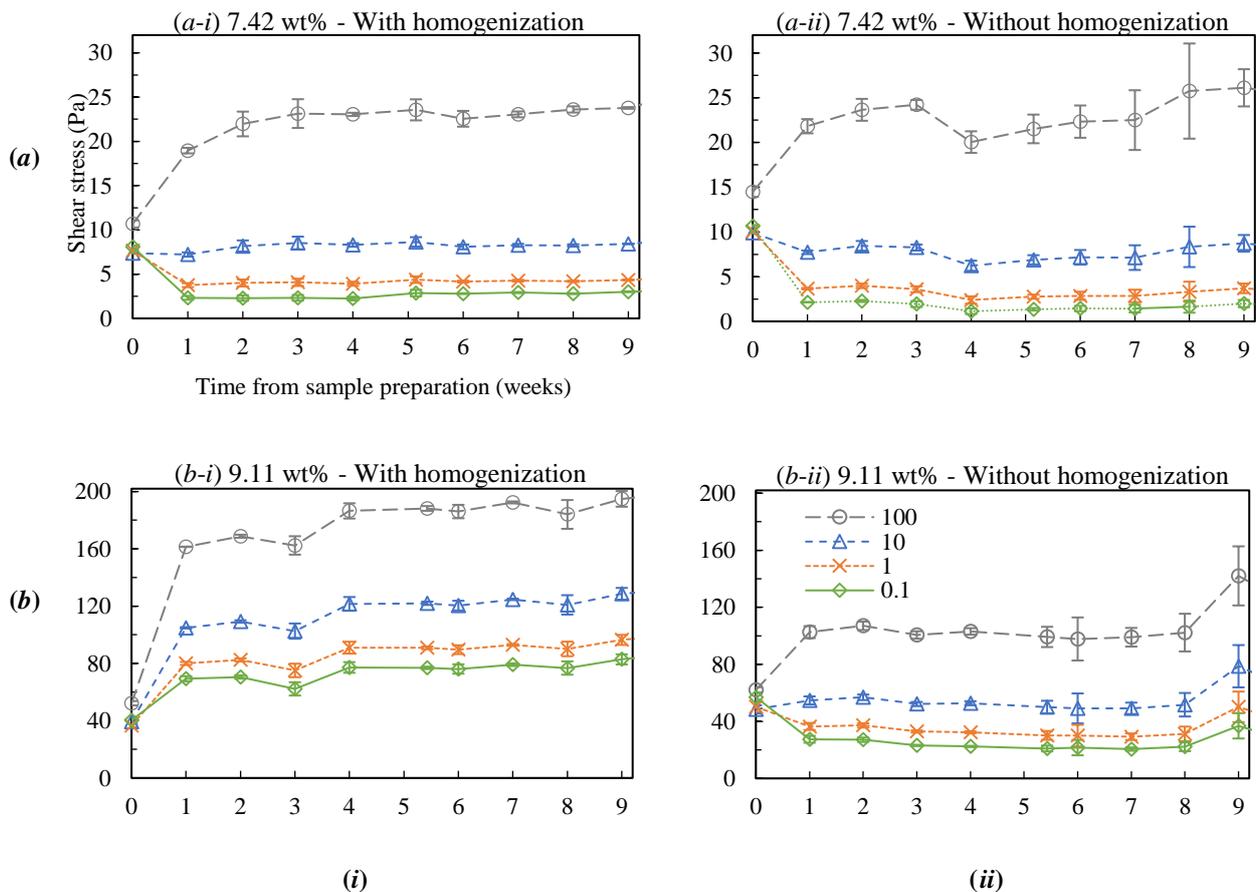

Figure 2. Shear stress for four different shear rates in function of time after sample preparation: (*a*) Suspension of 7.42 wt% bentonite (*b*) Suspension of 9.11 wt% bentonite. (*i*) With homogenization (*ii*) Without homogenization. The legend are presented on *ii-b* with the shear rates imposed in s^{-1}. The labels axis are on *i-a*. The error bars denote the standard deviation of the triplicate.

The biggest changes in viscosity were observed within the first week after sample preparation. This behavior is attributed to swelling of the particles by adsorption of water between clay layers (Norrish, 1954; Luckham and Rossi, 1999). The shear stresses measured at 100 s^{-1} doubled during this period (grey circles, Figure 2), with the exception of the sample with homogenization of 9.11 wt%, Figure 2 (*b-i*), in which the shear stresses increased fourfold. The shear stresses measured at the lowest shear rates, excluding the day of preparation, showed a behavior similar to that observed at 100 s^{-1}.

The shear stresses values did not show significant influence of the homogenization process at the concentration of 7.42 wt%, as can be observed in Figure 2 (*a*) *i* and *ii*. On the other hand, the homogenization presented a strong effect on the 9.11 wt% sample, as can be seen in Figure 2 (*b*) *i* and *ii*. The hypothesis of particle sedimentation was discarded since there has been no significant changes in the weight concentration measurements between samples. Therefore, the homogenization step for the more concentrated sample seems to increase its viscosity, which can be explained by the increase in the packing fraction promoted by the homogenization.

The error bars in error Figure 2 (a-*ii*) increase significantly after the fifth week for samples without homogenization. The growth of the error bars shows the importance of the samples homogenization processes prior to performing rheological tests, as suggested by the American Petroleum Institute (API SPECIFICATION 13A 2007) and Fernandes *et al.* (2017).

A variance analysis (ANOVA) was performed to identify at which week the shear stress measured at 100 s^{-1} of the homogenized samples (*a-i* and *b-i*) started to show insignificant variations at a significance level of 95%, indicating the stabilization of the suspension. The changes observed with the 7.42 wt% sample (Figure 2 *a-i*) were insignificant after two weeks. The 9.11 wt% (Figure 2 *b-i*), on the other hand, stabilized after four weeks.

The stability of formulated samples is essential for studying the rheology of complex materials. The results presented in Figure 2 indicate that a storage time of 16 h, as suggested by the American Petroleum Institute, is not enough to reach rheologically stable bentonite suspensions. The time required to sustain a constant viscosity over the shelf time seems to depend on the composition and formulation procedures.

3.3 pH

The pH as a function of storage time is shown in Figure 3 for samples (*a*) of 7.42 and (*b*) 9.11 wt%. The pH measurements for the homogeneized suspensions are slightly lower than those for the non-homogeneized ones for both concentrations. The pH decreased over time, as already reported by Choo and Bai (2015) and Kelessidis *et al.* (2007) when the sample during the preparation is alkaline. Kelessidis *et al.* (2007) observed a stable pH after 16 hours of formulating the samples, differently from the results reported in Figure 4 that shows a steady decrease over 9 weeks. The most intense changes in pH were observed during the first week, when intense changes in viscosity were notice as well. This result is similar to that observed by Choo and Bai (2015), where the decrease in pH was seen with an increase in the measured shear stress. According to Kelessidis *et al.* (2017), the pH of bentonite suspensions influence the mode of particle interaction: the edges of the bentonite particles are positively charged in acidic environments and negatively charged in alkaline environments (Caenn *et al.* 2017). Considering that the faces of the bentonite particles are negatively charged (Kelessidis *et al.* 2017), a decrease in the pH within the alkaline range (pH>7) indicates that the average electric charge of the suspension is gradually neutralized over the shelf time. This decrease in pH is more pronounced for the samples that underwent homogenization, possibly because mixing the samples promotes the dispersed phase redistribution and allows the hydration of more clay particles, accelerating the swelling process. This also explains the higher steady-state shear stresses observed for the homogeneized samples when compared to the non-homogeneized, as can be seen in Figure 3. Therefore, the pH can be used as a non-intrusive method to assess sample stability, without necessarily performing rheometric experiments.

4. CONCLUSIONS

Bentonite suspensions are thixotropic yield stress materials. A simple sample preparation methodology to perform rheological tests proposed by the American Petroleum Institute suggests a minimum storage time of 16 hours. This work investigated the effects of the storage time and the homogenization procedure on the steady-state viscosity and on the pH of bentonite suspensions.

Shear stresses for shear rates of 100, 10, 1 and 0.1 s^{-1} were measured over 9 weeks to assess the effects of storage time on the viscosity of bentonite suspensions. Concentration and pH measurements were also performed. 7.42 and 9.11 wt% bentonite in water suspensions were evaluated for the cases with and without homogenization before the rheological test. The measurement of the concentrations over time showed a constant behavior, indicating the absence of significant particle sedimentation.

The rheological behavior of the suspensions changed over the shelf time, and the highest shear stress variations were measured in the first week, when the swelling of particles is assumed to be more intense. The homogenization was shown to be relevant for obtaining repeatability of the results. For the homogenized samples, the steady-state shear stress of the

7.42 and 9.11 wt% samples stabilized two and four weeks, respectively, indicating that the 16 hours suggested by the American Petroleum Institute are not sufficient to reach stability.

The pH decreased from approximately 9.9 to approximately 8.7 over 9 weeks, and homogenization led to a decrease in the pH of the samples. In the first week, the most intense variations of pH and of shear stress took place simultaneously, indicating that pH measurements can be potentially used as a non-destructive procedure to probe sample stability.
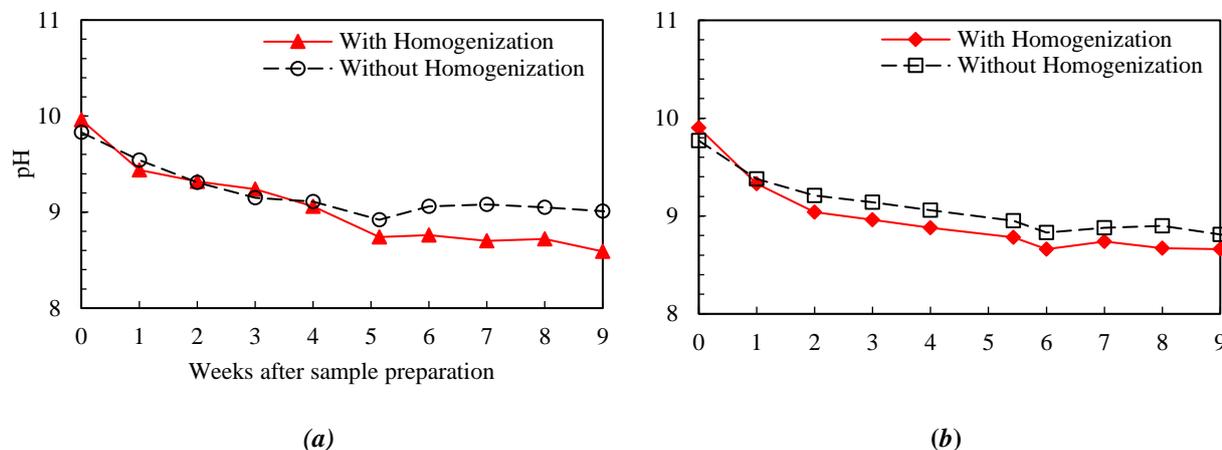

(a)   *(b)*

Figure 3. PH as a function of time after sample preparation: (*a*) Suspension of 7.42 wt% bentonite (*b*) Suspension of 9.11 wt% bentonite.

5. ACKNOWLEDGEMENTS

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