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EVALUATION OF MODIFIED STARCHES USED IN MINING FOR APPLICATION IN DRILLING FLUIDS

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Abstract: *The present work has proposed to evaluate the use of modified starches that are used in mining for application as filtration-control additive in polymeric drilling fluids for oil wells. For this, the starch samples were first tested in the standard EP-1E1-00066-B and those that were approved in the specifications, were evaluated in concentrations of 0 to 9g/350mL of water, in a typical formulation of polymeric fluid in order to analyze the optimization of filtration properties. According to the results, only the AM3 sample of the five samples studied was approved and can be used in the polymeric fluid to control filtration loss.*

Keywords: *starches, filtration reducer, standard.*

1. INTRODUCTION

During well drilling, the filtration process occurs through the pressure differential between the fluid and the formation. When the hydrostatic pressure of the fluid is greater than the pore pressure of the formation, the liquid phase of the drilling fluid is compressed against the permeable formation, and the solid particles filtered adhere to the wellbore forming the filter cake. The volume of fluid passing through the cake is called the filtrate, which must be controlled with the use of filtrate reducing additives (Arthur and Peden, 1988; Khodja *et al.*, 2010; Caenn, Darley and Gray, 2011; Amanullah *et al.*, 2016).

In recent years, growth in the development and synthesis of new types of starch derivatives for application as a filter reducer has been observed. Modification of starch provides a variety of physico-chemical properties and can be used for specific functions. The most widely used starch derivatives as additives for drilling fluids are pre gelatinized starches, water soluble starch ethers and water soluble starch graft copolymers (Zhang, 2001; Taiwo, Joel and Kazeem, 2011; Guo and Peng 2012; Sinava *et al.*, 2014; Ghazali *et al.*, 2015; Masina *et al.*, 2017).

Carboxymethyl starch (CMS) is a type of chemically modified starch used in the mining industry (Schmitt and Nobel, 2000; Heize, 2005). However, there is a shortage in articles that deal with the use of CMS as a filtering controller in fluids used in drilling operations in the mining sector, as well as in studies evaluating the filtration reduction mechanism with the addition of the polymeric fluid with CMS.

Amanullah and Yu (2005) described the characteristics of starch-based products and their performance as fluid loss additives over a widely used modified starch. Six different starches were prepared by gelatinization using reactive extrusion technology. This technology has been widely used to modify conventional polymers and has the advantages of flexibility, efficiency, no solvent requirement, lower production cost, and the ability to perform one-stage multi-

reactions. The filtrate and spurt loss volume values of the modified starch containing fluids indicated that some of these products have similar or better fluid loss control properties compared to the currently used modified starch.

Xu *et al.* (2017) investigated the potential use of HCMS (hydrophobic carboxymethyl starch) as an environmentally correct filter reducing additive in clayey drilling fluids. The HCMS was synthesized from corn CMS and the influences of the reaction parameters on the degree of substitution were evaluated. The physicochemical characteristics of HCMS and the properties of HCMS drilling fluids were also investigated. The VF of the drilling fluids ranged from 14,8mL to 4,4mL when the HCMS concentrations (DS=0,31) increased from 0,0wt% to 3,5wt%. In addition, the VF of the drilling fluids decreased as the HCMS concentration increased. The results showed that the VF of the drilling fluids was below 4,0mL when the concentrations of HCMS ranged from 3,5wt% to 4,0wt%. This result indicated that the HCMS could effectively contain the loss of filtrate when added to the drilling fluids, forming a thin cake with low permeability.

The increasing interest in the development and use of new filter reducers additives, with characteristics appropriate to a good performance during the process of filtration, has encouraged studies and research aimed to exploration of the potential of the modified starches. Considering the need for the use of starches in the market for drilling oil and gas wells, this work had the objective to evaluate the use of starches used in mining as a filter reducer in polymer drilling fluids for oil and gas wells.

2. METHODOLOGY

The following additives were used to prepare the polymeric drilling fluids: antifoam, viscosifier (xanthan gum), pH (magnesium oxide (MgO)), filter reducers (different types of modified starches (named in Table 1) and low viscosity carboxymethylcellulose (CMC BV), sodium chloride (NaCl), sealant (calcite (CaCO₃)) and bactericidal (sodium persulfate).

All additives were supplied by Company System Mud an Imdex Limited Company/SC.

Table 1. Identification of the starch samples studied.

Type of Starch	Nomenclature Used
Carboxymethylamido (CMS)	AM1
Low Viscosity Carboxymethylamido (CMS BV)	AM2
High Viscosity Carboxymethylamido (CMS AV)	AM3
Pre-gelatinized Starch of Manioc	AM4
Pre-gelatinized Corn Starch	AM5

The starch samples were tested according to standard PE-2POC-00727 (Petrobras, 2017). This standard specifies the characteristics required for qualification, acceptance and test method for the evaluation of the filter reducer for water-based drilling fluid in the exploration and production of oil wells, in accordance with Petrobras Procedures, Guidelines and Good Practices.

Were prepared 9 drilling fluids for the evaluation of the starch samples according to the standard PE-2POC-00727 (Petrobras, 2017). Table 2 shows the components and their respective concentrations for the formulation of the fluids.

Table 2. Components and their respective concentrations to be used in the formulation of the drilling fluids and subsequent filtration test (* Concentrations (g/350mL deionized water)).

Components	Concentrations (g)
Sodium chloride (NaCl)	21,0
Calcium chloride (CaCl ₂)	0,07
Magnesium chloride (MgCl ₂)	0,028
Sodium hydroxide (NaOH)	1,0
Filter reducer to be tested	5,0
Micronized aragonite limestone	40,0

For the preparation of the fluids, the additives were added according to the concentrations and order shown in Table 2. At low speed (13,000rpm), the salts were added to the water and remained under agitation for 15 minutes on Hamilton Beach mechanical stirrer, model 936. The filter reducer was then added to the mixer cup for 1 minute, stirring for a further 4 minutes at low speed. Finally, the limestone was added to the mixer cup, containing the water, the salts and the filter reducer, prolonging the stirring for 1 minute at low speed.

After preparation of the fluid, it was immediately poured into the API filter cell and allowed to stand for 15 minutes (time taken between the end of the shaking and the beginning of the filtration). After this resting time, a pressure of 345kPa \pm 35kPa (50psi \pm 5psi) was applied immediately, so that this value is reached at most in 30 seconds. The pressure was maintained for 30 minutes and at the end of that time all the filtrate contained in the 25mL beaker was collected for analysis based on requirements (Table 3) of standard PE-2POC-00727 (Petrobras, 2017).

Table 3. Requirements of the standard PE-2POC-00727 (Petrobras, 2017).

Time (minimum)	Statistical Method	Requirements (maximum)
Filtrate (mL)	Simple arithmetic average	10
	Uncertainty	2

2.1 Evaluation of Starches in Polymeric Drilling Fluids

Polymeric drilling fluids were formulated and tested with the starch samples approved in standard PE-2POC-00727 (Petrobras, 2017).

The fluids were formulated with four distinct compositions, the concentration of the starch samples ranging from 0 to 9g/350mL of water, according to Table 4.

Table 4. Formulations of polymeric drilling fluids (* Concentrations (g / 350mL deionized water)).

Additives	F1	F2	F3	F4
Anti-foaming agent (g)	0,4	0,4	0,4	0,4
Xanthan gum (g)	1,5	1,5	1,5	1,5
PH controller (g)	1,0	1,0	1,0	1,0
CMC BV (g)	3,5	3,5	3,5	3,5
Starch (g)	-	3,0	6,0	9,0
NaCl (g)	18,0	18,0	18,0	18,0
Calcite (g)	20,0	20,0	20,0	20,0
Bactericide (g)	0,01	0,01	0,01	0,01

The polymeric drilling fluids were prepared according to field practice, which consists in adding the additives, one by one, under constant agitation. A Hamilton Beach Model 936 mechanical stirrer was used. Following the order described in Table 4, the additives were added to 350mL of deionized water with a 10 minute interval between each of them, except for the antifoam which spent 5 minutes under stirring constant at a speed of 17,000rpm.

The final (VF) and initial (spurt loss - SPL) volumes were determined according to ANSI/API 13I (2009) in API press filters. The fluid was agitated for 1 minute under constant stirring, then it was transferred to the filter-press vessel, applying a pressure in the order of 100psi (7,0kgf/cm²) and the filtrate was collected at the times of 1 ; 5; 7,5; 10; 15; 25 and 30 minutes.

The thickness of the filter cake (h) was determined with the extensometer according to the methodology developed by Farias (2005), and the permeability of the cake (k) was determined according to ANSI/API 13I (2009), using Equation (1).

$$k = Q_f \cdot \varepsilon \cdot \mu \cdot 8,95 \times 10^{-5} \text{ (mD)} \quad (1)$$

Where, k is given in mD; Q_f the volume of filtrate, given in cm³; ε is the thickness of the filter cake, given in mm; and μ is the viscosity of the liquid phase of the fluid, given in cP.

3. DISCUSSION AND RESULTS

According to analysis of the results presented in Table 5 and based on the standard PE-2POC-00727, it was verified that only one of the starch samples studied, AM3, was considered approved for use as a filter reducer for oil and gas wells, since the maximum average filtrate and the uncertainty presented values according to the specifications (Vf <10mL and U (Vf) <2) (Petrobras, 2017). This result is probably due to the higher viscosity presented by sample AM3.

Table 5. Variables analyzed to evaluate the starch samples.

Variables	AM1	AM2	AM3	AM4	AM5
Medium Filtration - Vf (mL)	> 10	> 10	5,62	> 10	> 10
Standard Deviation - δv	-	-	0,3962	-	-
Uncertainty - U (Vf)	-	-	0,3125	-	-

Samples AM1, AM2, AM4 and AM5 were considered as faulty product, since the maximum average filtrate was higher than the requirement value.

Table 6 presents the results concerning the filtration properties (Filtering Volume - VF, Thickness of the cake - h and the Permeability of the cake - k) obtained for the polymeric fluids studied.

It was observed that the F1 fluid had higher values of VF (9,4mL) and k (0,655x10⁻³mD) compared to the fluids formulated with sample AM3, probably due to the greater amount of free water in the system and absence of the polymeric additive in its formulation.

For comparison purposes, the filtrate volume values presented in Table 6 were compared to filtrate values obtained with fluids formulated with a hydroxypropyl starch sample. The F4 fluid, formulated with a maximum concentration (9.0g/350mL) of AM3, had a filtrate volume of 4,8mL, while the value obtained by Leite (2014) was 5,4mL, showing that the use of this type of starch was able to reduce the FV to a satisfactory value.

Based on Table 6, it was also observed that the fluids added with the AM3 sample presented increasing values of filter cake thickness (from 0,698 to 1,002mm) as the polymer concentration in the fluid increased, which differs from the results presented in the literature. According to Blkooor and Fattah (2013) and Ghazali *et al.* (2015), the increase in filter cake thickness is inversely proportional to the increase in polymer concentration. This proportionality presented between concentration and thickness of the cake for fluids F2, F3 and F4 probably occurred because of the high viscosity of the AM3 sample and the higher concentrations of polymer in the formulation.

Fluids F2, F3 and F4 presented high and similar permeability values, being these values of 0,430; 0,512 and 0,441x10⁻³mD, respectively. The high permeability in this case is related to the high values of h and VF, since the permeability of the filter cake is determined with bases in these two properties. The greater the permeability acquired by the cake, the lower the filtration control (Leite, 2014).

According to Ferraz (2014), the formation of a thin, impermeable cake along the wellbore is a decisive factor for the correct performance of the drilling operations. The cake reduces filtration, preventing the continuous phase from invading the formation, reducing the filtrate volume.

Table 6. Filtration properties of the polymeric fluids studied.

Filtration Properties	F1	F2	F3	F4
SPL (mL)	1,08	0,25	0,11	-0,82
VF (mL)	9,4	7,0	6,1	4,8
ε (mm)	0,779	0,698	0,938	1,002
k (10 ⁻³ mD)	0,655	0,437	0,512	0,430

Figure 1 shows the results of the filtrate volume, obtained at different time intervals, plotted to determine the initial leakage loss, known as spurt loss. In Table 10, we present the equations of the curves, the determination coefficients (R²) and the spurt loss values.

The values of the coefficient of determination (R²) presented in Table 7 were very close to 1, which is in agreement with the proposed mathematical model (Linear Model). Only the F4 fluid presented a negative spurt loss value. According to Barkman and Davidson (1972), the spurt loss value is related to the diameter of the solid particles contained in the drilling fluid. When the particles have a larger diameter than the pores of the filter medium, spurt loss does not occur, and the intercept of the linear portion at time zero is negative. In the case where the particles have a much smaller diameter than the pores of the filter media, the invasion of solids occurs at the beginning of the filtration, resulting in a positive spurt loss value. It can be inferred that the addition of starch in a higher concentration (9.0g/350mL of water) to the F4 fluid, together with the presence of CMC BV, also used as a filter reducer, and calcite (solid sealant) conferred a negative spurt loss value.

Figure 1. Spurt loss curves for polymeric fluids formulated without starch (F1) and sample AM3 (F2, F3 and F4).

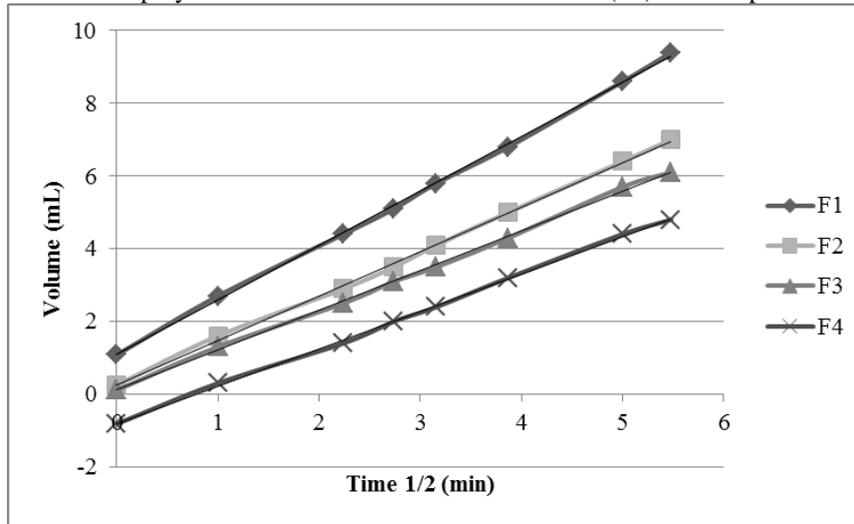


Table 7. Equations, parameters and spurt loss values of polymeric fluids formulated without starch (F1) and sample AM3 (F2, F3 and F4).

Fluid	Equation	R ²	Spurt loss
1	$y = 1,501x + 1,0776$	0,9992	1,08
2	$y = 1,2248x + 0,2476$	0,9999	0,25
3	$y = 1,0955x + 0,1096$	0,9989	0,11
4	$y = 1,0297x - 0,8135$	0,9991	-0,82

4. CONCLUSIONS

- The AM3 sample was considered approved according to the specifications of standard PE-2POC-00727;
- Addition of F4 fluid with high viscosity CMS (AM3) at the concentration of 9g/350mL of water resulted in lower API filtrate volume values, higher cake thickness and lower permeability;
- The sample of high viscosity CMS used in mining operations with the function of reducing the filtrate can also be used in the formulation of polymeric fluids for the same purpose.

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