

Effectiveness of Shale Inhibition by Anionic and Cationic Polyacrylamide Copolymers in Water Based Mud

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Abstract

Producing oil and gas from shale reservoir is currently increasing. Shale reservoir formations are mainly consist of water clay sensitive. Sensitive shale formations can cause the following operational drilling problems: stuck pipe, bit balling, increase torque and drag, and cutting disintegration. Due to environmental restrictions of oil based mud, formulating Water Based Mud (WBM) with shale inhibitor is essential to overcome these technical drilling problems.

The objectives of this study are to: (1) determine the possibility of using Cationic Friction Reducer (CFR) and Anionic Friction Reducer (AFR) as shale inhibitors in WBM; (2) identify the shale inhibition mechanism for the recommended inhibitor; and (3) present the effect of pressure and temperature on the formulated WBM with recommended shale inhibitor.

Common commercial CFR and AFR used in hydraulic fracturing were used in this study. Zeta potential, swelling test, shale dispersion, and anti-accretion test, mud ball immersion test were conducted to study the effectiveness of AFR and CFR as the shale inhibitor. The results show that CFR performs poorly as a shale inhibitor. AFR is much more effective for shale inhibition due to the encapsulation and wettability alteration mechanisms. Shale recovery from formulated WBM with 0.50 lbm/bbl AFR and 0.50 lbm/bbl CFR are 99%, and 60% respectively. The formulated WBM with AFR is powerful to prevent shale swelling, dispersion, and bit balling. Adding AFR in WBM improve thermal stability of the fluid rheology between 120 to 180° F. The effect of pressure from 0 to 2000 psi within temperature up to 180° F on the formulated WBM with AFR is practically negligible. This study presents a promising WBM to replace oil-based mud to drill sensitive problematic shale formations.

Introduction

The oil and gas industry has currently focused on developing unconventional reservoirs due to the rising demand for fossil fuels brought on by the growing population. In order to meet the present and anticipated future demand for hydrocarbons resources, the extraction of oil and gas from shale reservoirs has

increased recently (Haider et al. 2020). Shale reservoirs is mainly consists of water sensitive clay formations. Shale have a tendency to swelling and dispersion due to absorption of water inside clay lattice (Gautam et al. 2020). The drilling operations in shale reservoir often result in complex wellbore shale instability problems such as stuck pipe, wash out of borehole, bit balling, and poor hole cleaning. This can increase nonproductive time in drilling operation (Patel et al. 2007).

Optimum selection of drilling fluid plays a pivotal role in minimalizing the wellbore instability problems (Albooyeh et al. 2018). Oil based Mud (OBM) has superior shale inhibition performance when being used to drill sensitive water shale formations. OBM has many advantages besides shale inhibition such as lubricity, and stable rheology at high temperature (Hossain et al. 2015). However, there are restrictions to use OBM due to its detrimental effect on the environment. Hence, there is increasing in cost of treating OBM to meet environmental regulations. Besides, US Environmental protection Agency (EPA) approved stricter regulation criteria for cuttings discharge drilled by OBM. This means more costs associated with OBM cutting discharge (Friedheim et al. 2002).

On the other hand, Water Based Mud (WBM) has simplicity to be formulated in the drilling field, easiness to control its rheology and fluid loss, has better control of loss of circulation problems, and has better well control during gas kick (Hamdan et al. 2020). However, conventional WBM is very sensitive to shale and easily interact with shale formation and results in hydration of shale. Therefore, over the years, oil industry have been developed WBM to approach performance of OBM related to shale inhibition. These developed fluids are called high performance WBM (Huaike et al. 2019).

Hence, there are many drilling fluid additives used as shale inhibitor in WBM like inorganic salts, polymers, amines, glycols, nanoparticles, and surfactant. There are some limitations related to the applications of the previous additives. Inorganic KCl salt has high capability to prevent shale swelling, but high KCl concentrations are toxic for the marine environment (Young et al. 2013). Polymers and its derivative are effective additives as shale inhibition, but they are thermally degradation in high temperature conditions like in deep drilling

(Sun et al. 2019). The limitation of using amine based shale inhibitor are the toxicity, effect of pH on inhibition performance, and high-required dosage (Jia et al. 2020). The nanoparticles proved lab success in preventing shale swelling. Due to its homogenous distribution, its can highly affect drilling fluid rheology (Kang et al. 2016).

Based on the limitations of current solutions, developing a new shale inhibitor with excellent inhibition performance is still a hot research topic. The chemical engineers develops new class of synthetic polymers called emulsified polymers to resist to harsh conditions like high temperatures and high salinity. These polymers are soluble in water and emulsified in oil base. Recently, the emulsified polymers have recently been used in oil field applications (Guo et al. 2022). One of emulsified synthetic polymers is the polyacrylamide based polymer. This polymer is successfully used as a friction reducer in hydraulic fracturing to reduce the frictional pressure losses (Motiee et al. 2016). The commercial friction reducers used in this study are Cationic Friction Reducer (CFR), and Anionic Friction Reducer (AFR). The target is to study the possibility of using AFR and CFR as shale inhibitor.

The Objective

Clearly, the main objectives of this research are to (1) determine the possibility of using Cationic Friction Reducer (CFR) and Anionic Friction Reducer (AFR) as shale inhibitors in WBM; (2) identify the shale inhibition mechanism for the recommended inhibitor; and (3) present the effect of pressure and temperature on the formulated WBM with recommended shale inhibitor.

Experimental Preparation

Materials:

The test matrix of the formulated drilling fluids is shown in table 1. The table contains chemical additives with its quantities. The additives and its functions are as follow:

- Bentonite: used for the initial viscosity, suspension, and fluid loss control
- Starch, and PAC: provided fluid loss reducers
- KCl: salt used for shale inhibition purpose
- Xanthan Gum (XC) polymer: used to provide viscosity
- Soda Ash and caustic soda: Used to control water hardness, and pH, respectively
- Barite: used for controlling drilling fluid density

Experimental Apparatus:

The available equipment used in this research are mud mixer, pH meter, OFITE 900 rheometer, OFITE 1100 rheometer , OFITE roller oven, a zeta potential analyzer (Anton Paar Litesizer), shale swelling test, shale dispersion apparatus, accretion bar, and goniometer to test WBMs. OFITE means the manufacturing company, which is OFI Testing Equipment, inc. The pH meter was used to adjust the pH of the formulated WBM. The OFITE rheometer with model of 900 measured

automatically shear stress versus different shear speeds at different temperatures up to 200⁰ F and ambient pressure.

Table 1: Test matrix of the tested drilling fluids

	Basic WBM	WBM with KCl	WBM with AFR	WBM with CFR	Unit
	pH (8.5 – 9.5)	pH (8.5 – 9.5)	pH (8.5 – 9.5)	pH (8.5 – 9.5)	
Additives	Quantities	Quantities	Quantities	Quantities	
Water	1	1	1	1	bbbl
Bentonite	8	8	8	8	lbm/bbl
Caustic soda	0.3	0.3	0.3	0.3	lbm/bbl
AFR	0	0	0.5	0	lbm/bbl
Starch	3	3	3	3	lbm/bbl
KCl (Salt)	0	17.5	17.5	17.5	lbm/bbl
XC polymer	0.75	0.75	0.75	0.75	lbm/bbl
CFR	0	0	0	0.50	lbm/bbl
PAC-L	1	1	1	1	lbm/bbl
Barite	As required	As required	As required	As required	lbm/bbl

The OFITE 1100 rheometer is used to measure mud rheology at temperature up to 500° F and pressure up to 2000 psi. This device gives indication about effect of pressure on fluid rheology. Hemphill (1996) described new term called Relative Dial Readings (RDR) and can be used to correlate the changes in dial readings with temperature, pressure, and shear rate.

$$RDR = \frac{\tau_{p \text{ and } T}}{\tau_{\text{ambient } P \text{ and } T}} \quad (1)$$

OFITE Roller oven was used to simulate the drilling fluid inside the well as drilling fluid sample was put in a cell and rotated in the oven at any specific temperature. This oven has 5 rollers and the aging can be done under static or dynamic conditions from ambient temperature up to 600⁰ F.

There are many used techniques to evaluate shale inhibition performance. These techniques are zeta potential, linear swelling test, hot rolling dispersion test, capillary suction test, methylene blue test, and scanning electron microscope, accretion test, and mud ball immersion test (Ahmed et al. 2019). Zeta potential, shale swelling, shale dispersion test, accretion, and mud ball immersion test are used in this study for study shale inhibition performance for AFR and CFR in WBM.

Litesizer which manufactured by Anton Paar company was used to measure zeta potential by electrophoretic light scattering. The model used in this study is Litesizer 500. The test samples were prepared by mixing chemical additives with water and their pH values were adjusted manually by using pH meter. The samples were then loaded in to an omega cuvette using an inversion method to avoid any trapped air bubbles. Kalliope software was used along with its library of solvent properties such as refractive index, viscosity and relative permittivity for analysis. Water was used as the solvent as it was the base fluid for all formulations. Samples were equilibrated for 3 mins at temperature range from 0 to 90⁰ C and approximated using the Smoluchowski model with a Henry factor of 1.5 (Hiemenz 1977).

Shale dispersion test is also known as cutting dispersion test. The clay cuttings are ground and sieved by 20-30 mesh screens. According to API recommendations, the weighted sieved clay

cuttings are placed in the aging cell with the formulated drilling fluid in the roller oven for 16 hrs. Then shale cuttings are washed and recovered by sieve of 50 mesh. After that, the recovered shale cuttings are heated again in the roller oven for 3 hrs to make sure all water is evaporated. Finally, the recovered shale after heating over the original shale weight is indication of shale recovery percentage. Clearly, higher shale recovery means better shale fluid inhibitor (Jain et al. 2015).

$$\text{Shale recovery (\%)} = \frac{M_2}{M_1} \times 100 \quad (2)$$

Where:

M_1 : Weight of the shale cuttings before hot rolling

M_2 : Weight of recovered shale cutting after drying

The immersion test is easy visual method to evaluate inhibition performance. The mud ball was created by mixing bentonite with distilled water with mass ratio 2:1. Then, mud balls were immersed for different times in distilled water, and water with shale inhibitors. Finally, the samples were photographed to evaluate visually the swelling, dispersion, and inhibition (Lv et al. 2020).

Swelling test is an easy way to evaluate shale swelling tendency. Mass of 1 g sodium bentonite was added into three flasks with volume 20 ml, and then 10 mL of three different solutions (water, water with KCl, and water with KCl and AFR, respectively) were added. The pH was adjusted between 8.5 and 9.5. The swollen bentonite volume were recorded to evaluate shale inhibition of the formulated solution (Zhao et al., 2017).

Accretion tests have been used extensively to study the sticking tendency of clay in the presence of different drilling fluids on the bit and bottom hole assembly. Accretion test is comparatively unsophisticated and cost-effective method. Accretion was conducted in the laboratory using a steal bar and jar. The test star with placing a clean hollow steel bar in a jar containing 1 barrel of drilling fluid. Then, adding specific grams (W_1) of ¼" bentonite tablets as a shale cuttings is the following step. Then close jar and place it horizontally in the roller oven for 30 minutes at 120 °F. After 30 minutes, remove the bar from the jar and Photograph the accreted bar for qualitative analysis. Finally remove the sticking solids from steel par and dry them in the oven for 3 hours at 240° F and measure its weight (W_2). The accretion percentage is calculated using the equation 3 (May et al., 2022).

$$\text{Accretion(\%)} = \frac{W_2}{\left[\frac{(100 - M)}{100}\right] \times W_1} \times 100 \quad (3)$$

Where:

M : Water content of unexposed bentonite tablets which in our case was 0.1

W_1 : Weight of the shale cuttings added initially to the jar

W_2 : Weight of sticking shale cutting after drying

Results and discussion

The results of the measured zeta potential in mV of AFR at a concentration of 0.5 lbm/bbl with water versus pH at 25° C were plotted and presented in Fig. 1. Zeta potential showed a trend of increasing negativity with respect to pH. This observation further substantiated that the surface charge of this FR is negative. The negatively charges increased due to hydrolyzed of carboxylic neutralized (COOH) group on AFR backbone to carboxylate negative group(COO-). This leads to raise negativity of the measured zeta potential.

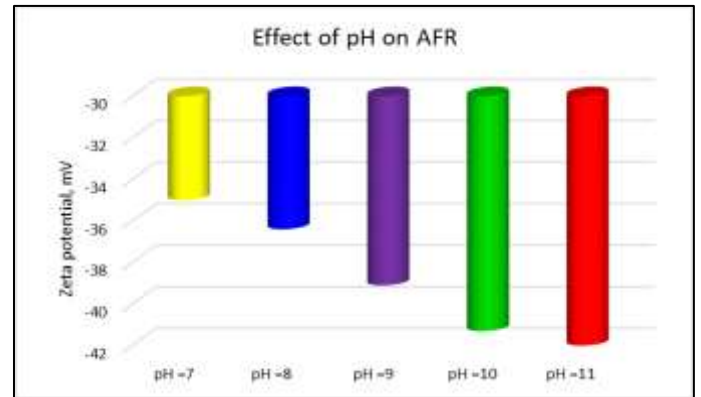


Figure 1: Zeta potential measurements of the pH effect on AFR

On the other hand, CFR has different zeta potential measurements in comparison with AFR. As the zeta potential decreased with increasing pH from 7 to 8.5 as shown in Fig 2. Zeta potential values at pH of 7 and 8 were 12 mV and 6 mV, respectively. This reduction in surface positive charge when pH increases from 7 to 8 is because of the elimination of cationic group from CFR chain. The isoelectric point of CFR is at pH of 8.5 because of zero charge. This means CFR is very sensitive to pH. Furthermore, the negative value of Zeta potential increased above pH 8.5 and become have negative charges higher than positive ones.

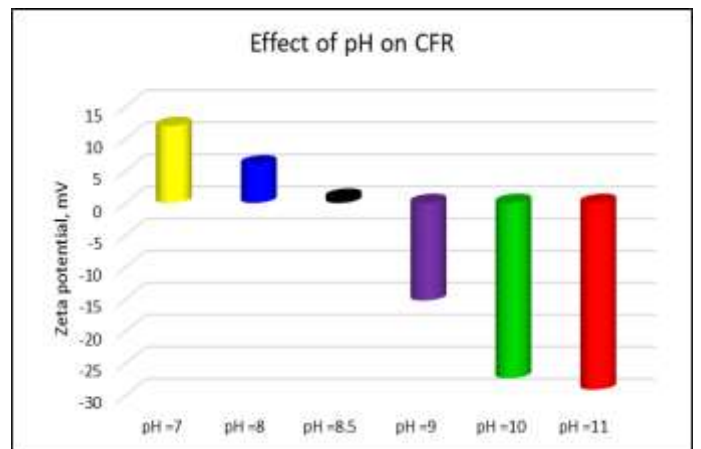


Figure 2: Zeta potential measurements of the pH effect on CFR

The evaluation of used AFR and CFR as shale inhibitors in WBM were based on measuring zeta potential, swelling test,

shale dispersion test, mud ball immersion test, and accretion test. The zeta potential measurements of the formulated solutions at different temperatures are shown in Fig. 3. When KCl sat was added to the bentonite, there is decline in absolute value of measured zeta potential, this means KCl interacted with bentonite surface and decreased zeta potential value. It is expected to have small zeta potential values when adding CFR because CFR supposed to neutralize negative bentonite surface. But, CFR leads to raise negatively zeta potential and this means no interaction between CFR and bentonite or shale surface. The reason is KCl repeals with positive charges of CFR and prevents CFR attraction to shale surface.

On the other hand, addition of AFR to bentonite solution with KCl resulted in decreasing zeta potential with all temperatures. Also, when AFR concentration raised from 0.25 lbm/bbl to 0.50 lbm/bbl, it caused for more decline in zeta potential measurements. This means KCl works as a bridge between AFR and bentonite surface. Also, this attraction improved with temperature raised from 80 to 150° F. This proves another attraction by the hydrogen bond between non-hydrolyzed polyacrylamide groups with negative surface clay (Mohamed et al. 2023). This results in more decreasing in zeta potential magnitude. Therefore, this the first good sign for using AFR as shale inhibition.

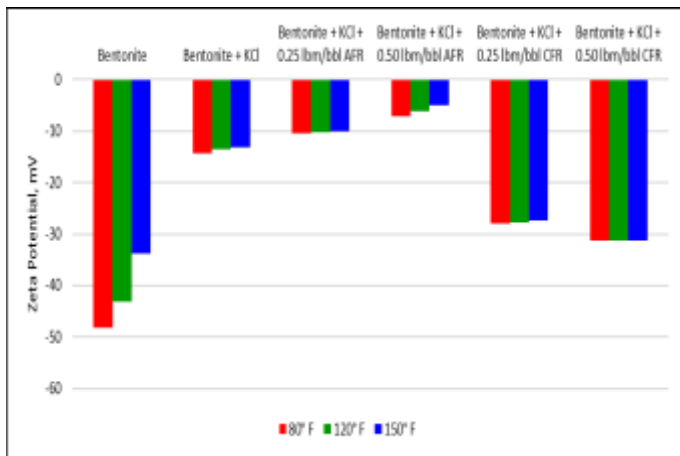


Figure 3: Zeta potential measurements for the different solutions

The swelling test is another method for shale inhibition performance. The swelling test for 1 gm bentonite had volume of 2.6 ml at time zero. This volume was added to different solutions as the results of this test with time are shown in (Fig. 4). It is clear that water absorb in bentonite and make it swelling as the volume of bentonite increase from 2.6 ml to 6 ml after 3 hr. on the other hand, the solutions with CFR had less swollen volume than water solution. Nevertheless, when 0.5 lbm/bbl AFR was added to the solution of water with KCl, AFR prevent bentonite from swelling and its expansion volume became constant after 0.5 hour at 3 ml. this means after AFR interact with shale, it prevent water absorption quickly and inhibit swelling and this can lead to stabilize shale during drilling.

Shale dispersion test is another way to evaluate shale stabilization capability of proposed shale inhibitor. Dispersion tests were done to determine percentage of shale recovery when using formulated WBM with 0.50 lbm/bbl of AFR and CFR. The results of the shale dispersion tests for the formulated muds were illustrated in Fig. 5. The shale cuttings used in the test were obtained from the Wolfcamp shaly formation. The formulated WBM with AFR had high shale recovery of 95% in comparison of 60% shale recovery for WBM with CFR. This means AFR prevent shale dispersion by encapsulating shale surface and prevent water shale interaction. Hence, the formulated WBM with AFR is capable to prevent shale dispersion better than formulated WBM with CFR.

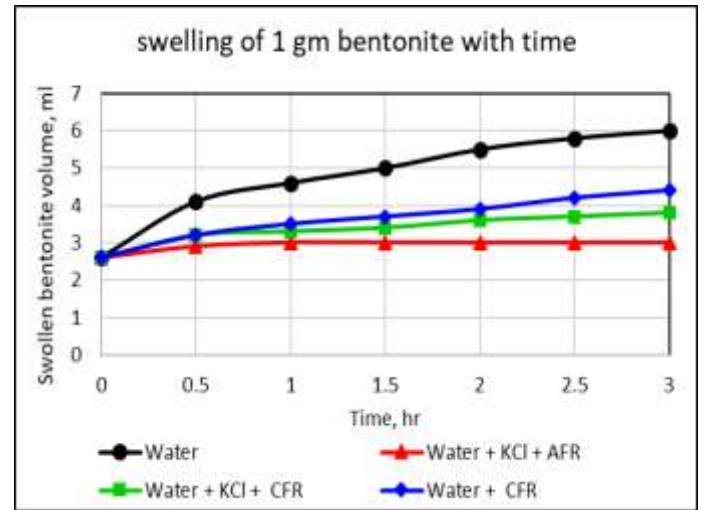


Figure 4: swollen bentonite volume in different solutions

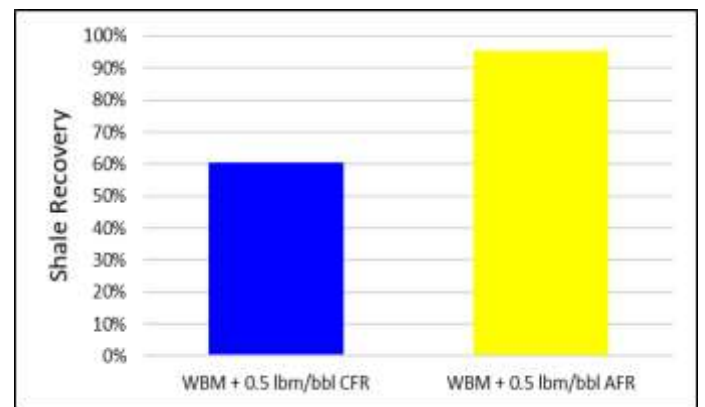


Figure 5: Shale dispersion test of the formulated WBM with CFR and AFR

Additionally, mud ball immersion test is a visual method to evaluate shale stabilization performance of shale inhibitors. This test is based on taking physical pictures of the mud balls after immersed in different formulated solutions. The pictures of mud balls were taken after 0 hr, 24 hr, and 48 hr as shown in (Fig. 6).The mud ball in water swelled and then dispersed.

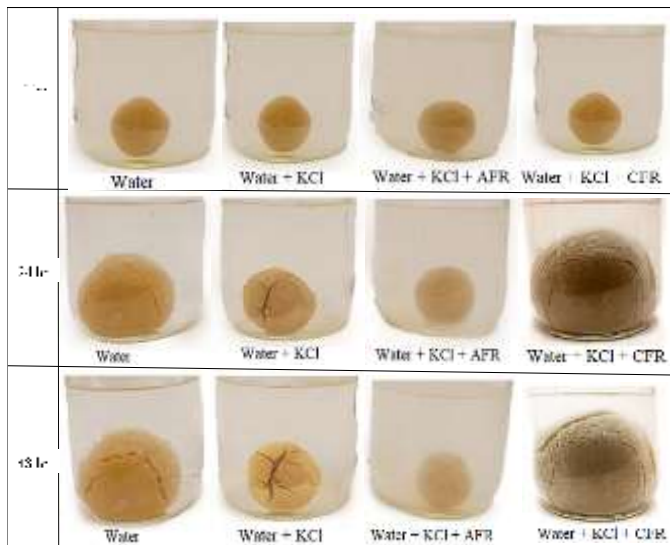


Figure 6: Pictures of Mud Ball after immersed in different fluids at different times

In addition, the water solution with 5% KCl and 0.07% CFR has swelled and dispersed mud ball like water solution. But, the mud ball in water with 5% KCl showed cracks or dispersion without swelling. This dispersion increased with time.

It is clear that the mud ball maintained its spherical shape after being immersed in a solution with 0.07% AFR for 48 hr. This means AFR adsorbed on mud or clay ball, formed thin or protective layer, and prevent water to interact with shale. This protective layer increased radial stress and minimized difference between hoop stress and radial stress and this helps prevent cracking or dispersion. It is obvious from zeta potential, swelling test, dispersion test, and mud ball immersion test; that the developed WBM with AFR prevent both shale swelling and dispersion better than the formulated WBM with CFR. This means CFR performs poorly as a shale inhibitor.

The zeta potential measurements give indication about attraction of shale inhibitor to clay surface. Swelling test, dispersion test, and mud ball immersion test show ability of shale inhibitor to prevent clay swelling and dispersion. The accretion test is still the practical way to know the tendency of shale/clay to adhere to steel surfaces. The accretion test provides a qualitative indicator of the likelihood of experiencing bit balling and ROP reduction problems (Van Oort, 2018). Personnel may eventually need to pull out of hole the bottom hole assembly in order to clear the balling issue at the bit. The bentonite tablets used in this study has Cation Exchange Capacity (CEC) is 40 meq/100 gm), which means it has high swelling capability. The accretion tests were performed using different clay weights (25, 50, 75, and 100 gm. These additives were put in different WBM formulations as mentioned in table 1.

The results of accretion test was shown in Fig. 7. The basic WBM and WBM with CFR had accretion percentages higher

than 30% when adding at least 50 gm of clay. Therefore, WBM with CFR had poor performance to eliminate sticking to bit and cause bit balling problems. On the other hand, the accretion percentage of shale in case of WBM with AFR was less than 1%, when clay was added up to 100 gm. the formulated WBM with AFR had the lowest accretion value in comparison with all formulated WBMs. Consequently, Adding AFR to WBM minimized shale sticking and bit balling and increased ROP.

The mechanism behind the ability of AFR to preclude bit balling is the manufacturing itself of AFR. This AFR is emulsified copolymer which means it is synthesized in presence of surfactant. This surfactant will form between the clay surface and solid bar and inhibit sticking. Hence, AFR not only inhibit shale swelling and dispersion, but also able to prevent shale accretion and minimize bit balling problem. It became clear that CFR has poor shale inhibition while AFR is much more effective to stabilize sensitive problematic shale formations.

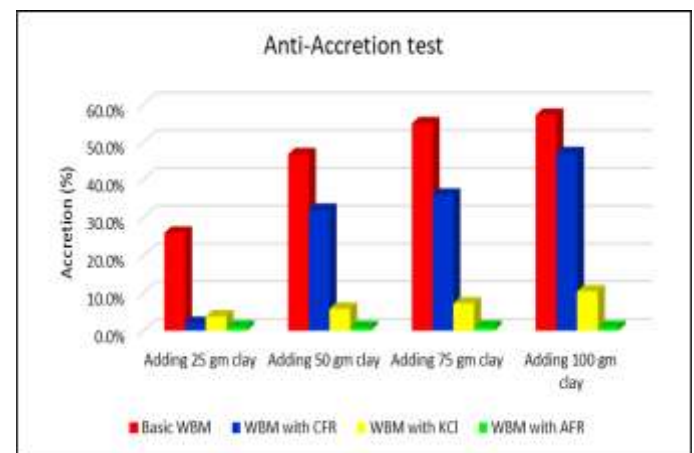


Figure 7: Accretion percentage of the different formulated WBMs

It became clear in this study that CFR has poor shale inhibition while AFR is much more effective to stabilize sensitive problematic shale formations. The next target is to determine the shale inhibition mechanism of using AFR in WBM. Both shale dispersion and contact angle measurement were used for this purpose. A series of shale dispersion tests were done. These series were based on the following steps: Step 1 was adding the shale cuttings to WBF with 4 pptg AFR and performing shale dispersion test to calculate shale recovery. Step 2 was performed by adding the recovered shale cuttings from the previous step to new WBF with AFR concentration of 8 pptg and shale dispersion tests will be repeated to estimate shale recovery. Step 3 was conducted by repeating step 2 but with increasing the AFR concentration by 4 pptg in the new WBM. The obtained results of shale recovery from shale dispersion tests are illustrated in (Fig. 8). It is obvious that the recovered percentage of shale increased with every step of the shale dispersion test series. This gives indication about adsorption of AFR on clay particles and this adsorption encapsulate the clay surface. The encapsulation formed a thin film around clay and prevented water to adsorb and interact with clay. This proves

the encapsulation is one of shale inhibition mechanism.

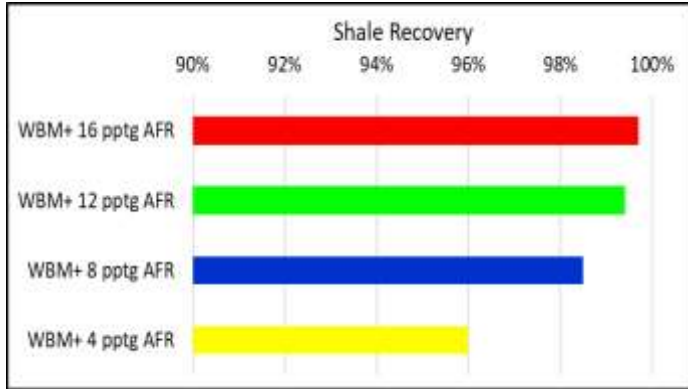


Figure 8: Shale recovery from the formulated WBF with different AFR concentrations

The contact angle measurement provides an indication of the wettability alteration of clay surfaces in terms of hydrophilic and hydrophobic surface. Figure 9 shows the contact angles of based mud. The based mud without AFR shows the approximate contact angle 12.1°. The means the shale surface is hydrophilic and tends to adsorb water. On the other hand, adding AFR to WBM leads to increase the contact angle from 12.1° to 50.7° as illustrated in Fig. 10. This means the shale surface wettability has changed and become less hydrophilic.

The shale dispersion test proved there was thin film formed around clay/shale surface and encapsulated this surface. AFR is type of emulsified polymer that already being emulsified in oil phase by using neutral surfactant. This surfactant modifies the wettability of the film surface as it increased the hydrophobicity of the clay surface. In conclusion, AFR encapsulated the clay surface and formed a thin hydrophobic layer that prevents the water penetration into the shale.

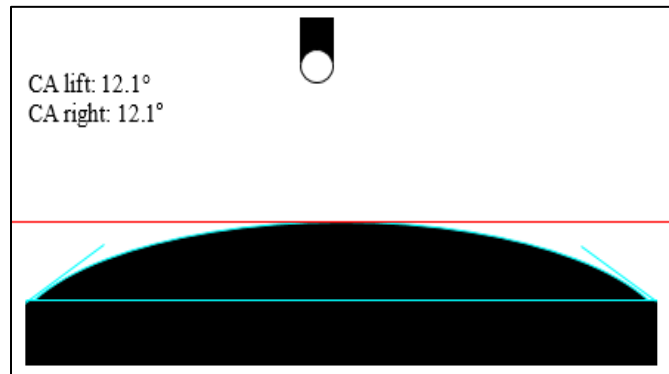


Figure 9: Contact angle measurements of basis WBM

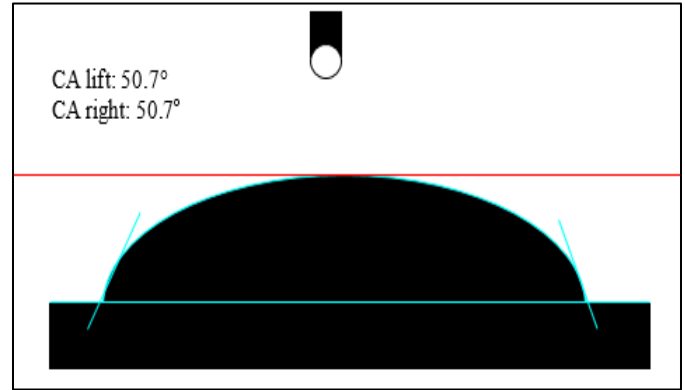


Figure 10: Contact angle measurements of the formulated WBM with AFR

The formulated WBM with AFR is not only able to prevent shale swelling, and dispersion, but also minimize bit balling problems by both encapsulation and wettability alteration mechanisms. The following step is know the effects of temperature and pressure on the formulated WBM with AFR to simulate its performance under downhole conditions. Fluid rheology of the two formulated WBM with and without AFR were measured at different temperatures range from 120° to 180° F. (Fig. 11 and Fig. 12) illustrate the shear stress versus shear rate. The formulated mud with AFR of concentration ranging from 0.25 to 0.50 lbm/bbl showed shear thinning behavior. The formulated WBM without AFR was degraded with temperature. Nevertheless, WBM with 0.25 and 0.50 lbm/bbl had thermal stability and high resistant to viscosity thermal degradation. This thermal stability was based on interaction between AFR and bentonite in the formulated mud and this interaction increased with temperature rising. The formed hydrogen bond between amide group on AFR backbone and oxygen in the bentonite surface is the main interaction behind this temperature stability.

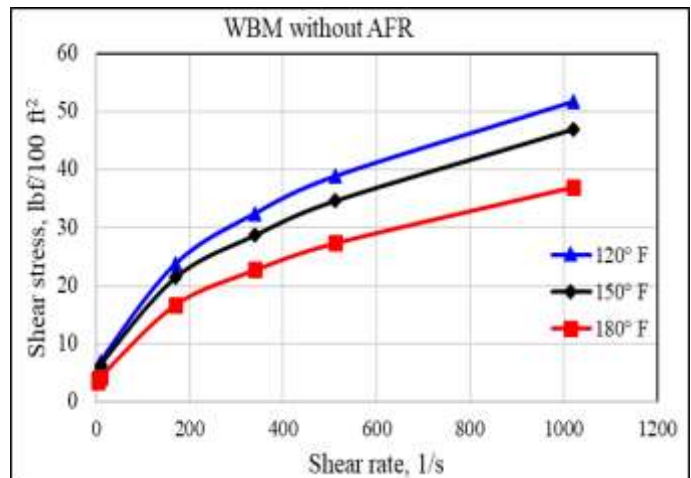


Figure 11: Shear stress of the formulated WBM without AFR

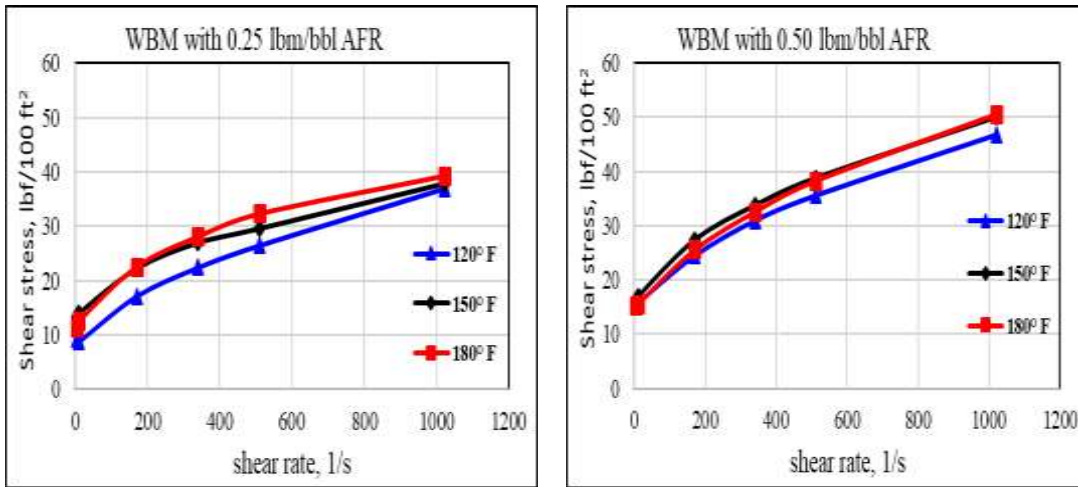


Figure 12: Shear stress of the formulated WBM with different AFR concentrations

The formulated WBM with AFR showed less degradation with temperature from 120 to 180° F. It is important to determine changes of mud rheology with pressure. The OFITE 1100 rheometer was used to measure shear stress versus shear rate under pressures of 500, 1000, 1500, and 2000 psi within temperature from 120 to 180° F. The calculated RDRs for the formulated WBM with 0.5 lbm/bbl AFR are demonstrated in Fig. 13 through Fig. 15. In the range from (0 – 2000 psi), the effect of pressure on measured shear stress versus shear rate is less than 5%, which is practically negligible.

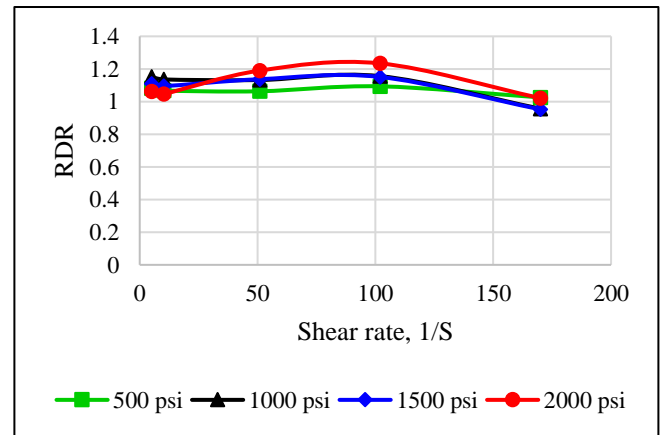


Figure 14: WBM with 0.5 lbm/bbl AFR at 150° F

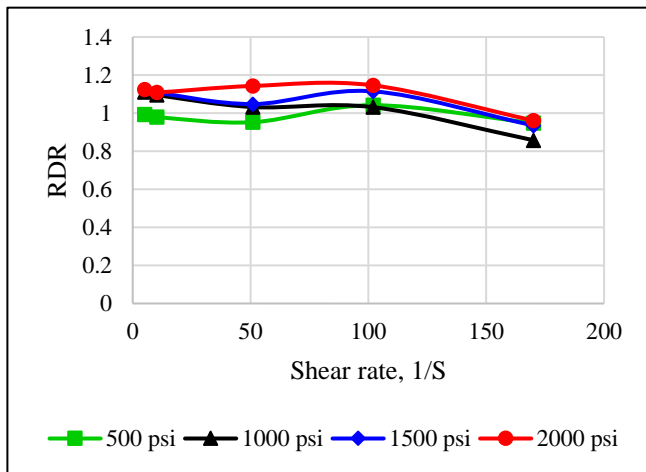


Figure 13: WBM with 0.5 lbm/bbl AFR at 120° F

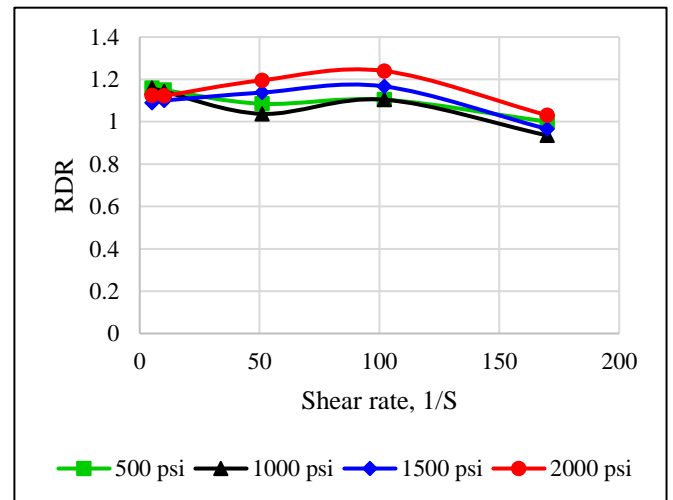


Figure 15: WBM with 0.5 lbm/bbl AFR at 180° F

Conclusion

This paper focused experimentally on evaluation shale inhibition performance of AFR and CFR in WBM. Besides, it concentrated on determination shale stabilization mechanism of the proposed shale inhibitor and knowing effect of pressure and temperature on the developed WBM. The following conclusions are drawn from the study:

- CFR performs poorly as a shale inhibitor
- The formulated WBM with AFR is effective to prevent shale swelling and dispersion
- The Accretion tests show the formulate WBM with AFR is effective to prevent bit balling and increase ROP
- AFR is much more effective for shale inhibition due to the encapsulation and wettability alteration mechanisms
- The formulated WBM with AFR has better thermal stability up to 180° F
- The effect of pressure (0- 2000 psi) on fluid rheology of formulated WBM with AFR is practical negligible

Abbreviations

AFR	Anionic Friction Reducer
CFR	Cationic Friction Reducer
WBM	Water Based Mud
lbm	Pound mass
XC	Xanthan gum
mV	millivolt
bbl	Barrel
pptg	Pound per thousand gallon
OFITE	OFI Testing Equipment®
PAC	Polyanionic Cellulose
CaCl ₂	Calcium Chloride salt
RPM	Revolution Per Minute

Conversions

$$\text{Lbm/bbl} = 0.04 \times \text{pptg}$$

$$1/S = 1.703 \times \text{RPM}$$

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