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Research paper

Design of experiments to evaluate clay swelling inhibition by different combinations of organic compounds and inorganic salts for application in water base drilling fluids

Rosangela de Carvalho Balaban [a], Emanuella Layne Ferreira Vidal [b], Maurício Rodrigues Borges [c,*]

[a] Laboratório de Pesquisa em Petróleo (LAPET), Universidade Federal do Rio Grande do Norte (UFRN), 59.078-970 Natal, Brazil
[b] Newpark Drilling Fluids do Brasil, 59.064-390 Natal, Brazil
[c] Quimpetro Engenharia, Cidade Verde, Parnamirim 59.152-200, Brazil

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ABSTRACT

In this study the synergistic behavior that occurs when three different cationic inhibitors for clay swelling were associated with brines containing NaCl and KCl was evaluated. These commercial inhibitors are based on a cationic quaternary polyamine chloride with quaternary ammonium group (INIB 1), on a cationic polyacrylamide chloride with quaternary ammonium group (INIB 2) and on a quaternary ammonium chloride salt (INIB 3). Each inhibitor was characterized considering the amount of chlorides and content of active matter. The tests were performed with a commercial bentonite. Capillary suction timer (CST) and linear swell meter (LSM) were used for the evaluation of clay–water interaction in the presence of various fluids. For a better interpretation of the experimental results statistical analysis (DOE — design of experiments) via response surface methodology (RSM) was used, taking into account the type and concentration of inhibitors, the type and concentration of brines as well as the contact time of the inhibitor solutions with clay. The results showed different efficiencies, in other words, inhibitors mixed with brines were more effective than the inhibitors alone. The best results were obtained for cationic polyacrylamide chloride with quaternary ammonium group at 7 lb/bbl (pounds per barrel) in KCl brine at 18.74 lb/bbl with contact time of brine and clay of 7.6 h. Solutions containing these combinations presented greater inhibition of clay swelling. However, for field operations, other parameters should be considered as operating cost, environmental requirements and the application time of each product.
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1. Introduction

During the drilling of oil wells, it is common to detect different types and amounts of clay minerals in the rock formation. The particularly interesting group of smectites can swell with changing ionic conditions and eventually disperse and migrate with the flowing fluid. Swelling clays reduce the effective area for flow and cause reduction of the permeability of the rock formation (Mohan et al., 1993). The larger the amount of smectites the larger will be the swelling degree of clays, because of the relatively weak intercrystalline bonds in the clay structure, which allow the entrance of water or other polar substances that result in increased interlayer distance (Laird, 2006). The hydration of the clays is a function of the extent and location of layer charge, the interlayer cation species, the water activity, the temperature, the external pressure and the salinity of the bulk solution (Villar et al., 2012). In drilling oil wells, this swelling can cause a lot of problems in production operations, such as trapping the bit, collapsing, widening wellbore and commitment of reservoir rock permeability (Boek et al., 1995; Richard et al., 2010). Despite these problems, the oil industry uses water-based fluids for drilling wells as much as possible, because they are relatively cheap and more environmentally friendly than oil-based formulations (Nunes et al., 2014).

There are organic and inorganic chemical additives capable of minimizing the clay–fluid interactions, hindering the entrance of water molecules and effectively reducing the hydration of the clay minerals. The main organic additives used as clay swelling inhibitors are cationic molecules containing quaternary ammonium groups in their structures (Qu et al., 2009; Anderson et al., 2010; Peng et al., 2013; Zhong et al., 2013; Pham and Nguyen, 2014). Cationic organic compounds as quaternary ammonium salts and diammonium methyl sulfate with different alkyl chain lengths can lie flatly as a monolayer between the siloxane layers, decreasing the swelling of bentonites (Hu et al., 2014). Cationic organic polymers are also used as additives for stabilization and swelling inhibition of clay. The most common are the quaternary polyamines and quaternary polyacrylamides. While the cationic nitrogen of these polymers binds to the anionic surface of the clay, the hydrophobic carbon chains form a network structure, preventing the migration of fines (clay particle displacement) and also reducing water molecule sorption (Fig. 1). The sodium and potassium chlorides are inorganic compounds extensively used to reduce

* Corresponding author. Tel.: +55 84 30825230; fax: +55 84 32153803.
E-mail addresses: balaban@supercabo.com.br (R.C. Balaban), layne_ufrn@yahoo.com.br (E.L.F. Vidal), mauriborges@hotmail.com (M.R. Borges).

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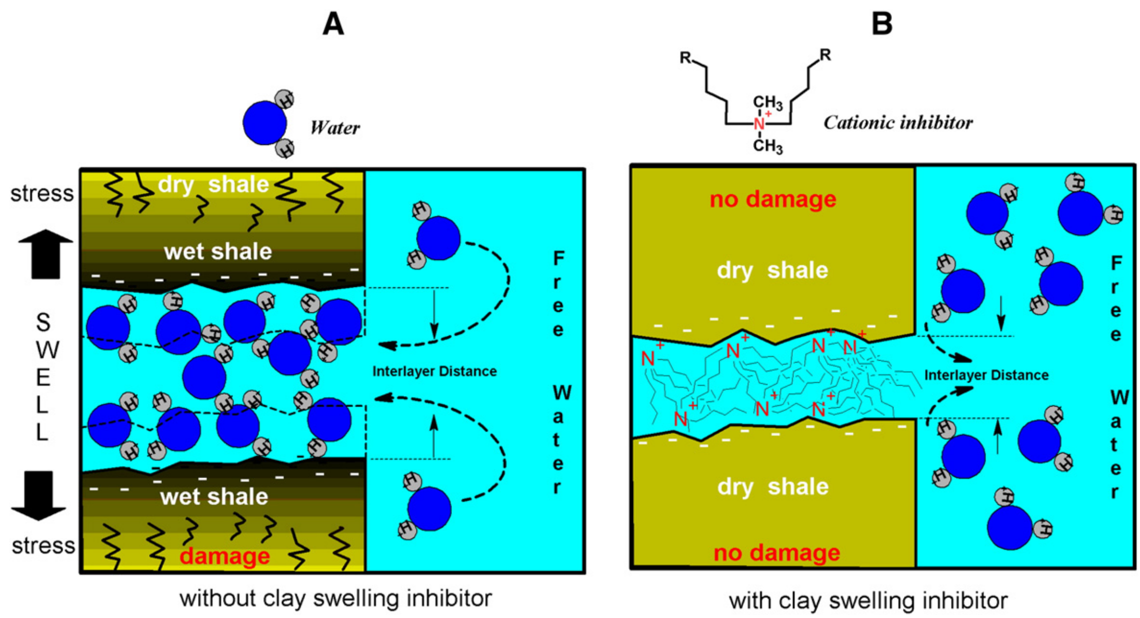

Fig. 1. Schematic representation of clay swelling inhibition mechanism: (a) without cationic inhibitors' action, and (b) under the cationic inhibitors' action.

the hydraulic flow to the argillaceous formation by mechanisms of ion adsorption on clay surface and osmotic pressure due to higher cation concentration in the drilling fluid, stimulating the water flow from the formation to the drilling fluid and, consequently, reducing the hydration around the well (Liu and Lu, 2006; Zhong et al., 2011; Teixeira et al., 2014; Zhao et al., 2014).

It is very important to differentiate chemicals designed to minimize the hydration of clays from those designed to promote the stability of clays. The first type refers to inhibitors that prevent the water penetration between the clay basal spacing, while the second has the ability of preventing clay swelling as well as the migration of fines. In both the last cases, the mechanism of action is to fix the cationic fraction of product structure in the negative clay surface, releasing the exchangeable cation present in the clay structure (Hamdi and Srasra, 2014). However, in the case of clay stabilizers, the cationic polymeric additives form a network structure at basal spacing, preventing the migration of fines. The misconception concerning the application of these commercial products in formulations of drilling and completion fluids has caused collapse of shale formations during drilling operations in oil wells, causing serious damages.

The organic inhibitors are considered expensive by the oil industry. For this reason, they are usually applied associated with inorganic salts of sodium and potassium (Ghimici and Dragan, 2002). In this paper, the efficiencies of different mixtures of inorganic and organic salts in aqueous media as clay-swelling inhibitors in water-based drilling fluids (WBDF) were compared. The selected inorganic salts were the sodium and potassium chlorides, whereas the organic compounds were commercial organic salts of quaternary ammonium chloride, cationic polyacrylamide chloride with quaternary ammonium group and cationic quaternary polyamine chloride with quaternary ammonium group. The different brines were subjected to the analysis of CST and LSM (linear swell meter) in order to assess the ability of blocking the water penetration in samples of activated clay. Aiming to determine the best organic–inorganic system, the responses were submitted to design of experiments by response surface methodology, using Modde™ 7.0 software.

2. Materials and methods

2.1. Materials

Bentonite was acquired from Poland Quimica Ltda and used in the study of hydration. Sodium chloride (NaCl) was purchased from Chemco Indústria e Comércio Ltda; potassium chloride (KCl) was purchased from Biotec Produtos Químicos; and calcium chloride ($CaCl_2$) was acquired from Cromoline Química Fina Ltda and used for humidity standardization of the commercial clay test. The drilling fluids were prepared with the following chemicals: xanthan gum purchased from CP Kelco Brasil, S.A.; magnesium oxide (MgO) was purchased from Cromoline Química Fina Ltda; carboxymethylcellulose (CMC ADS) was purchased from System Mud Co.; hydroxypropylstarch (HP-starch) and calcite ($CaCO_3$) were purchased from Carboflex Ltda; the biocide triazine was purchased from M-I Drilling Fluids Ltda; the commercial clay-swelling inhibitors were supplied by Laboratório de Pesquisa em Petróleo (LAPET): cationic quaternary polyamine chloride with quaternary ammonium group (INIB 1); cationic polyacrylamide chloride with quaternary ammonium group (INIB 2); and quaternary ammonium chloride salt-based inhibitor (INIB 3). All inorganic chemicals used were P.A. (Pro Analysis) grade and all other chemicals used were of the best grade available from suppliers.

2.2. Chloride content

The amount of total chlorides present in the organic inhibitors was determined by volumetric titration. Initially 1 g of inhibitor in 100 mL of distilled water was added. Then, an aliquot of 25 mL of this solution was taken off and supplemented with distilled water until 100 mL of volume. Afterwards, the indicator potassium chromate (K_2CrO_4 5%) was added and the solution was titrated with 0.282 N (NORMAL) of silver nitrate ($AgNO_3$). For the determination of the amount of ammonium chloride, 1 g of inhibitor and 5 mL of sodium hydroxide (NaOH 0.01 N) in 100 mL of water were added, and the solution was submitted to heating at boiling for 30 min. After cooling at room temperature, 1 mL of methyl orange indicator was added and the solution was titrated with sulfuric acid (H_2SO_4 0.02 N).

2.3. Active matter amount in the commercial organic inhibitors

About 1 g of each inhibitor was freeze dried in a Thermo Savant Modulyo-D freeze dryer, for enough time to obtain a constant mass of the sample. The active matter content was determined by mass balance between initial and final mass.

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