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Improving Thermal Stability of Starch in Formate Fluids for Drilling High Temperature Shales

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Abstract
Starch is one of the most widely used biopolymers in water based drilling fluids to control fluid loss. The thermal stability of starch in common drilling fluids is low (93 °C). In this study, the thermal stability of starch has been evaluated in sodium/potassium formate and potassium chloride fluids. Samples of mud were prepared by formate salts (sodium and potassium) and potassium chloride with the same formulations. The rheological and filter loss properties and shale recovery were studied at different temperatures. The results showed that despite the relatively low concentration of starch ($4\ ^{gr}/_{350\,cm^3}$) and low density of mud, the sodium and potassium formate salts increased the thermal stability of starch up to 150 °C for 16 hours. The rheological and fluid loss properties of formate fluid after 16 hours hot rolling slightly changed compared with potassium chloride fluid. Also, the results showed that the shale recovery of formate fluid is better than that of potassium chloride fluid. Thus, formate salts improved the thermal stability of starch in water based drilling fluids

Key words: Starch, Formate Fluids, Thermal Stability, Shale Recovery, Rheological Properties

Introduction
Drilling fluid is the most important factor affecting the cost of drilling operation. Any problem in drilling fluid properties directly affects the drilling process. Therefore, maintaining the fluid properties under the pressure and temperature of the hole will increase the efficiency of the drilling operation.
Today, with the drilling of the deeper wells, we encounter higher bottomhole pressures and temperatures. Thus, we need mud additives with high thermal stability for drilling such deep drilling operations. There are basically two types of water soluble polymers used in muds, namely natural polymers such as polysaccharides and the synthetic ones such as vinyl polymers. Starch is one of the most common natural polymers used as a fluid loss controller in drilling fluid formulations. Also, this additive is cost effective and affluent [1]. Starch is the principal component of the seeds of cereal grains (such as corn, wheat, and rice) and of tubers (such as potato and tapioca). Starch is degraded by heat and agitation. With continued circulation in a hole at the temperatures of 200 °F (93 °C) and higher, starch breaks down rapidly and loses the sealing action of the filter cake [2]. Therefore, the thermal stability of starch should be increased for applications at higher temperatures. Formate salts are capable of increasing thermal stability of polymers like starch [3].
The formate salts of alkali metals are very soluble in water and form brines of very high densities. The three salts that have been found useful for drilling and completion fluids are sodium formate (NaCOOH), potassium formate (KCOOH), and cesium formate monohydrate ($CsCOOH.H_20$). Sodium formate is the least soluble of the three and can reach a density of about 1.33 SG. Potassium formate is more soluble, with a maximum brine density of about 1.59 SG, and cesium formate can reach as far as 2.3 SG [4]. Formate brine was first used in 1993 by NAM in the Netherlands as a coiled-tubing drilling fluid in a well sidetracking operation in the Berkel field [5].
The alkali metal cations (Na^+, K^+, and Cs^+) are all monovalent, giving them their unique compatibility with biopolymers while at the same time contributing to their non-damaging behavior in reservoirs. The alkali metal formates in solution also exert a structuring effect on surrounding water molecules, making water more ice-like in nature. This water structuring behavior has a beneficial effect on the conformation of dissolved macromolecules, making them more ordered, rigid, and stable at high temperatures. The combination of anti-oxidant and

water structuring properties imparts the potential for increasing the thermal stability of many common drilling fluid polymers to formate brines [6].

In this study, the effect of sodium and potassium formate salts on increasing the thermal stability of starch has been investigated. The comparison of the rheological and filtration properties of fluid after being heated at different temperatures proved the effect of formate salts on increasing the thermal stability of polymers in the fluid.

Experimental and the Technical Aspects Material and Equipment

The salts of sodium formate with a minimum purity of 99% and a molecular weight of 68.01 and the potassium formate with a minimum purity of 99% and a molecular weight of 84.12 were used in the mud composition. The rheological properties of the fluid were measured directly using a rotational viscometer (model Chan35) and the filtration properties of the fluids were measured by Multi filter press (model Fann 12BL). A rolling oven (model Fann) was used for dynamic heating of the fluids at different temperatures.

Method

For the evaluation of the thermal stability of starch and other polymers, two samples with the same concentration of additive in the formulation were prepared. The difference between these samples was the salt type. One of these contained potassium and sodium formate salts and the other contained KCl salt (Table. 1). The rheological and filtration properties of the samples were evaluated after exposure to different temperatures from ambient up to 175 °C. Also, shale recovery tests based on API RP 13-I method were carried out on the samples at different temperatures.

Table 1- The typical formulation of KCl and sodium/potassium formate fluids

Fluid Composition	unit	KCl fluid	Na/K Formate fluid
Sea water	ml	350	350
Soda Ash	gr	0.3	0.3
Starch	gr	4	4
PHPA	gr	1	1
Xanthan Gum	gr	1	1
Potassium chloride	gr	121	21
Sodium formate	gr	-	50
Potassium formate	gr	-	50
Limestone powder	gr	50	50

Rheological measurement tests were run at ambient temperature with Chan 35 viscometer for each sample after hot rolling. Rheological parameters (A_v, P_v, and Y_p) were calculated based on Bingham plastic model by using the following equations:

$$Av = \frac{\theta_{600}}{2} \quad (1)$$

$$P_v = \theta_{600} - \theta_{300} \quad (2)$$

$$Y_p = \theta_{300} - P_v \quad (3)$$

Filtration tests were run at ambient temperature and at the pressure of 100 psi with a multi filter press (Model 12BL Fann) and the filtrate volume collected in 30 minutes was reported as a filter loss of fluid.

The shale recovery test was performed by American Petroleum Instituted method (API RP 13 I). This test was intended to mimic the exposure of drilled cuttings to a particular drilling fluid during transport to the surface through a well bore annulus. A sample of dried shale was ground and sieved through both a 4 mm (mesh 5) and a 2 mm (mesh 10) sieve. Ground shale particles, which passed through the 4 mm sieve, but collected on the 2 mm sieve, were selected for use in this particular test. For each fluid to be tested, a 20 gram sample of sized shale was weighed and selected. Next, approximately 350 mls of each fluid to be tested was poured into a cell. The 20 gram sized shale sample was added to the fluid and the cell was capped and shaken to ensure even distribution. The sample was then placed in an oven and hot rolled at different temperatures for 16 hours. When the 16 hour hot roll was complete, the sample was cooled to room temperature. Next, a large quantity blend of approximately 15 pounds per barrel of potassium chloride solution and saturated salt water was prepared. The contents of the sample cell were then poured onto a 500 micrometer (mesh 35) sieve. The inside of the cell was carefully rinsed with potassium chloride solution and poured again onto the 500 micrometer sieve. The cell was repeatedly rinsed and poured until all shale had been removed from the cell. Next, the shale retained by the 500 micrometer sieve was carefully washed with potassium chloride solution. Special care was taken to ensure that none of the samples spilled over the side of the sieve. The washed particles of shale were then washed with water to remove any remnants of the potassium chloride brine. Then, the shale particles were placed in a pre-heated oven at 250 °F to dry to a constant weight. Having been dried, the shale sample was then weighed. The percentage recovery of shale was then determined by the following equation [7]:

$$\text{Shale recovery } \% = \frac{\text{Weight of drierd shale (gr)}}{\text{Weight of initial shale (20gr)}} \times 10 \quad (4)$$

Results and Discussion

In this study, the thermal stability of starch was examined in the presence of potassium chloride and sodium/potassium formate brines at different temperatures (120 °C, 130 °C, 150 °C, 160 °C, and 175 °C). All the samples were hot rolled for 16 hours at the above temperatures. the rheological and filtration properties of potassium/sodium formate and potassium chloride fluids are given in Table 2. In Figure 1, the apparent viscosity of formate and KCl muds is shown at different temperatures. As observed in Figure 1, the apparent viscosity decreases by increasing temperature, but the decrease in the apparent viscosity of KCl mud is more than the drop in the apparent viscosity of formate mud.

Table 2- The rheological and filtration properties of potassium/sodium formate fluid and potassium chloride fluid after 16 hours hot rolling at different temperatures

Fluid type	KCl fluid					Na/K Formate fluid				
Properties Temperature °C	Av (cp)	Pv (cp)	Yp (lb/100ft²)	Gel	Fl (ml)	Av (cp)	Pv (cp)	Yp (lb/100ft²)	Gel	Fl (ml)
25	17	13	14	3/4	6.5	23	15	16	3.5/4.5	4.3
120	8	7	2	1.5/2.5	8.5	21	14	14	3/4	4.4
130	11	8	6	2/3	31.6	19	13	12	2/3	6.2
150	4.5	4	1	0.5/1	No.C	15.5	11	9	2/3	7.6
160	2.5	2	1	0/0	No.C	13	11	4	1.5/2	93
175	3	3	0	0/0	No.C	4	4	0	0.5/1	104

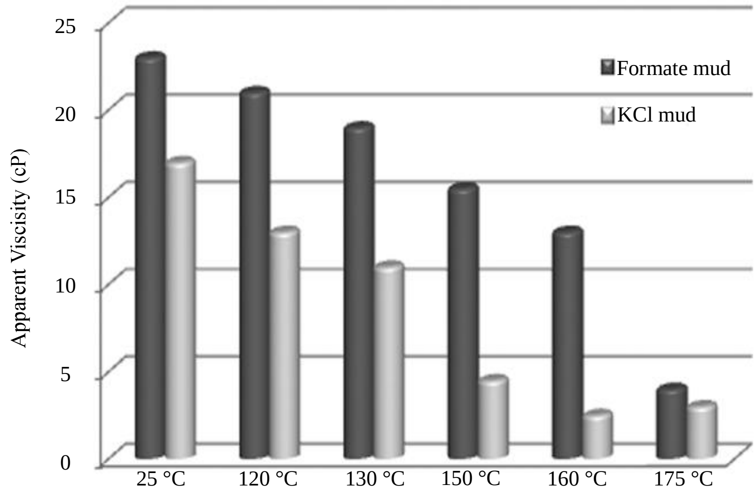

Figure 1- The apparent viscosity of formate mud and KCl mud after 16 hours hot rolling at different temperatures

The apparent viscosity of formate mud was maintained up to 160 °C (50% of its original properties are retained), but in the case of KCl mud, the apparent viscosity was maintained just up to 130 °C.

Figure 2 shows the yield point of formate and KCl mud at different temperatures. According to Figure 2, the reduction in the yield point is greater in KCl muds than formate mud.

One of the important parameters in evaluating the efficiency of starch is the amount of API fluid loss. In Figure 3, the fluid loss of formate and KCl muds is shown at different temperatures. As observed, the fluid loss of KCl mud after hot rolling at different temperatures is more than that of formate mud. According to Figure 3, the starch maintains its fluid loss controlling role up to 150 °C in the presence of potassium and sodium formate salts, while the starch decomposes at temperatures above 130 °C in the case of KCl mud.

Shale recovery values for formate and KCl muds at 120 °C, 150 °C, and 175 °C are given in Table 3. The shale recovery of formate mud is better than that of KCl mud at higher temperatures.

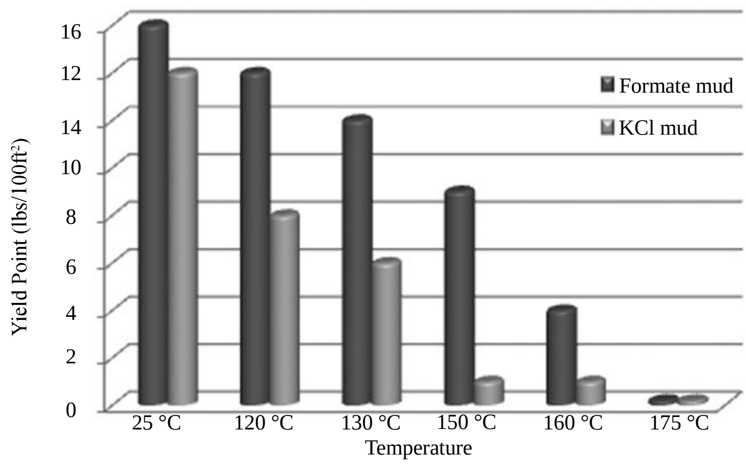

Figure 2- The yield point of formate mud and KCl mud after 16 hours hot rolling at different temperatures

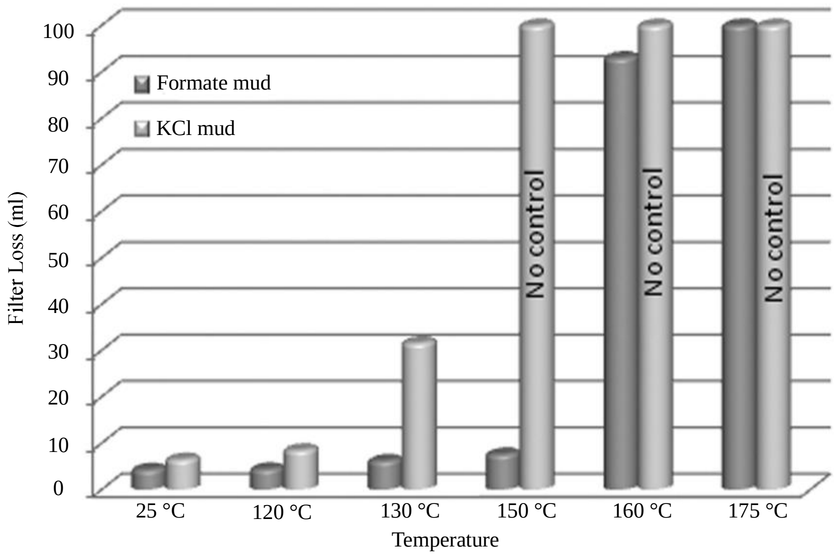

Figure 3- The filter loss of formate mud and KCl mud after 16 hours hot rolling at different temperatures

Table 3- Shale recovery values for formate and KCl mud after 16 hours hot rolling at different temperatures

Fluid Type Temperature (°C)	KCl fluid	Na/K Formate fluid
120	88%	95%
150	87%	92%
175	84%	92%

Conclusion

The present study clarified the effect of potassium and sodium formate salts on increasing the thermal stability of polymers in water based drilling fluids. The results show that starch can be used at 150 °C in formate drilling fluids and potassium and sodium formate salts increase the thermal stability of starch from 120 °C in KCl mud to 150 °C in formate mud. Also, the test results show that the thermal stability of xanthan (XC polymer) increases in the presence of formate salts.

According to the results of shale recovery tests, the formate salt has better shale inhibition properties than potassium chloride.

Formate fluids are a suitable alternative for conventional drilling fluids for drilling shale and HPHT wells. Also, these fluids are environmentally responsible and readily biodegradable.

Nomenclature

API: American Petroleum Institute

A_v: Apparent Viscosity (cP)

P_v: Plastic Viscosity (cP)

Y_p: Yield Point (lbs/100ft^2)

θ_{600}: Dial reading at 600 rpm

θ_{300}: Dial reading at 300 rpm

References

[1]. Annis Max R and Smith Martin V, *Drilling Fluids Technology. Revised edition*, August 1996, Page 127-132.

[2]. Darley H.C.H and Gray George R, "*Composition and Properties of Drilling and Completion Fluids",* Fifth Edition, 1988, pp. 565-568.

[3]. Formate Technical Manual, Part B, Compatibilities and Interactions, SectionB5: "*Compatibility with Additives*" www.formatebrines.com/technicalinformation/formatetechnical manual. By Cabot Specialty Fluid, Available in Sep 2010.

[4]. Howard S.K.: "*Formate Brines for Drilling and Completion: State of the Art*" , SPE 30498, 1995.

[5]. Bungert D., Maikranz S. Sundermann, R., Downs, J., Benton, W. and Dick, M.A.: "*The Evolution and Application of Formate Brines in High Temperature/Pressure Operations*", SPE 59191, 2000.

[6]. Formate Technical Manual, Part A, Chemical and Physical Properties, and SectionA1:"*Chemistry*"www.formatebrines.com/technicalinformation/formatetechnicalmanual. By Cabot Specialty Fluid, Available in Sep 2010.

[7]. API RP 13I, *Recommended practice for laboratory testing of drilling fluids*, - 6th edition, MAY 2000.