IOP Conf. Series: Earth and Environmental Science **21** (2014) 012035 doi:10.1088/1755-1315/21/1/012035

Influence of Primary Glyoxal on Properties of Tested Drilling Mud

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Abstract. The research was done to observe the influence of primary glyoxal on properties of tested drilling mud. Glyoxal was used as a reagent to reduce viscosity and stabilize shale. Drilling mud processing parameters were estimated before and after affecting by glyoxal. Suggested is the method of polysaccharide modification by glyoxal for improving its resistance to microorganisms; carried out the research of bio- and thermal resistance of starchy and xanthan reagents.

1. Introduction

According to the present knowledge, it has been found that microorganisms negatively affect the process of oil production starting from well drilling to commercial oil transport.

At drilling process, the activity of cellulose-decomposing and other bacteria leads to a rapid deterioration of processing properties of drilling mud based on polysaccharide (starch, xanthan gum, various types of cellulose). This results in changing of the flow properties and the increasing of fluid loss indicator [1. № 2. P.23]. Loss in flow and processing properties of mud, resulted from biodegradation, leads to the necessity of extra processing with costly chemical reagents and thus increases the cost of drilling operations. Therefore, critical task is to prevent biodegradation of polysaccharide.

The most rational and promising way to suppress bacteria is to use special antimicrobial agents - bactericides. In this case, bactericides should meet the following requirements: to have broad spectrum of activity, to be of high activity at low concentration, non-corrosive, safe for humans and environmentally friendly, do not affect processing properties of drilling mud, to have available resource base and low cost [2 . P.15].

High biodegradability of polysaccharides affected by bacteria gives the ground to carry out the study aimed to determine the effect of bactericidal agents on the consistency of bio-polymer mud.
Phenol and formaldehyde (paraformaldehyde) have antibacterial effect, but their usage for drilling mud treatment is limited by hygienic and ecological restrictions. Formaldehyde has found wide application as an antibacterial additive to the drilling mud and a corrosion inhibitor. However, this reagent has several drawbacks, in particular, low efficiency and duration of antibacterial effect, as well as high toxicity index (2nd hazard class according to GOST 12.1.007-76) [3. C.1]. Thus, the most optimal bactericide agent is primary glyoxal.

Glyoxal is more than twice as active as formaldehyde and greatly exceeds in environmental characteristics. One molecule of glyoxal is able to fix four sulfur-containing molecules (hydrogen sulphide, mercaptans, etc.), hence it is possible to use it for prevention of H2S corrosion [4. P.34]. Biocidal properties of glyoxal are widely used to extend the service life of drilling mud and for oil decontamination, in particular, to prevent the growth of sulfate-reducing bacteria. High cost of glyoxal reduced its application. Currently "Novokhim" company, firstly in Russia, launched the production of glyoxal by using unique technology, hence the products became competitive. Thus, the aim of present research was to study the flow and processing properties of tested drilling mud modified by glyoxal.

2. Experiment

2.1 Preparation

Drilling mud was prepared by dissolution of bentonite clay (PBMA) in distilled water, than the required amount of glyoxal was added.

2.2 Characterization

Study of flow properties was performed on a rotor viscometer OFITE 1100. Glyoxal showed the highest chemical reactivity in a temperature interval of 50-60 º C, and therefore the study of drilling mud rheology was carried out at temperature of 20 º C and 55 º C. Filtration characteristics of drilling mud was determined by pressure filter OFITE. Effect of drilling mud on clay swelling was studied by longitudinal swelling tester OFITE in dynamic regime.

Antibacterial activity was evaluated by the number of colony-forming bacteria and by observing the structural change in flowing properties of 1% biopolymer aqueous solution during 7 days.

3. Results and discussion

Research of flow and processing properties of drilling mud containing glyoxal.

During the study of drilling mud rheology it was defined that processing of bentonite slurry by glyoxal leads to the considerable reduction of drilling mud funnel viscosity (table 1). With the increase of glyoxal concentration the effect becomes more obvious, thus when using glyoxal in clay mud, thin properties of the reagent should be taken into account. Despite the fact that viscosity of drilling mud decreases when adding glyoxal, the filtration index is slightly changing during glyoxal concentration increasing.

Table 1. Flow and processing properties of tested glyoxal and bentonite drilling mud.

Mud	ρ, g/cm^3	Funnel viscosity, sec.	Filtration, cm^3/30 min.	SGS, pound/100ft^2,		PV, cPs		DSS, pound/100ft^2	
				20 ºC	55 ºC	20 ºC	55 ºC	20 º C	55 º C
Bentonite 5%	1,035	28,5	19,5	4,0/6,0	6,0/8,0	3,3	3	3,3	4,1
Bentonite 5%+ glyoxal 0,25%	1,035	22,0	19,4	2,0/3,0	3,0/4,0	2,9	2,3	1,8	2,3
Bentonite 5%+ glyoxal 0,5 %	1,035	20,0	19,3	2,0/2,0	2,0/2,0	2,4	1,9	1,6	1,8
Bentonite 5%+ glyoxal 1,0 %	1,035	18,0	19,2	1,0/2,0	2,0/2,0	2,5	1,9	1	1,3
Bentonite 5%+ glyoxal 2,0 %	1,035	18,0	19,0	1,0/2,0	2,0/2,0	2,2	2,2	1,3	1,3

Static gel stress (SGS), plastic viscosity (PV) and dynamic shear stress (DSS) decrease with the increasing of glyoxal concentration in mud

Glyoxal has the ability to fix polymer reagents containing hydroxyl groups. This can result in viscosity increaing and mud shearling. Therefore, flow properties study of tested starch and glyoxal-containing drilling mud (5% bentonite and 0.25% starch) was made. Measurement of rheology was done one day after mud preparation.

Table 2. Flow and processing properties of tested drilling mud containing glyoxal and starchy additives (5% bentonite, 0.25% starch).

Glyoxal concentration, %	ρ, g/cm^3	Funnel viscosity, sec.	Filtration, cm^3/30min	SGS, pound/100ft^2,	PV, cPs	DSS, pound/100ft^2
				20 ºC	20 ºC	20 ºC
0,025	1,035	23.8	14	4,0/6,0	10,2	3,5
0,075	1,035	25	14	4,0/7,0	10,4	4,8
0,10	1,035	25.2	14,4	5,0/8,0	10,7	4,9
0,25	1,035	27	13	6,0/9,0	11,4	5,6
0,50	1,035	24.5	15	5,0/8,0	10.3	4,4
0,75	1,035	23.5	15	4,0/7,0	9,8	3,4
1,0	1,035	23	14.6	4,0/6,0	8,9	3,7

From the results of drilling mud flow properties measurements, shown in table 2, it can be seen that increasing of glyoxal concentration to 0.25% results in the increase of the tested mud viscosity. This may be the result of glyoxal and starch interaction, at which polysaccharide polymer units are fixing and shearling is increased. Further increasing of glyoxal concentration in drilling mud leads to the decrease in viscosity. Thus, it can be assumed that excess of glyoxal reacts with bentonite clay developing thin effect as it was shown above (table 1).

Effects of glyoxal on colloidal clay mud in water can be used to reduce the swelling of shale clay. The swelling process is accompanied by increase in humidity, rock volume and swelling pressure. As a result, during the process of drilling, challenges associated with sidewall sticking, cavings and rock falls may emerge due to water-based drilling mud application [5. P.42].

Studies (figure 1) show the interaction between bentonite and sodium during 70 hours of analysis. The graph clearly displays a discrepancy of four fluids. Water demonstrates the highest degree of swelling, exceeding approximately in 4 times the axial size of bentonite sample.

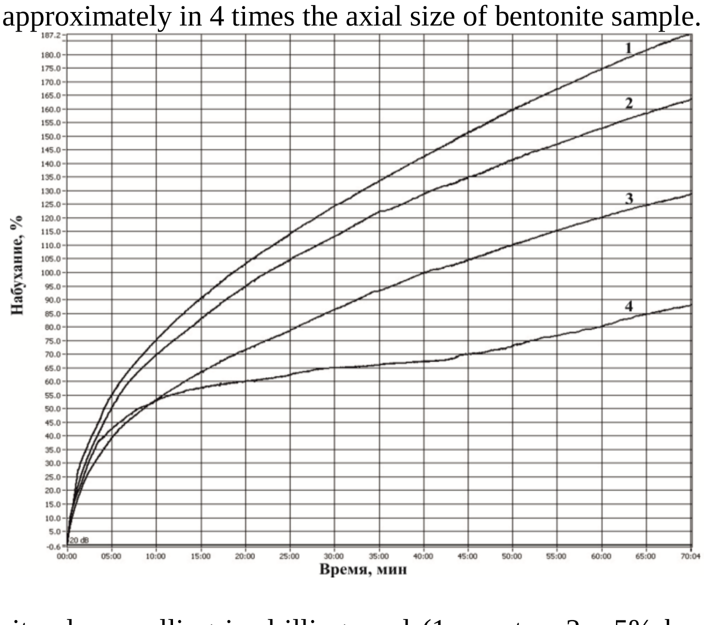

Figure 1. Bentonite clay swelling in drilling mud (1 - water: 2 - 5% bentonite + 0.25% Bur-S (modified starch); 3 - 5% of bentonite + 0.25% starch; 4 - 5% bentonite + 0.25% starch + glyoxal 1%)

Clay mud containing Bur-S and starch demonstrate shale stabilizing ability, although it inferiors to the drilling mud modified by glyoxal. The glyoxal add into drilling mud containing starch, results in significant inhibition of the swelling process of compacted bentonite clay samples. This effect starts to emerge only after 9 hours of drilling mud affecting on clay sample. Apparently, the highest swelling property of mud containing glyoxal, before that period, is determined by lower viscosity, which in its turn resulted in high diffusion of water into the bentonite. Reduction of samples linear swelling placed in starch drilling mud modified by glyoxal reaches 40% as compared to non-glyoxal mud.

Study of antibacterial properties.

Addition of bactericidal reagents allows reducing the number of microorganisms and extends the drilling mud life. In course of research the attempt to increase polysaccharides enzyme resistance was made. In this case, drilling mud was glyoxal free. Glyoxal was used as a modifier of biocidal properties to starch reagent.

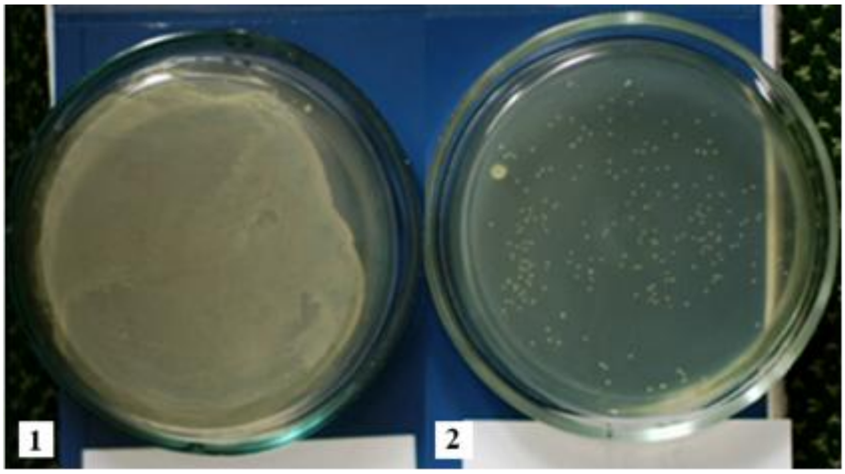

Figure 2. Visual determination of microorganisms colonies.

Table 3. Number of colony-forming units of starch drilling mud samples.

Composition	1st day	2nd day
Natural starch	$1,2 \cdot 10^{8}$ CFU/ml	$8,3 \cdot 10^{10}$ CFU/ml
Starch with bactericide additive MI CIDE	$7,8 \cdot 10^{5}$ CFU/ml	–
Glyoxal-modified starch	$3,6 \cdot 10^{5}$ CFU/ml	$2,3 \cdot 10^{6}$ CFU/ml

As criteria to measure the dynamics of structural and rheological characteristics changing, dynamic shear stress and static gel stress was selected. From the results shown in table 4, it can be seen that modified starch solution saves primary flow properties for a long period of time. While the source starch reactant, under the influence of bacteria, completely degraded after 7 days. Thus, the use of modified starch allows refusing from bactericide additives in drilling mud, this in its turn will reduce the total costs.

Table 4. Rheological stability of starch reagent (1 - natural starch reagent, 2 – glyoxal-modified starch).

Flow properties	1st day		3rd day		7th day	
	1	2	1	2	1	2
Plastic Viscosity, cPs.	40,0	45,0	29,6	41,7	6,09	39,9
DSS, pound/100ft^2	19,7	20,2	11,93	21,2	0	20,5
SGS pound/100ft^2	4/5	7/8	2/2	7/8	0/0	6/7

Research of bactericide influence on flow properties of xanthan gum based drilling mud.
For qualitative processing of biopolymer 0.1% of potassium hydroxide was added by stirring in a triaxial mixer till homogeneous substance for alkaline condition, while xanthan gum DUO-VIS was added smoothly and strictly on time.

Comparative analysis of dynamic shear stress of xanthan gum solution, with and without glyoxal bactericides additives (figure 3) and MI CIDE (figure 4), showed that glyoxal as well as starch, demonstrate good stabilizing properties. Stability of polymeric solutions increases with growth of bactericide concentration. However, xanthan gum DUO-VIS has sufficient resistance to bacteria (gum solution is resistant to 15 days), so it is possible to assume, without bactericides addition, that present reagent has been already modified by the producer. Static gel stress of researched solutions varies slightly within a month.

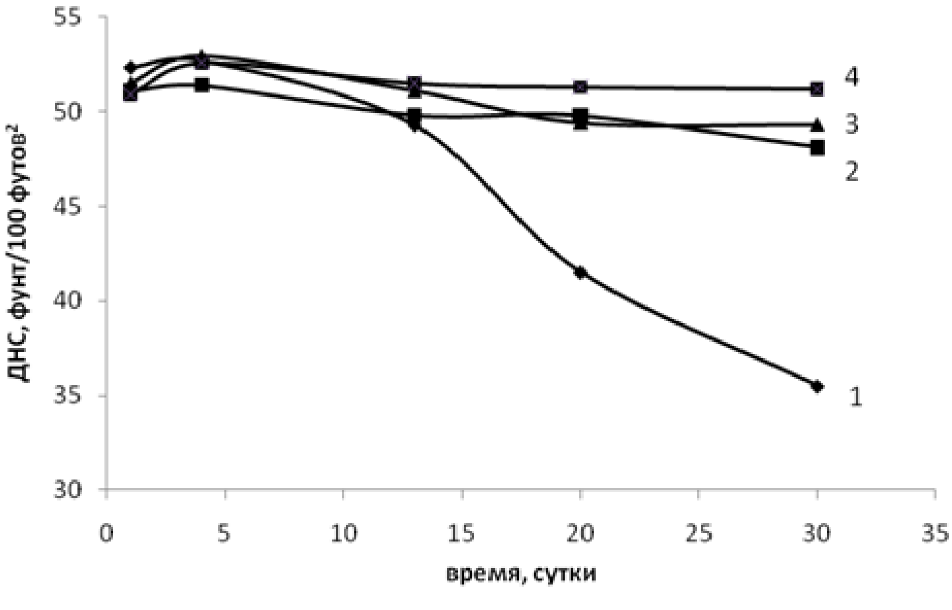

Figure 3. Time variation of the dynamic shear stress limit of 1% water xanthan solution DUO-VIS, processed by glyoxal bactericide (1 - xanthan solution without bactericide, 2 - 0.25% glyoxal, 3 - 0.5% glyoxal, 4 - 1 0% glyoxal).

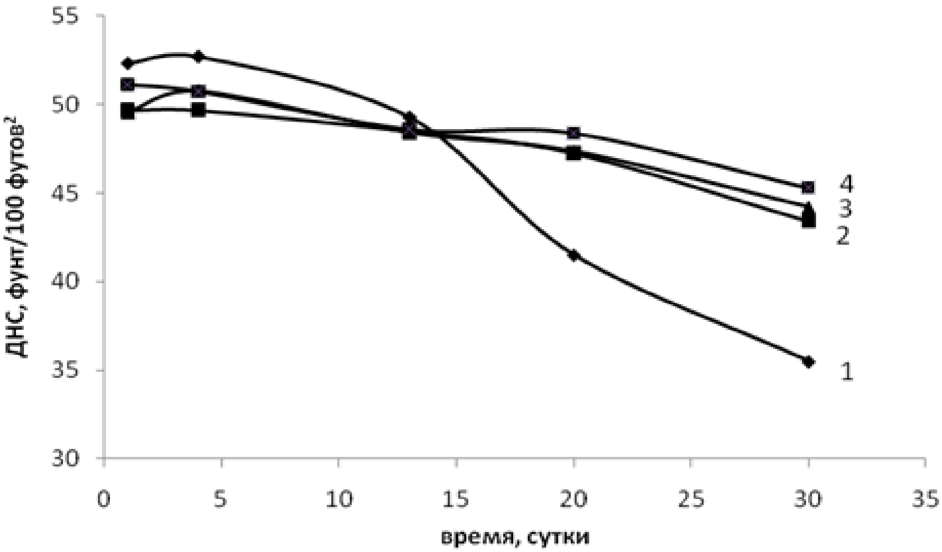

Figure 4. Time variation of the dynamic shear stress limit of 1% aqueous xanthan DUO-VIS, processed by bactericide MI CIDE (1 - xanthan solution without bactericide, 2 - 0,25% MI CIDE, 3 - 0,5% MI CIDE, 4 - 1,0% MI CIDE).

An important aspect of polysaccharides polymeric reagents application is temperature resistance. Study of xanthan reagent solution thermal stability, before and after bactericide addition, was carried out by aging test and cylinder stove, simulating the circulation of drilling mud in the borehole during the process of drilling. Temperature was maintained at 125 ° C and pressure at 2 atm. during 24 hours, after which flow properties of polymer solutions were analyzed. Studies have shown that initial solution, not containing the studied bactericides, retains rheological characteristics to a greater degree than the solution with the addition of glyoxal and MI CIDE, therefore it can be concluded that the addition of bactericide solution of xanthan gum results in the decrease of solution thermal stability.

3. Conclusion

1. Liquefying effect of glyoxal on colloidal clay solutions was determined.
2. In the presence of starch, along with clay mud liquefying, glyoxal textural properties are observed.
3. Glyoxal adding into the drilling mud results in a significant inhibition of shale swelling.
4. Glyoxal modified starch demonstrates biocidal properties and saves the original rheological parameters for a long period of time.
5. Glyoxal at equal concentrations shows better bactericidal properties for polysaccharides under study as compared to MI CIDE bactericide.
6. Processing of xanthan gum with bactericides results in a reduction of polymer solution thermal stability.

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