

# APPLICATION OF SALTS FREE OF CHLORINE AS INHIBITORS OF CLAYS IN AQUEOUS DRILLING FLUIDS

D. V. Lucena\*; P. R. Borges\*\*; L. V. Amorim\*\*\*, H. L. Lira\*\*\*\*

\* Doutorado em Ciências e Engenharia de Materiais, Bolsista Capes/ CNPQ – UFCG, Campina Grande, PB-Brazil, daniellymateriais@yahoo.com.br.

\*\* Graduação em Engenharia de Petróleo, Bolsista PIBIC/CCT – UFCG, Campina Grande, PB-Brazil, priscilla@yahoo.com.br.

\*\*\* Departamento de Engenharia de Petróleo, UFCG, Campina Grande, PB-Brazil, luciana@dem.ufcg.edu.br.

\*\*\*\* Departamento de Engenharia de Materiais, UFCG, Campina Grande, PB-Brazil, helio@dema.edu.br.

## ABSTRACT

At present, concern with the environment damage and the costs involved in the disposing of contaminated cuttings have led to find drilling fluids water based, but during the well drilling it is common the presence of formations with shales and hydratable clays, in these cases, it is necessary the use of swelling inhibitors, that are chemical compounds with capacity of to reduce, in a effective way, the hydration of clays.

The aim of this work is to develop formulations of water base drilling fluids with high power of inhibition, ecological correct and with low toxicity, to be applied in deep drilling well with shale and hydratable clays formations.

The results reached until now are promising and the prepared fluids can maintain the values of filtrate volume almost constant before and after the contamination and this suggest that the studied inhibitors are efficient after clay contamination.

**Keywords:** drilling fluids, expansive clay inhibitor, environmental protection.

## 1 INTRODUÇÃO

During perforation oil well is common the detection of layer constituted by clay minerals with high degree of hydration, organized in lamellar package. When in contact with water, this package of clays separated as the water penetrates in the basal space. Clay formations containing smectites are sensible to the presence of water. Many of these formations contain several types and different amount of clays. The higher the amount of smectite, the greater the reactivity in the presence of water, due to the relative weak of intercrystalline bonds that allow the entry of water or other polar substances, which results in increase of the interplanar or basal distance. This phenomenon is known by swelling [1].

The water based fluids can present highly hydrophilic clays in their composition, as those found in shales or

“active solids” (typical sedimentary rock rich in hydrophilic clays, in specially those found in offshore locations or younger sedimentary basins, characterizing much water sensible formations). These clays react chemically with the water from drilling fluid, causing its expansion and dispersing the particles in the fluid and for all well. The presence of clay in the fluid composition can cause a phenomenon that affects mechanically in the drilling, causing an effect of intrusion of expanded clay in the pores of the formations cut by the drill, forming an barrier that paralyzes or restricts significantly the flux of production of hydrocarbons [2], [3], [4].

This is a serious performance problem caused by the use of water based fluid, provoking also well instability and loss of fluid to the formations. In parallel, this material expansion leads to a generation of extra volume of waste from perforation. The solution for the pointed problem above is inhibiting the fluid through the addition of substances that prevent or decrease the reaction with water [5].

The inhibited fluids are planned to drill rocks of high degree of activity in the presence of fresh water. It was added to the inhibited fluids chemical products, such as polymers and/or electrolytes, which has the properties of hinder or decrease these effects [6].

The inhibit systems provide special properties to the drilling fluids, such as: low viscosity, low gel consistency, greater tolerance to the solids and resistance to contamination. Its prevent the shale and clays hydration and achieve better results in the well stabilization [7].

With inhibit fluids it is possible to work with salty contaminations, cements and anhydrite, even when these contaminations are generated by the drilling in great amounts [7].

In the inhibition of swelling by hydration of clay, the additives more commonly used are the inorganic and monovalent cation, such as KCl and NaCl, and bivalent cations, such as, CaCl<sub>2</sub>. To stabilization of clays, it was used quaternary ammonium salt. Several cationic inhibitors are added to the drilling fluids. These salts are considered of high cost by the petroleum industry to be used in drilling

fluids, therefore, are usually associated with sodium and potassium salts, which are cheaper [8].

The chloride salts, like KCl, are inexpensive and at high content present inhibiting action. However, intensify the fluid density and cause damage to the polymers, which lose in viscosity. In addition, cause damage to the environment and to the humans due to its toxicity and are currently being replaced by chlorine free salts [9].

In this way, the aim of this work is to develop inhibited fluids without the presence of chlorine for application in drilling well with reactive formation.

## 2 MATERIALS AND METHODS

### 2.1. Materials

It was developed drilling fluids with ternary mixtures of inhibitors of expansive clays with free chlorine. For the preparation of these fluids it was used the following additives: antifoam, viscosificante, filtrate reducer, pH controller, inhibitor of expansive clay (potassium sulphate, potassium acetate, potassium citrate and KCl), bactericide, lubricant and sealant.

For the contamination of the fluids it was used Brasgel PA clay.

Table 1: Additives and concentration used in the formulations of drilling fluids.

Aditives	Unities	Concentration
Antifoam	drop/ bbl	6
Viscosificante	lb/ bbl	0.75 a 1.5
Filtrate reducer	lb/ bbl	2.5 a 3.5
pH controller	lb/ bbl	1.0
Clay inhibitor	lb/ bbl	16.0
Bactericide	lb/ bbl	0.7
Lubricant	lb/ bbl	1.0 a 3.0
Sealant	lb/ bbl	15.0 a 25.0

\* lb/bbl x 0,00285301 = 1 g/mL

### 2.2. Methods

#### 2.2.1. Factorial plain

The fluid preparation was based in the factorial plain presented in Table 2.

The levels of independent variables used in ascending order (-1, 0, +1) were: 0.75, 1, 1.125 and 1.5 lb/bbl of water to viscosificante (V), 2.5, 3.0 and 3.5 lb/bbl water to filtrate reducer (R), 1.0, 20, and 3.0% to lubricant (L) and 15.0, 20.0 and 25.0 lb/bbl of water to the sealant (S).

The regression of experimental data was done by using STATISTICA™ program (STATSOFT) [10].

Table 2: Matrix of factorial plan 2<sup>4</sup>, with three replays at central point.

Fluid	(V)	(R)	(L)	(S)
F1	-1	-1	-1	-1
F2	+1	-1	-1	-1
F3	-1	+1	-1	-1
F4	+1	+1	-1	-1
F5	-1	-1	+1	-1
F6	+1	-1	+1	-1
F7	-1	+1	+1	-1
F8	+1	+1	+1	-1
F9	-1	-1	-1	+1
F10	+1	-1	-1	+1
F11	-1	+1	-1	+1
F12	+1	+1	-1	+1
F13	-1	-1	+1	+1
F14	+1	-1	+1	+1
F15	-1	+1	+1	+1
F16	+1	+1	+1	+1
F17	0	0	0	0
F18	0	0	0	0
F19	0	0	0	0

#### 2.2.2. Preparation of drilling fluids

The drilling fluids were prepared according to the field practice, which consists in adding the additives, one by one, under stirring at a constant speed of 13,000 rpm using a Hamilton Beach stirrer, 936 model, following the order described in Table 1.

The additives and concentrations range that were used in the development of the inhibited fluid formulations are shown in Table 1.

It was considered as contaminated fluid the one present in their composition sodium clay bentonite with high degree of swelling. For the preparation of these it was followed the same procedure performed for the preparation of fluids above. After the addition of latest additive (sealant), it was added clay, which remained under stirring for 10 min. Then the fluid remained at rest for 24 h.

#### 2.2.3. Rheological study of drilling fluids

After rest of 24h it was done the rheological study of drilling fluids. To do this, the fluid was stirred for 5min in a mechanical stirrer Hamilton Beach, 936 model, at a speed of 17,000 rpm. After stirring, the fluid was transferred to the container of the viscometer Fann 35A model. The viscometer was started at a speed of 600 rpm for a period of 2 min and making the reading after 15 s.

With the data of the readings from the viscometer, it was calculated the apparent viscosity (VA), plastic viscosity and yield point (LE) according to the PETROBRAS norm N-2605 [11].

VA is the value obtained from the reading at 600rpm divided by 2, given in cP. Plastic viscosity (VP) is the difference between the readings at 600 rpm and 300 rpm, given also in cP and LE is the difference between the value obtained with the reading at 300 rpm and plastic viscosity, given in N/m<sup>2</sup>.

To obtain the initial gel strength, the fluid was stirred at speed of 600rpm for 15s and after the speed was changed to 3 rpm and the reading was took after 10 s of rest. Then, to obtain the final gel strength, the fluid was left in rest for 10min and the reading was took at a speed of 3 rpm, according to the API norm 13 B-1 [12].

#### 2.2.4. Filtrate volume

For measurement of filtrate volume, the fluids were stirred for 1 min, with mechanical stirrer Hamilton Beach, 936 model and at speed of 17,000rpm. Then the fluid was transferred to the API filter press container, with an applied pressure of 100psi.

After 30 min, the filtrate volume was measured, given in mL.

### 3 RESULTS E DISCUSION

The influence of the chemical inhibitors was evaluated through the properties of the drilling fluids, comparing the results before and after contamination.

In Table 3 are presented the results of the rheological properties and filtration for the fluids with and without inhibitors, as well as those of contaminated fluids.

It was observed significant variations in the values of rheological properties and filtration of the studied fluids. The fluids F8, F12 and F16 have in their compositions great amount of viscosificante and filtrate reducer. These fluids presented the greatest values of VA, VP and LE, indicating that the increase in concentration of these additives providing an increase in the value of those properties.

This behavior with respect to the additives concentrations is expected and arising, for example, from the viscosificante action, which is an additive that has as main function to increase the viscosity of the fluid, and the filtrate reducer (composed by polymer) can also act as a viscosificante.

The increase in the amount of filtrate reducer promoted, in general, in addition to the reduction of the filtrate volume, a significant increase in the rheological properties values. This behavior can be justified by the composition of filtrate reducer, which is composed by a cellulose based polymer; carboxymethylcellulose (CMC) of low viscosity, and according to the supplier, this additive was produced with greater size chain cellulose than the traditionally used in the preparation of these additives. In higher concentrations, such as 3.5 lb/bbl of water, the additive act as a viscosificante, justifying the high values observed the rheological properties [13].

Table 1 – Rheological properties and filtration of drilling fluids.

Fluids	VA (cP)	VP (cP)	LE (N/m <sup>2</sup> )	VF (mL)	ER (mm)
<b>F1</b>	<b>41.75</b>	<b>27.5</b>	<b>28.5</b>	<b>8.4</b>	<b>0.5194</b>
F1*	71.0	36.5	69.0	7.2	0.8616
<b>F2</b>	<b>51.0</b>	<b>22.5</b>	<b>57.0</b>	<b>6.8</b>	0.5946
F2*	52.0	22.0	60.0	4.8	0.4572
<b>F3</b>	<b>47.0</b>	<b>26.5</b>	<b>41.0</b>	<b>7.6</b>	<b>0.5138</b>
F3*	70.75	37.0	67.5	7.4	0.5914
<b>F4</b>	<b>54.0</b>	<b>27.0</b>	<b>54.0</b>	<b>6.6</b>	<b>0.5540</b>
F4*	76.0	40.0	72.0	5.4	0.5558
<b>F5</b>	<b>47.75</b>	<b>27.5</b>	<b>40.5</b>	<b>7.4</b>	<b>0.4786</b>
F5*	57.5	31.5	32.5	7.4	0.4586
<b>F6</b>	<b>58.0</b>	<b>26.0</b>	<b>64.0</b>	<b>6.4</b>	<b>0.4896</b>
F6*	65.75	40.0	51.5	4.6	0.5198
<b>F7</b>	<b>56.5</b>	<b>27.0</b>	<b>59.0</b>	<b>5.8</b>	<b>0.5510</b>
F7*	66.0	41.5	49.0	3.2	0.5586
<b>F8</b>	<b>71.5</b>	<b>29.5</b>	<b>84.0</b>	<b>5.6</b>	<b>0.7814</b>
F8*	81.0	48.0	66.0	5.2	0.5836
<b>F9</b>	<b>43.25</b>	<b>27.0</b>	<b>32.5</b>	<b>9.2</b>	<b>0.7964</b>
F9*	46.25	28.5	35.5	6.8	0.6226
<b>F10</b>	<b>64.5</b>	<b>34.0</b>	<b>61.0</b>	<b>4.0</b>	<b>0.4658</b>
F10*	56.5	33.0	47.0	2.6	0.4340
<b>F11</b>	<b>71.0</b>	<b>40.0</b>	<b>62.0</b>	<b>7.6</b>	<b>0.5568</b>
F11*	73.5	38.0	71.0	7.0	0.5844
<b>F12</b>	<b>72.0</b>	<b>39.0</b>	<b>66.0</b>	<b>6.0</b>	<b>0.7042</b>
F12*	95.0	49.5	91.0	5.4	0.6314
<b>F13</b>	<b>48.0</b>	<b>29.0</b>	<b>38.0</b>	<b>7.8</b>	<b>0.3844</b>
F13*	18.0	15.0	6.0	4.6	0.3432
<b>F14</b>	<b>63.5</b>	<b>38.0</b>	<b>51.0</b>	<b>4.8</b>	<b>0.6222</b>
F14*	65.0	41.0	48.0	2.4	0.3722
<b>F15</b>	<b>60.5</b>	<b>34.0</b>	<b>53.0</b>	<b>7.0</b>	<b>0.8410</b>
F15*	83.5	56.0	55.0	5.6	0.4976
<b>F16</b>	<b>88.5</b>	<b>54.0</b>	<b>69.0</b>	<b>4.6</b>	<b>0.4466</b>
F16*	86.5	59.0	55.0	3.6	0.4090
<b>F17</b>	<b>65.25</b>	<b>38.5</b>	<b>53.5</b>	<b>5.2</b>	<b>0.5130</b>
F17*	76.5	43.0	67.0	3.6	0.4298
<b>F18</b>	<b>67.5</b>	<b>45.0</b>	<b>45.0</b>	<b>5.4</b>	<b>0.5642</b>
F18*	78.5	47.0	63.0	4.8	0.4688
<b>F19</b>	<b>66.0</b>	<b>36.0</b>	<b>60.0</b>	<b>6.8</b>	<b>0.3992</b>
F19*	71.5	31.0	81.0	6.8	0.4826
<b>FSI</b>	<b>40.3</b>	<b>21.0</b>	<b>38.5</b>	<b>9.8</b>	<b>0.6360</b>
FSI*	74.7	34.8	79.9	8.1	1.0980

When it was established a comparison between the fluids prepared with and without expansion inhibitors it can be observed that the presence of inhibitor changed the rheological behavior and filtration of the fluids; the fluids with inhibitors showed best results for filtrate volume in relation to the fluids without inhibitors, as well as present higher values of VA and VP than the fluid without inhibitors. Comparing the values of rheological properties and filtration of fluids with and without contamination, it was observed that the addition of clay to the fluid without

inhibitor (FSI\*) increase significantly the values of VA, VP, LE and ER and reduced the value of VF. This is due to the fact that the clay to be added to the system acted as a viscosificante agent, since the clay used is a sodium bentonite with high degree of swelling. Also, the addition of clay resulted in an increase of solids concentration and may have interacted with other additives that make up the fluid. Points out that this behavior has been observed in the fluids that do not have inhibitors, because its presence should avoid or minimize the dispersion and swelling of the clay.

After addition of clay, most of the fluids with inhibitors, except F16, presented an increase in the VA, VP and LE values. This behavior suggests that the clay interacted with aqueous phase of the fluid, modifying its properties.

The fluids F5 and F19 remaining with constant values of VF after contamination with clay, indicating the efficiency of the inhibitors in the inhibition of clay swelling.

The maximum observed variation in the VF values of the fluids before and after contamination was 2.6mL (F7 and F7\*), that is, the presence of clay gave to the fluids a reduction in VF values. However, this reduction can be considered small.

In previous studies, it was proven the efficiency of the salts studied in this work as inhibitors of clay swelling through Foster swelling and Linear (LSM) [14].

Thus, through these studies and from the results presented in this article, it was suggested that the filtrate volume tests are carried out in conjunction with others techniques, such as CST and LSM, to evaluate the efficiency of inhibition of aqueous drilling fluids contaminated with clay.

Currently, environmental agencies, with recent changes in government laws, have regarded as primordial chemical composition of products which are used in the preparation of drilling fluids for oil wells, since toxic products such as KCl, can cause serious damage to the environment and the the human been [15]. Thus, the use of chlorine free inhibitors such as potassium sulphate, potassium acetate and potassium citrate emerge as an alternative environmentally correct for the use in inhibited fluid formulations.

## 4 CONCLUSIONS

With the aim to evaluate the efficiency of several chemical additives as inhibitor agents of expansive clay, by means of rheological and filtration properties, it was conclude that: (i) the fluids developed with higher concentrations of viscosificante and filtrate reducer presented the greatest values on the rheological properties; (ii) the presence of the inhibitors changed the rheological and filtration behavior of the fluids; (iii) the fluids with the presence of inhibitors showed best results of VF, as well as presented values of VA and VP higher than those fluids without inhibitors; (iv) the fluids contaminated with clay

presented an increase in the values of VA, VP and LE and reduced values of VF and (v) filtrate volume tests can be used to evaluate the degree of inhibition of the drilling fluids contaminated with clays since in conjunction with other tests to have a more precise assessment of the results.

## REFERENCES

- [1] Amorim, L. V.; Viana, J. D.; Fárias, K. V.; Barbosa, M. I. R.; Ferreira, H. C. "Estudo comparativo entre variedades de argilas bentoníticas de Boa Vista, Paraíba". *Revista Matéria*, v.11. p. 30-40, 2006.
- [2] Bleier, R., Leuteran, A.J.J., Stark, C.L., "Drilling Fluids: Making Peace with the Environment", SPE 24553, Washington, DC, USA, 4-7 October, 1992.
- [3] Lummus, J.L E Azar, J.J., *Drillings fluids optimization a practical field approach*, PennWell Publishing Company, Tulsa, Oklahoma, 1986.
- [4] Khondaker, A. N., *Modeling the fate of drilling waste in marine environment – an overview*, computers & geosciences, 26 pp. 531-540, 2000.
- [5] Schaffel, S. B., *A Questão Ambiental na Etapa de Perfuração de Poços Marítimos de Óleo e Gás no Brasil*. Tese de Doutorado. COPPE- UFRJ. Rio de Janeiro, 2002.
- [6] Thomas J.E., "Fundamentos de engenharia de petróleo", Editora Interciência, 2001.
- [7] Ferraz, A.I. *Manual de engenharia dos fluidos de Perfuração*, Divisão Magcobar Grupo Oilfield Products Dresser Industries, 1977.
- [8] Vidal, E. L. F. *Avaliação do comportamento de argila ativada na presença de água destilada, de soluções salinas e de inibidores de hidratação catiônicos*. Dissertação de Mestrado- UFRN, 2009
- [9] PEREIRA, E., "Fluidos e perfuração: o uso de inibidores de argila como solução de problemas de sondagem". *Anais Encontro Nacional de Perfuradores de Petróleo*, Recife, 2001.
- [10] STATSOFT, Inc. *STATISTICA for Windows*, version 5.0, 2000, 1 CD
- [11] PETROBRAS, *Ensaio de viscosificante para fluido de perfuração base de água na exploração e produção de petróleo*, Método, N-2605, 1998.
- [12] API, *Norma API Recommended Practice 13B-1*, novembro, 2003.
- [13] Farias, K.V., *Desenvolvimento de fluidos de alto desempenho para perfuração de poços de petróleo*, Tese em Engenharia de Processos, UFCG, 2009.
- [14] LUCENA, D. V., "Desenvolvimento de fluidos de perfuração com alto grau de inibição ambientalmente corretos", *Dissertação de Mestrado*, Mestrado em Ciências e Engenharia de Materiais, CCT/UFCG, Campina Grande, 2011.
- [15] Nascimento, R. C. A. M. *et al* . *Avaliação da eficiência de inibidores de argilas expansivas para o uso em fluidos de perfuração*, *Revista Eletrônica de Materiais e Processos*, v.4.2, 2009.