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RESEARCH OF THERMAL STABILITY OF BIOPOLYMER SYSTEMS WEIGHTED BY FORMIC ACID SALT

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ABSTRACT: The paper considers the utilization of clay-less drilling fluids under conditions of abnormally high formation pressures and temperatures. The solution of this problem is possible through the utilization of water-soluble formic acid salt. Results of the laboratory research of formate salt impact on the biopolymer drilling fluids thermal stability are presented.

Depths of drilling are constantly increasing. Not so long ago the area of application for clay-less systems was limited by abnormally low or hydrostatic formation pressures, whereas nowadays there is a problem with the utilization of those systems in the conditions of abnormally high formation pressures and temperatures.

Utilization of clay-less drilling fluids weighted with traditional weighting agents (barite, hematite, marble, etc.), under the conditions of high formation temperatures, is limited due to uncontrollable increase of HTHP filtration loss [1]. Density of such systems can be increased with adding water-soluble salt to their composition which gives the possibility to avoid the increase of HTHP filtration and preserve all benefits that those fluids provide.

Utilization of salts of alkali metals of formic acid allows to receive stable high-density systems. Thus, in case of sodium formate utilization, drilling fluid density can reach up to 1330 kg/m^3, potassium formate – up to 1570 kg/m^3, cesium formate – up to 2300 kg/m^3 [2, 4]. Herewith, such heavyweight formate-based systems maintain low filtration indexes under high temperatures (Tab. 1).

Table 1. Comparison of HTHP filtration of clay-less system Biocar® weighted with barite and HCOOK up to the density of 1500 kg/m^3

Experiment temperature, ΔP = 5 MPa	Biocar® + barite up to 1.50 g/cm^3	Biocar® + HCOOK up to 1.50 g/cm^3
120°C	25 cm^3/30 min	10 cm^3/30 min
140°C	36 cm^3/30 min	15 cm^3/30 min
150°C	44 cm^3/30 min	18 cm^3/30 min
160°C	62 cm^3/30 min	20 cm^3/30 min

It is known that rheological properties of biopolymer clay-less systems are the most sensitive to the change of external factors [3]. As a result, the results of testing of rheological parameters can be used for evaluating thermal resistance of such drilling fluids.

Rheological properties under high temperature conditions were explored with the utilization of rotational viscometer OFI TE 1100. Thermal stability of a system can be evaluated on the basis of either shear stress or viscosity depending on temperature. On a graph there is a characteristic point, so called "melting point" (T_m), where sharp decrease of rheological properties begins. T_m index is proposed by us as the criterion determining the starting temperature point of biopolymer destruction.

When such temperature point is achieved, spatial structure of polymer molecules undergoes conformational changes – molecules that have been in ordered state become less ordered (Fig. 1). Those changes lead to the sharp decrease of drilling fluid rheological indexes and increase the speed of thermal destruction.

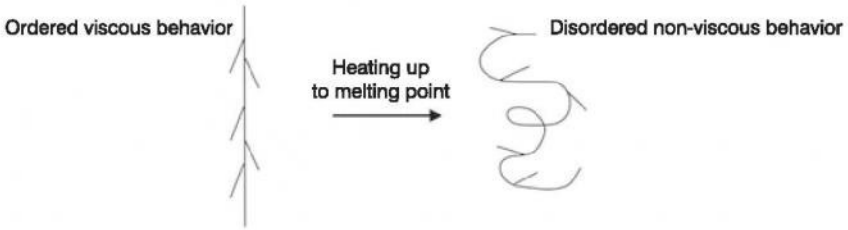

Fig. 1. Conformational changes of xanthan gum molecule when heated to melting point

Adding of salts of formic acid to the clay-less system Biocar® allows increase the starting point of thermal destruction. With the increase of salt concentration thermal stability of drilling fluid is also risen. When the amount of potassium formate in drilling fluid equals 300% T_m index increases from the initial 110 up to 174°C (Fig. 2). For comparison, in case of potassium and sodium chlorides utilization when the limit of their solubility is achieved, maximum index for T_m index does not reach 138°C. Such temperature of destruction responds to 30% concentration of potassium formate.

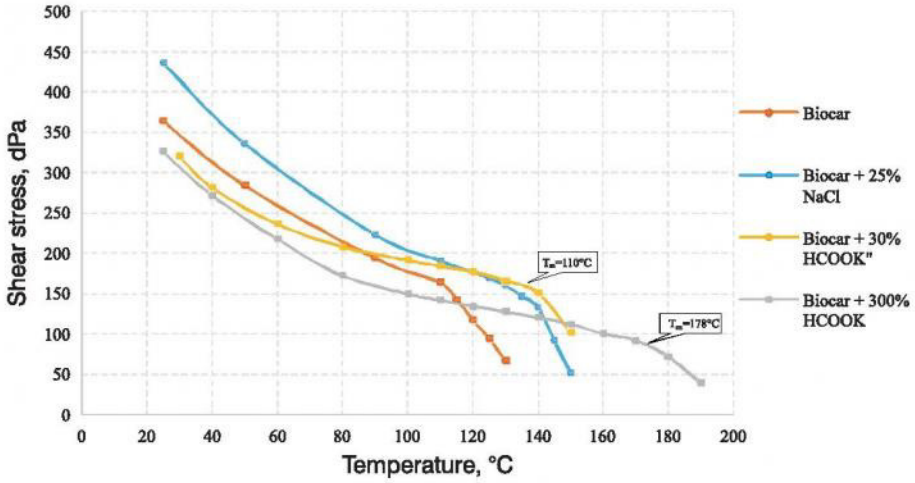

Fig. 2. Influence of salt on the temperature of thermal destruction start in Biocar® drilling mud

Thus, formic acid salts can produce efficient influence on macromolecules of polysaccharide components of clay-less drilling fluids conformation and provide for the maintenance

of their ordered state. Therefore, temperature stability of clay-less drilling system is significantly increased.

On the graph the value of T_m from potassium formate concentration changes in logarithmic dependence, due to the rapid rise in the range from 0 to 100% and further gradual stabilization (Fig. 3). Thereby, with the concentration of potassium formate exceeding 100%, its role as thermo-stabilizing agent decreases. At high concentrations it seems to serve more as a weighting agent.

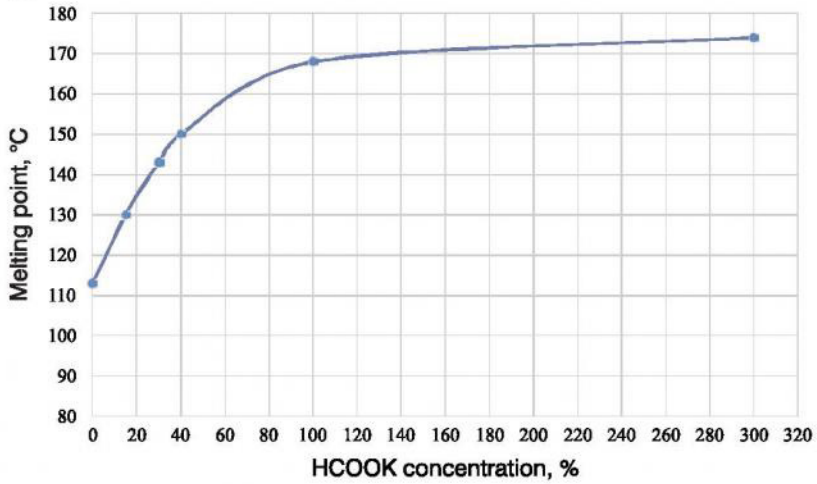

Fig. 3. Dependence of thermal degradation point on the content of potassium formate in biopolymer system Biocar®

High thermal stability of biopolymer systems, weighed with formic salts, is also confirmed by the results of their long-term thermostating at various temperatures (Tab. 2). Collected data demonstrated that potassium formate ensures stable structural-rheological and filtration properties of system up to the temperature of 170°C, whereas sodium or potassium chloride-based fluids shall be entirely destroyed already at the temperature of 150°C.

Table 2. Comparative table of drilling fluid parameters after 8 hours of thermostating under different temperatures

T [°C]	Fresh Biocar®				Biocar® + 3% KCl + + 27% NaCl				Biocar® + 110% HCOOK			
	PV [cP]	YP [dPa]	Gel [dPa]	Fl [cm³/ 30 min]	PV [cP]	YP [dPa]	Gel [dPa]	Fl [cm³/ 30 min]	PV [cP]	YP [dPa]	Gel [dPa]	Fl [cm³/ 30 min]
25°C	15	134	43/53	4	25	172	53/58	3.5	35	168	53/58	3
85°C	15	134	43/48	3.5	25	168	53/58	3	30	168	43/53	2.5
120°C	11	95	28/28	3.5	23	168	48/53	3	34	168	43/58	2.5
140°C	10	19	17/17	n.m.	12	86	48/53	8.5	30	163	48/53	2.5
150°C	Full system distraction				10	17	15/15	n.m.	30	163	43/58	2.5
160°C	Full system distraction				Full system distraction				35	124	24/38	2.5
170°C	Full system distraction				Full system distraction				30	101	29/34	3

Thereby, conducted research established that introduction of formic acid salts, especially potassium formate, provides a number of unique properties to clay-less drilling fluids. These

properties essentially increase the range of their application at HTHP conditions. Drilling fluids, weighed with formate salts, are characterized by high density, low bottomhole filtration and extremely high thermal stability, that is more than 20°C higher than the thermal stability of traditional clay-less fluids weighed with sodium or potassium chlorides. Taking into account environmental safety, high lubricity and inhibiting properties we can conclude that systems based on formate salts are extremely promising for drilling deep wells in Ukraine.

Literatura

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Исследование термической устойчивости биополимерных систем, утяжеленных солями муравьиной кислоты

СОДЕРЖАНИЕ: В статье рассмотрены вопросы применения безглинистых промывочных жидкостей в условиях аномально высоких пластовых давлений и температур. Показано, что проблема может быть решена путем применения водорастворимых солей муравьиной кислоты. Приведены результаты лабораторных исследований влияния солей формиата на термическую устойчивость биополимерных систем.

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