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TÍTULO DO TRABALHO:

PAC: a multifunctional additive for water-based drilling fluids

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PAC: a multifunctional additive for water-based drilling fluids**Abstract**

The composition-physicochemical properties relation of a number of WBF was studied, focusing on the polysaccharide content. The rheological behavior, fluid loss and shale inhibition properties of the drilling fluids were investigated according to conventional evaluation methods. All WBF flow was well described by the Ostwald-de Waele (OW) model, and the rheological parameters could be calculated. The nature of water diffusion into the shale follows an anomalous pattern. Polyanionic cellulose (PAC) acted as a rheology modifier, remarkably promoted the shale inhibition and led to a desirable fluid loss.

Introduction

The design of an adequate drilling fluid depends on the operating parameters of the well to be drilled, as well as its cost. Synthetic-based fluids (SBF) show unique properties such as high temperature stability and lubricity, but they are expensive and request serious environmental concerns. Water-based fluids (WBF) show good well cleaning ability and solubilize easily most of the polymers commonly used, but they are not stable at high temperatures and request a larger number of additives to optimize their performance. Meanwhile, most of the world's drilling fluid operations use WBF (Caenn & Chillingar, 1996).

Usually, drilling operations request adjustments of some parameters of the fluid during flow. WBF provides desirable conditions to quickly modify parameters such as salinity and low-end rheology. An important aspect of a WBF is to evaluate water-soluble polymers to control the main drilling fluid's functions: rheology, fluid loss, and shale inhibition (Hughes, Jones & Houven, 1993). Polysaccharides are known as interesting materials mainly due to their variety of functional structures, physicochemical properties, abundance on nature and cost (Cunha, Paula & Feitosa, 2009).

It is known that the physicochemical properties of a polymer blend differ remarkably from a single polymer component (Wu, 2009). Thus, efforts have been made to design polymer blends with improved properties.

The aim of this work is to evaluate the composition and some physicochemical properties of water-based drilling fluids, focusing on the polysaccharide content.

Experimental*Materials, fluid preparation and fluid loss test*

Hydroxypropyl starch (HPS), polyanionic cellulose (PAC), Magnesium oxide (MgO), and calcite (CaCO_3) were provided by NewPark Drilling Fluids do Brasil. The bactericidal (BC) was supplied by Lambra Ltda. Hydroxypropyl guar (HPG), the shale inhibitor (SI) (its composition is basically a cationic polymer), NaCl, and the antifoaming (AF) were all available in ordinary markets.

In a given fluid, the following additives were added to 1 bbl of water, in the order: HPG, HPS, PAC (when present), SI, MgO, NaCl (when present), AF, BC, and calcite. Each additive cited above, respectively, was shaken for 10, 10, 10 (when present), 5, 10, 10 (when present), 5, 5, and 10 minutes, in a model 5009 Fann Hamilton Beach shaker, under 18000 rpm.

The fluid loss evaluation was performed through API standard procedures.

Rheological analysis

The apparent viscosity for F1, F1-S21 and F1-S40 fluids was 37, 45 and 39 cP, respectively. In the other hand, the apparent viscosity for F2, F2-S21 and F2-S40 fluids was 40, 46 and 44 cP, respectively. The increased AV in the formulations F1-S21 and F2-S21 (when compared to their standards fluids) was attributed to the molar mass of the shale inhibitor. The decrease in AV observed when NaCl concentration is approximately doubled is related to the Salting Out effect. When more electrolytes are added to the fluid, some of the water molecules are attracted by the salt ions, decreasing the number of water molecules available to interact with the polymers. As a result of the increased demand for solvent molecules, the polymer-polymer interactions become stronger, leading to compact polymer structures, and decreasing the viscosity (Reichardt, 2003). Once the negative charges along PAC backbone also attract part of the salt ions, Salting Out effect is less significant in formulation 2. It is noteworthy to say that F2 had a higher AV than F1 even with a lower total polymer concentration.

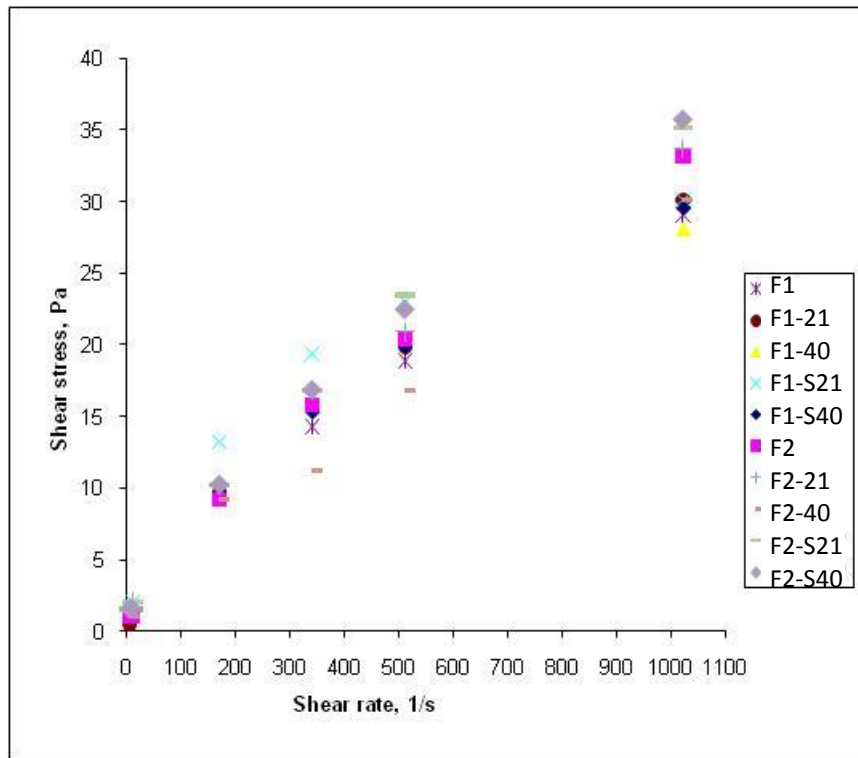


Figure 1. Flow curves for the drilling fluids, at 25°C

The deflection (ϕ) was converted to shear stress (τ) by equation 3:

$$\tau = \left(\frac{k_a}{2\pi r_1^2 H} \right) \phi \quad (3)$$

The shear rate ($d\gamma/dt$) was calculated from rotation rate (N) using equation 4:

$$d\gamma/dt = \Psi \left(\frac{2r_2^2}{r_2^2 - r_1^2} \right) \left(\frac{2\pi}{60} \right) N \quad (4)$$

where k_a , r_2 , r_1 , and H are constants from the apparatus' geometry, and Ψ is a correction parameter for non-Newtonian fluids, given by equation 5:

$$\Psi = \left[\frac{\beta^{2/n}}{n\beta^2} \right] \left[\frac{\beta^2 - 1}{\beta^{2/n} - 1} \right] \quad (5)$$

where $\beta = r_2/r_1$, and n is the flow index – pseudoplastic fluids ($n < 1$), dilatants ($n > 1$) and Newtonians ($n = 1$) (Machado, 2002; Carl Gatlin, 1960).

Initially, regarding there is not any information about the flow properties of the fluids, it was assumed that the fluids are Newtonian, implying that $\Psi = 1$. Figure 1 shows the flow curves (shear stress versus shear rate) for the drilling fluids, at 25 °C.

The Ostwald-de Waele (OW) model (equation 6) is widely used because it fairly accurately describes the flow of a large number of aqueous fluids containing polysaccharides (Khunawattanakul et al, 2008; Bezerril et al, 2006; Desbrières, 2002; Nikolova, 1998; Werner & Mersmann, 1998). This model was used to evaluate shear stress-shear rate dependence and to determine the rheological parameters of the fluids.

$$\tau = K \left(d\gamma/dt \right)^n \quad (6)$$

where K is the consistency index.

It should be pointed out that for fluids with marked pseudoplastic behavior ($n < 1$), the Ostwald-de Waele model denotes that apparent viscosity increases indefinitely with a decrease in shear rate and vice versa. Both phenomena are physicochemically incoherent (Darby, 2001).

Table 2. Evaluation of the drilling fluids at room temperature

Fluid sample	Rheology				Swelling kinetic		Fluid loss	
	n (*)	K (Pa.s ⁿ)	R^2	S_{180} (%)	n' (*)	k (10 ³ min ⁻ⁿ)	R^2	v (ml)
F1	0.763	0.162	0.9973	24.26	0.532	63.40	0.9981	22.0
F1-21	0.776	0.159	0.9964	22.58	0.590	48.45	0.9933	
F1-40	0.682	0.275	0.9879	21.10	0.578	54.24	0.9910	16.8
F1-S21	0.592	0.566	0.9946	20.59	0.633	37.34	0.9982	
F1-S40	0.644	0.352	0.9997	19.05	0.549	57.53	0.9995	11.0
F2	0.697	0.261	0.9898	23.69	0.602	43.62	0.9970	9.2
F2-21	0.585	0.550	0.9978	22.27	0.638	37.15	0.9707	
F2-40	0.619	0.363	0.9944	21.35	0.680	31.34	0.9950	8.4
F2-S21	0.597	0.535	0.9966	12.06	0.567	52.05	0.9959	
F2-S40	0.623	0.447	0.9890	11.76	0.587	47.07	0.9998	5.5

(*): dimensionless.

Table 2 shows the rheological parameters calculated using the OW model. This model satisfactorily described all the fluids studied, exhibiting R^2 values above 0.989.

All fluids showed a pseudoplastic pattern. In general, the pseudoplasticity decreased with salt addition. The consistence index increased with SI addition, but decreased when NaCl

concentration was approximately doubled. Such effects can also be understood by salting out assimilation, as previously discussed for apparent viscosity results.

Since the flow indexes for the different drilling fluids could be calculated, and all fluids were non-Newtonian, it provided a correction parameter different from that assumed. The Ψ values for the drilling fluids ranged from 1.018 to 1.046. The corrected shear rate was calculated for all fluids, and then the OW model was fitted again. Since the correction parameter showed a negligible variation from 1, practically the same OW parameters were reached.

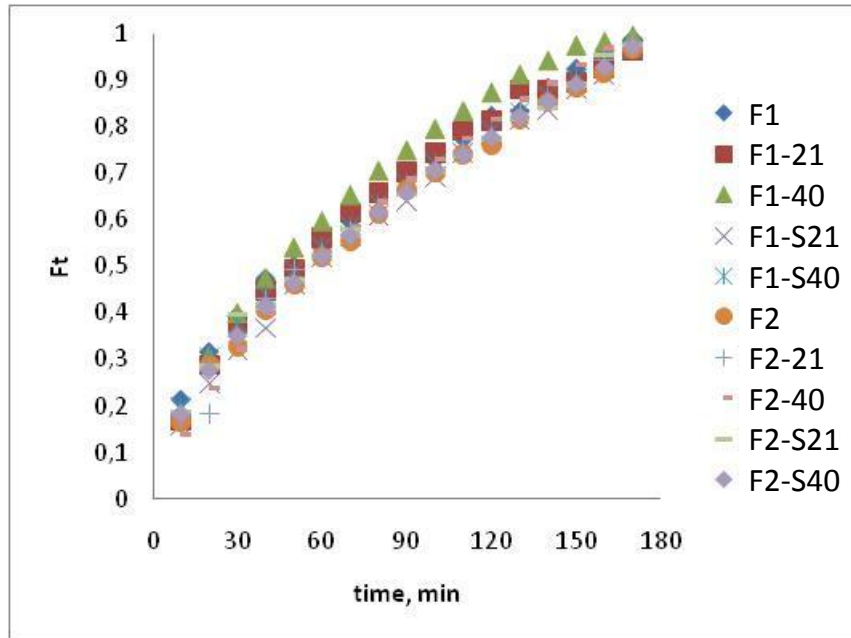


Figure 2. Plot of swelling fraction as a function of time, at room temperature

It was observed that salt addition inhibited the shale swelling (table 2). The higher is the NaCl concentration, the higher is the inhibition. The best results were achieved in the presence of SI, PAC and NaCl (F2-S21 and F2-S40 formulations). Such effect can be understood by the fact that the cationic shale inhibitor and the anionic polysaccharide PAC have strong interaction with the shale surfaces and interlayers. Bentonite has positively charged surfaces and negatively charged interlayers. Thus, the additives would be able to penetrate in the interlayer and to surround the surface, preventing the entrance of water. In parallel, salt ions also play a role, minimizing the electrostatic repulsion between clay's surface-surface and interlayer-interlayer during water uptake (Qu et al, 2009; Anderson et al, 2010; Mahto & Sharma, 2004).

At $t > 0$, swelling of the bentonite pellets against water-based drilling fluids occurs. The nature of water diffusion into the shale was evaluated through kinetic models. First- and Second-order integrated rate laws were fitted. Also, the swelling fraction was taken as a function of time, F_t , and the following semi-empirical equation (equation 7) was used to describe the water diffusion (Katime, Novoa & Zuluaga, 2001; Maltais, Remondetto & Subirade, 2010):

$$F_t = \frac{S_t}{S_{180}} = kt^{n'} \quad (7)$$

where S_t and S_{180} are the degree of swelling at a given time and at 180 minutes, respectively, k is a constant characteristic of the system, and n' is an exponent which indicates the mode of water

transport. A n' value of 0.5 indicates a Fickian diffusion mechanism, and a value of $0.5 < n < 1$ indicates that diffusion is anomalous.

The First and Second order kinetic models poorly described the swelling, since they exhibited R^2 values lower than 0.876 and 0.687, respectively.

Figure 2 shows the swelling fraction as a function of time for the different fluids, at 25 °C. The kinetic parameters were obtained through linearization of equation 7, and the results are shown in the table 2. It satisfactorily described all the fluids studied, exhibiting R^2 values above 0.991. When only nonionic polymers compose the drilling fluid (formulation 1), the kinetic constant increases when NaCl concentration is doubled (with and without SI). Such effect is related to the freer mobility of the salt ions. When PAC is added (formulation 2), one can see the opposite effect. An increase of salt concentration leads to an increase of electrostatic interactions between PAC and salt ions. Thus, less salt ions are available in the system, resulting in a smaller k (Mortimer, 2000). No significant variance of the diffusional exponent is observed for the different fluid samples, and the water diffusion follows an anomalous pattern.

Table 2 shows the static fluid loss results. As expected, salt, as well as SI addition diminished the volume of filtrate for both formulations. However, the cake formation mechanism is driven primarily by PAC, since it caused a marked shift in the fluid loss behavior (Hughes, Jones & Houven, 1993). The best result was achieved with F2-S40 formulation. The stronger electrostatic interactions between PAC, SI and salt ions seem to provide a more compact complex structure, leading to a thinner filter cake with low permeability, resulting in a lower fluid loss (Petri & Neto, 2010).

Conclusions

Different WBF were formulated, and the composition-physicochemical properties relation was evaluated. According to OW model, which well described all samples, the drilling fluids are pseudoplastic – in general, the pseudoplasticity decreased with salt addition. The clay's swelling kinetic was not described by classical First- and Second-order kinetic models, and the nature of water diffusion into shale follows an anomalous pattern for all drilling fluids evaluated. Polyanionic cellulose (PAC) acted as a rheology modifier, remarkably promoted the shale inhibition and led to a desirable fluid loss. Thus, it can be considered as a multifunctional additive for WBF.

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Referências Bibliográficas

1. R. Caenn; G. V. Chillingar. *Journal of Petroleum Science & Engineering*. 14, 221-230, 1996.
2. T. L. Hughes; T. G. J. Jones; O. H. Houven. *SPE Drilling & Completion*. 8, 3, 157-164, 1993.
3. P. L. R. Cunha; R. C. M. Paula; J. P. A. Feitosa. *Química Nova*. 32, 3, 649, 2009.

4. M. Wu. *Polymer Bulletin*. 63, 853, 2009.
5. C. Reichardt. *Solvents and solvents effects in organic chemistry*. Wiley-VCH, Weinheim, 2003.
6. J. C. Machado. *Reologia e escoamento de fluidos – ênfase na indústria do petróleo*. Editora Interciência, Rio de Janeiro, 2002.
7. C. Gatlin. *Petroleum Engineering: Drilling and Well Completion*. Hardcover, New York, 1960.
8. W. Khunawattanakul; S. Puttipipatkachorn; T. Rades; T. Pongjanyajul. *International Journal of Pharmaceutics*. 351, 227, 2008.
9. L. M. Bezerril; C. L. Vasconcelos; T. N. C. Dantas; M. R. Pereira; J. L. C. Fonseca. *Colloids and Surfaces A: Physicochemical & Engineering Aspects*. 287, 24, 2006.
10. J. Desbrières. *Biomacromolecules*. 3, 342, 2002.
11. A. Nikolova; N. Manolova; I. Rashkov. *Polymer Bulletin*. 41, 115, 1998.
12. F. Werner; A. Mersmann. *Chemical Engineering Technology*. 21, 559, 1998.
13. R. Darby. *Chemical Engineering Fluid Mechanics*. Marcel Dekker, New York, 2001.
14. Y. Qu; X. Lai; L. Zou; Y. Su. *Applied Clay Science*. 44, 265, 2009.
15. R. L. Anderson; I. Ratcliffe; H. C. Greenwell; P. A. Williams; S. Cliffe; P. V. Coveney *Earth-science Reviews*. 98, 201, 2010.
16. V. Mahto; V. P. Sharma. *Journal of Petroleum Science and Engineering*. 45, 123, 2004.
17. I. Katime; R. Novoa; F. Zuluaga. *European Polymer Journal*. 37, 1465, 2001.
18. A. Maltais; G. E. Remondetto; M. Subirade. *Food Hydrocolloids*. 24, 518, 2010.
19. Mortimer, R.G. *Physical chemistry*. 2nd ed. Academic Press: New York, 2000.
20. D. F. S. Petri; J. Q. C. Neto. *Journal of Petroleum Science and Engineering*. 70, 89, 2010.