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EFFECTS OF THERMAL AGING ON THE RHEOLOGY OF WATER-BASED DRILLING FLUID WITH XANTHAN GUM AND LIMESTONE

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Abstract. *Drilling fluids must have the ability to transport cuttings during well drilling operations. Thermal gradients during the drilling process degrade the fluid, altering its rheological properties. The effect of thermal aging is significant in calculations of hydraulic projects under HPHT conditions. In the present work, flow curves were performed on the Anton Paar MCR 702TD rheometer to investigate the influence of temperature in a range of 4 to 70 °C on water-based drilling fluids with Xanthan gum. The viscosity variation was fitted to the WLF model through the consistency coefficient, showing a decrease with temperature. Also, dynamic thermal aging tests were carried out at 90 and 125 °C. Its comparison is made employing flow curves, evidencing a decrease in shear stress and the decrease in transition temperature with an increase in the aging temperature. Likewise, qualitative experimental tests showed a greater solubility of the electrolytes, an increase in the pH, and reduction in phase separation time, evidencing the thermal structural degradation of the fluid. The results evidenced physical-chemical alterations in the components of the drilling fluid. Experimental fit can be used successfully in the oil & gas industry to aid in the decision-making process.*

Keywords: *water-based drilling fluid, thermal aging, Xanthan gum, degradation.*

1. INTRODUCTION

As the energy demand for oil & gas worldwide has rapidly increased in the 21th century, the oil companies are always pursuing new hydrocarbon reservoirs, once the conventional reserves are being depleted. Therefore, companies are now focusing their effort to drill and explore deeper wells. Nowadays, the oil & gas companies are dealing with the strong challenges presented by HPHT conditions at the bottom of the well. One key factor for the success of the drilling operation is drilling fluid design that has a significant impact on the total costs of petroleum well hole that vary between 15 and 18% (Hossain, 2015). Thus, the successful drilling depends remarkably on a broad understanding of the drilling fluids properties, which must be designed to adapt to the formation conditions during the entire drilling process (Hermoso *et al.*, 2014a). Drilling fluids are complex materials that display elastoviscoplastic and thixotropic characteristics. They present a reversible time-dependent decreasing viscosity under shear rate and also display yield stress that characterizes the transition from a structured state to an unstructured one induced by shear stress. In oil exploration, water-based drilling fluids pioneered drilling fluids due to its capacity to carry cuttings from the bottom of well to the surface and at the same time working as well controllers. However, many other news challenges appeared, and operation conditions, such as high pressure and high temperature, presented the degradation of the water-based drilling fluid. Today, due to scientific advances, water-based drilling fluids are overcoming their limitations at HPHT conditions, based on the addition of new compounds or materials, which have shown to improve their rheological properties allowing deeper well drilling (Mohideen *et al.*, 2019). Many constituents of water-based drilling fluid degrade slowly at high temperatures. Such degradation occurs during fluid circulation but is more severe with the drilling fluid left in the lower part of the hole, due to the high temperature. Consequently, the effect of thermal aging can be observed on all water-based drilling fluid compositions. To simulate the conditions of the bottom hole temperature and to investigate its effects, aging tests on different temperatures can be performed.

Therefore, the objective of this work is to investigate the effects of temperature and thermal history on the rheological properties of water-based drilling fluid with Xanthan gum. Temperature effects were investigated by flow curves at different temperatures of 4, 10, 25, 40, 55, and 70 °C. The thermal stability of the fluid was investigated with thermal aging tests in a rotating oven for 16 hours at 90 and 125 °C. The shear stress was compared with the non-aged fluid, through flow curves at 25 and 55 °C with atmospheric pressure. In the same way, samples of the aged fluids were dried in ambient conditions, identifying crystallization of the dissolved electrolyte, as well as the comparison of the time required for phase separation of the fluid. Besides, an equation was fitted to model the behavior of the drilling fluid viscosity as a function of temperature.

2. MATERIALS AND METHODS

2.1 Drilling fluid

The drilling fluid used in the test was kindly provided by Petrobras S.A. The fluid is a water-based drilling fluid with Xanthan gum as a viscosifier, whose composition is shown in Tab. 1.

Table 1. Chemical composition of water drilling fluid.

Chemical Composition.		
WBM-Xanthan	Industrial Water	QSP
	NaCl brine $[kg/m^3]$	156.7
	Anti-foamer (Polifoan) $[mL/m^3]$	1.19
	Xanthan Gum $[kg/m^3]$	5.7
	Starch HP $[kg/m^3]$	22.8
	Magnesium Oxide $[kg/m^3]$	4.3
	Lubricant (Liovac 4260) $[\%\ v/v]$	2
	Bactericidal (Polibac TC) $[kg/m^3]$	1.4
	Magnesium Peroxide $[kg/m^3]$	2.8
	Rheological Modifier (BDF 990) $[kg/m^3]$	2.8
	Limestone $Ca(OH)_2$ $[m^3]$	QSP p/1.51

2.2 Experiments

The rheological characterization of drilling fluid was carried out in a rheometer Anton Paar MCR 702TD with chamber CTD 180. The temperature control was performed with the air convection system off and the Peltier system on. Additionally, to avoid evaporation of the sample pieces of cotton saturated with water were placed within the chamber. The geometry used was a sandblasted coaxial cylinders of 20 mm inner diameter with a radius ratio of 0.909 and a bottom gap of 0.051 mm, avoiding slip at boundaries, migration of the sample, and edge fracture. The annular gap of the geometry must be greater than 10 to 100 times the size of the particles in suspension, to avoid errors due to interaction between the walls that increase the measured torque (Hermoso *et al.*, 2014a).

The procedure for rheological measurements flow curves consists of homogenizing the fluid in a mixer Hamilton Beach HMD200 for 10 minutes. After, 10 ml of sample is placed inside the rheometer geometry at 25 °C for 5 minutes at atmospheric pressure. An oscillatory test of amplitude sweep with a frequency 1 Hz is performed to evaluate the fluid-structure before and after the temperature rise. Temperature ramps are implemented to reach the test temperature, a rate of 4 °C/min^{-1} for heating and 3 °C/min^{-1} for cooling, followed by a pre-shear of 600 s^{-1} during 10 minutes to eliminate possible flocculation and erase any shear history. Finally, the flow curve is obtained for different constant shear rate 400, 350, 300, 250, 200, 150, 100, 50, 10 and 1 s^{-1} were applied for 1000 seconds each until reaching steady-state shear stress, the criteria used is based on the moving average with 50 seconds intervals, with variations less and equal to 1%. The shear rate was imposed starting from the highest value to the lowest, allowing the steady-state to be reached more quickly, especially in materials presenting thixotropy (Da Cruz *et al.*, 2002; Divoux *et al.*, 2013).

The thermal aging tests were performed according to the API 13B-1 (2016) standard procedure. A Roller Oven Fann was used to aged tests dynamically at 90 and 125°C. Firstly, the sample was homogenized for 10 minutes, before being placed inside the aging cell. Then, the aging temperature was kept constant for 16 h, simulating the flow in the annular zone when the well is in operation. Finally, the cell was removed from the oven and cooled for 24 hours at room temperature. Thereafter, the drilling fluid was then tested to determine its rheological properties.

In order to verify the possible thermal degradation of the fluid after being subjected to thermal aging, the pH was measured through a pH meter Quimis Q400AS. Also, electrolyte crystallization tests at ambient conditions and measurement of phase separation times were carried out allowing to develop a qualitative analysis.

3. RESULTS AND DISCUSSION

3.1 Flow Curves at Different Temperatures

The characterization of the rheological behavior of drilling fluids subjected to increases in temperature and thermal history are important in the oil & gas industry. Flow curves of a steady-state material are the most traditional way of correlating viscosity variations with their dependent variables. Fig. 1 depicts the shear stress as a function of 10 different shear rates, that are within the operational range of the annular zone of the drilling rig, plateaus ranging from 400 to 1 s^{-1}, where the dotted dasher line shows a fit of the power-law model has been satisfactorily modeled (Song *et al.*, 2006). The parameters of fitting are shown in Table 2.

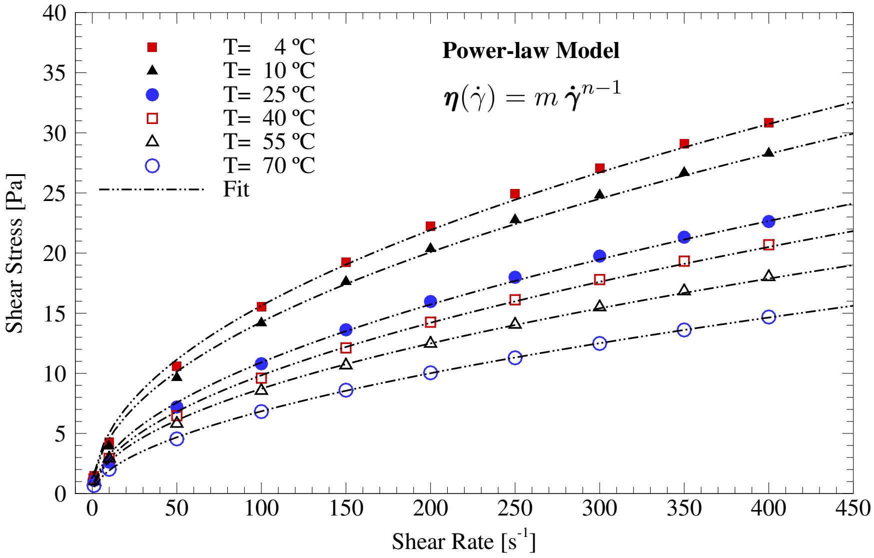

Figure 1. Equilibrium flow curve fitted by the power-law model in the temperature range from 4 to 70 °C for water-based drilling fluid. Power-law model describes the apparent viscosity as proportional function to shear rate, where m is the consistency coefficient, $\dot{\gamma}$ the shear rate, n the flow behavior index and η apparent viscosity.

The analysis of Figure 1 shows a shear thinning behavior at all temperatures. Shear stress also shows a decrease with increasing temperature, indicating that the material loses its viscosity with temperature. Shear stress decreased approximately 10% for every rise of 15 °C, for most intervals. The effect of decreasing shear stress with temperature is reflected through the consistency coefficient in fluid with shear thinning behavior, as reported by Reinoso *et al.* (2019). Due to the increase in the thermodynamic state of the molecules, the collision rate and the thermal motion gradually increases, resulting in a weakening in the hydrogen bonds of the water (Mao *et al.*, 2019), and polymeric chains of the Xanthan gum take a partially transition from ordered random broken helix conformation to disordered random coil conformation (Pelletier *et al.*, 2001; Xie and Lecourtier, 1992).

The shear-thinning behavior of the solutions is attributed to the disruption of internal structures entanglements formed by the molecules (Osaki, 1987). This characteristic is represented by the flow behavior index, which in the case of polymer solutions, the backbone of the chains goes from an ordered to a disordered state when the values of n increase. Therefore, the flow behavior index had a slightly less variation with increased temperature, due to it has not yet exceeded the transition temperature. According to Reinoso *et al.* (2019), the thermal transition region of native Xanthan gum solutions is between 70 to 120 °C.

In order to evaluate the variations of viscosity with temperature, Fig. 2 (a) presents the consistency coefficients as a function of temperature obtained from the power-law model, fitting the data to the model proposed by Williams *et al.* (1955) according to the following equation:

$$m = m'\,10^{-\left(\dfrac{A'''\,(T-T_0)}{B'''+(T-T_0)}\right)} \tag{1}$$

where m' is the consistency coefficient at the temperature of reference, A''' and B''' are adjustment constant. As indicated, the correlation coefficient R^2, for all the fit is higher than 0.95. Whereas, it was observed that the values at the

Table 2. The fit parameters of the consistency coefficient and flow index of the power-law model for the rheological behavior of water-based drilling fluid with increasing temperature, with their respective R^2.

Power-law Model			
T [°C]	**m**	**n**	**R^2**
4	1.65	0.48	0.997
10	1.47	0.49	0.998
25	0.96	0.52	0.998
40	0.85	0.53	0.998
55	0.80	0.51	0.999
70	0.54	0.54	0.999

temperatures of 25 and 55 °C had a greater deviation for the proposed fitting.

Figure 2(b) represents the viscosity as a function of the shear rate for different temperatures with its respective fit, where Eq. (1) was incorporated in the power-law model. When fitting this equation to rheological measurements, once can notice a good agreement with calculated data. The fitting parameters were m'=1.67, A'''=0.90 and B'''=72.46 respectively, for the reference temperature of 4°C. The analysis of the curves in Fig. 2(b) reveals that the viscosity decreases with increasing temperature. This effect is greater for temperatures above 60 °C, due to the polymer chains of the Xanthan gum beginning to random coil conformation (Reinoso *et al.*, 2019).

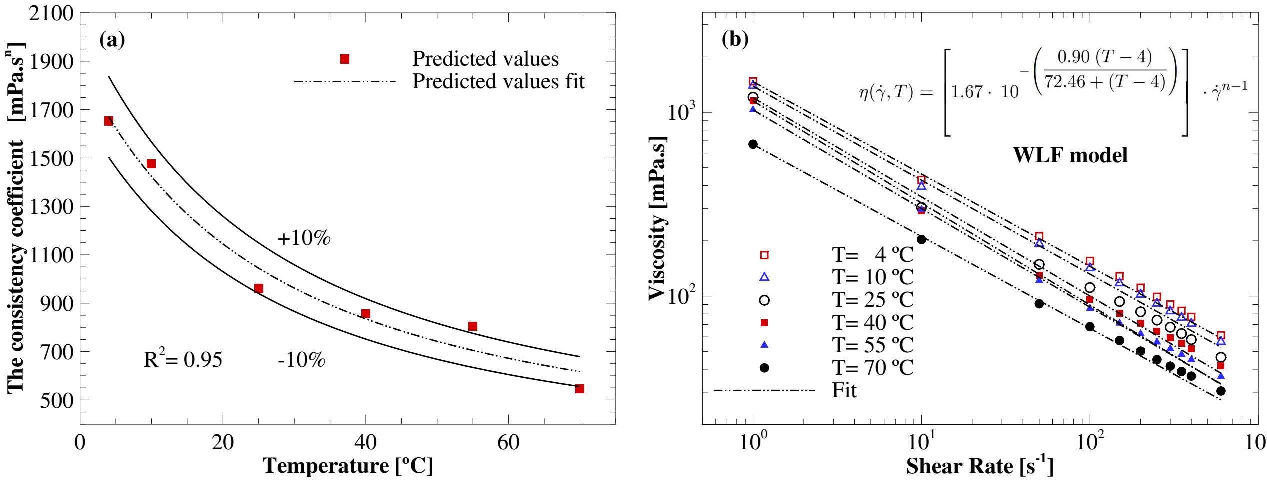

Figure 2. (a) Fitting of the predicted values of the consistency coefficient of the power-law model as a function of temperature through a non-linear regression proposed by Williams *et al.* (1955); (b) Equilibrium viscosity curve with the fit for the viscosity dependence model with temperature and shear rate for water-based drilling fluid.

3.2 Thermal Aging

Tests of thermal aging in a dynamic way allow to characterize the conditions of thermal history in rheological properties while observing the degradation or possible physical alteration in the fluid. Figure 3(a) shows the shear stress as a function of shear rate at 25 °C for non-aged and two aging fluids at 90 and 125 °C. The rheological data were fit to the power-law model due to the absence of the yield stress as shown in Table (3).

As can be seen in Fig. 3(a), the shear stress decreased with the increase of the aging temperature for both cases, with an average decrease of 12% for fluid aged at 90 °C and 60% at 125 °C one, when compared to the not aged fluid. This may indicate that the suspension experienced strong chemical alterations. The rheological behavior is affected by thermal history. Once the consistency coefficient decreased, it indicates a decrease in apparent viscosity. On the other hand, Table. 3 shows the flow behavior index at 25 °C was 0.57 and 0.74 for 90, and 125 °C respectively, indicating that for 125 °C the transition temperature of the polymer was exceeded, generating irreversible modifications in its structure. Besides, it was observed that for the flow curve at 55 °C for fluid aged at 90 °C, the flow behavior index increased reaching the same value of the fluid aged at 125 °C, therefore the imposition of a thermal history decreases the transition temperature. It is observed a trend to reach the behavior Newtonian as reported by Reinoso *et al.* (2019) for Xanthan gum solutions above 120 °C.

A comparison of the flow curves at 55 °C for all fluids is shown in Fig. 3(b), evidencing decreases of 29% and 67%

Table 3. Parameters of the power-law model at different temperatures for fluid aged at 25 and 55 °C.

Power-law Model				
Aging Temperature	**Test Temperature**	**m**	**n**	**R^2**
90 °C	25 °C	0.66	0.57	0.999
	55 °C	0.22	0.70	0.995
125 °C	25 °C	0.14	0.74	0.999
	55 °C	0.09	0.74	0.997

of shear stress compared to the non-aged. This also suggests that physical, electrochemical, and chemical modifications occurred during the aging process, as mentioned by Alderman *et al.* (1988).

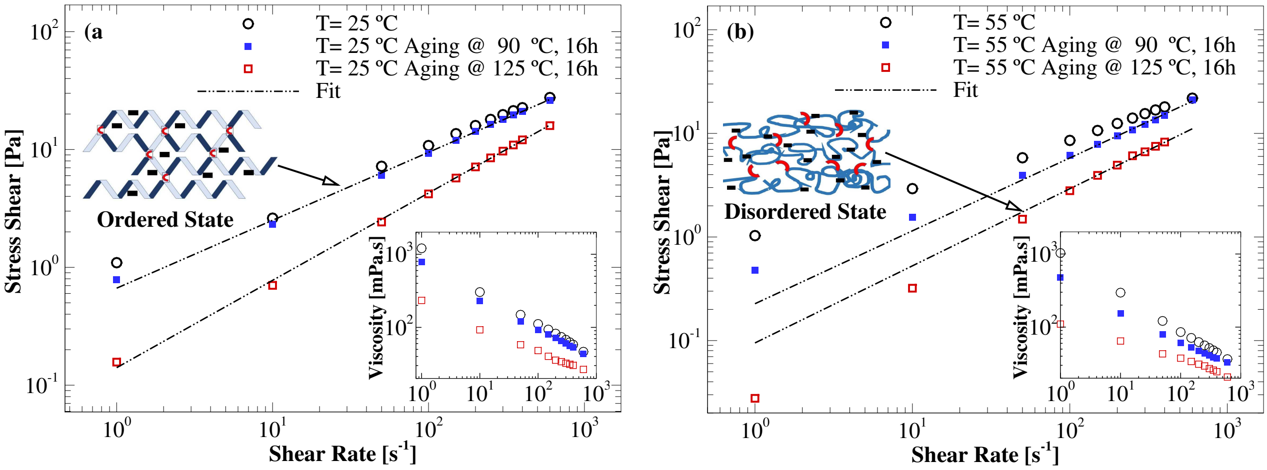

Figure 3. Comparison between equilibrium flow curves of non-aged fluid and fluids dynamically aged for 16 hours based on the ANSI/API Recommended Practice 13B-1 procedure. For temperatures of 90 and 125 °C with the adjustment of the power-law model, the tests were performed (a) at 25 °C and (b) at 55 °C, both at atmospheric pressure. The schematic representation of ordered and disordered states of crosslinked chains adapted from Bueno and Petri (2014).

Figure 3 shows the viscosity as a function of the shear rate for the aged fluids. A significant reduction was identified when compared to the non-aged fluid. When comparing the shear rate of 400 and 1 s^{-1}, these values indicate two important functions during the drilling process. The first represents the transport of cuttings to the surface of the well and other the cuttings suspension during the stops. In general, the higher temperature reduces the viscosity. However, the increase in the aging temperature also increases the losses of this property. The tests at 25 °C show that for 125 °C it decreased by 47.96 and 80.65% for the shear rates mentioned above, and for 90 °C of aging temperature its reduction was 8.82 and 35.1%.

Figure 4 shows the crystallization of sodium chloride for the three fluids used in the thermal aging comparison. Fluids aged at 90 and 125 °C are shown in Figs. 4(b) - (c) respectively. The samples were left for 3 days at 20 °C and 50% of relative humidity when the evaporation of the liquid part was evidenced. The crystallization of the electrolytes shows a higher supersaturation as the solvent evaporates, due to the increase in the thermal history imposed. Producing more crystals and reducing its size (Quilaqueo and Aguilera, 2016), indicating that the solubility of the salt in the suspension increased. Mao *et al.* (2019) highlighted that the solubility of electrolytes has significant effects on rheological properties, in the same way, that is mentioned by Reinoso *et al.* (2019) in xanthan gum solutions with brines. Furthermore, Fig. 4 it is observed that the pH values of the fluids increase with aging temperature, therefore a lower ionization causes degradation of the rheological properties, as other physicochemical modifications of the fluid as evidenced by Akpan *et al.* (2019).

The imposition of thermal history leads to the degradation of the fluid, this effect is observed through the rheological properties and visually through the flocculation and sedimentation of the particles over time under static conditions. Fig. 5 presents the separation between the liquid and solid phases over time for aging drilling fluids. For the image sequence of Fig. 5 (a) - (b) is observed that the speed of phase separation is greater with increasing aging temperature.

The observations of the current work indicate that possible molecule interactions with temperature decrease the relative dielectric constant of water (Fernandez *et al.*, 1995; Sprik, 1991; Suresh and Naik, 2000) by decreasing the polarity of

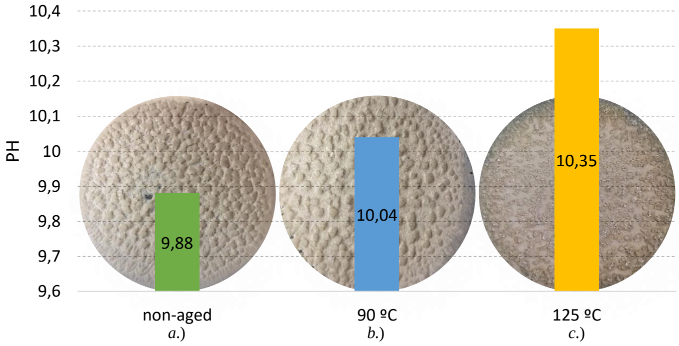

Figure 4. Comparison of values pH for each of the fluids performed at 20±0.5 °C with a standard deviation of ±0.02, and experiment visual of dry samples of aged drilling fluid, (a) non-aged; (b) the thermally aged at 90 °C and (c) thermally aged at 125 °C.

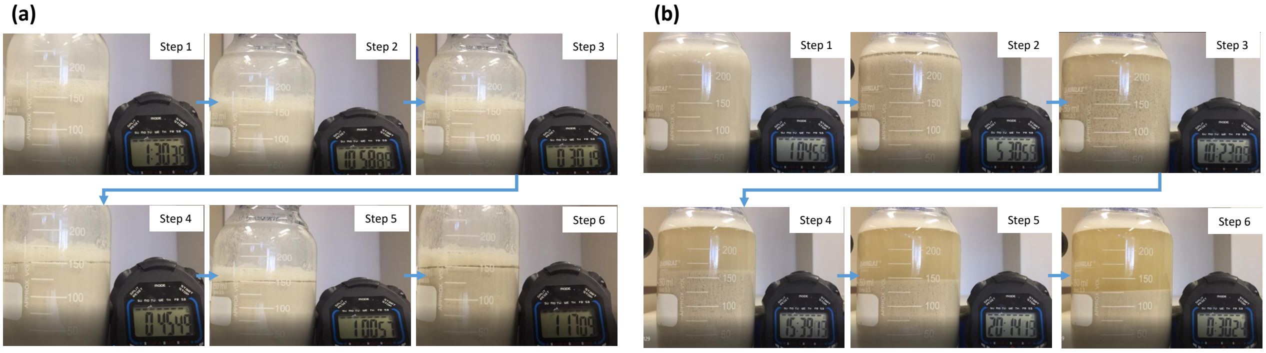

Figure 5. Visual appearance of suspensions stabilized for samples of the aged water-based drilling fluid by (a) at 90 °C for 77 minutes and (b) at 125 °C for 30 minutes.

water and promoting thermally induced phase separation (TIPS) precipitating the macromolecules dissolved in the drilling fluid (Mao *et al.*, 2019). Therefore, functions such as transport and suspension of cuttings are diminished with the aging of the water-based drilling fluid.

4. CONCLUSIONS

This work investigated the effects of temperature and thermal history observed through rheological measurements, where the thermal degradation of the fluid was analyzed and discussed. The results of the current work show a decrease in viscosity with the increase of temperature and aging time under atmospheric pressure conditions, maintaining its shear-thinning behavior and none dynamic yield stress. The influence of temperature and shear rate were fitted with the WLF model of Williams *et al.* (1955), where the behavior of the Arrhenius equation is not characteristic. The results suggest that there is a strong effect of temperature on the rheological and physicochemical properties of the water-based drilling fluid. The main conclusions of this work can be summarized as:

- The results of the viscosity fitting performed with the WLF model between temperature and shear stress depict a good fit with R^2=0.74.
- Thermal aging decreases the transition temperature of the fluid. This is represented by the increase in the flow behavior index, indicating that the higher the thermal gradient, the lower the non-Newtonian behavior of the drilling fluid due to changes in the polymer chains of the Xanthan gum.
- The pH present in the drilling fluid increases with the temperature of the thermal history, giving rise to a reduction in viscosity.
- Temperature increases over long periods decrease the polarity of the base of fluid, causing states of phase separation in shorter time intervals.

5. ACKNOWLEDGEMENTS

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