



## Article Enzymatic and Oxidizing Agents for the Decomposition of Polymers Used in the Composition of Drilling Muds

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Abstract: The article presents the results of research on the influence of enzymatic and oxidizing agents on polymers used in drilling mud technology. The research used calcium hypochlorite, urea peroxide, sodium persulfate, amylase and cellulase. This allowed us to determine the optimal concentrations of these agents in order to reduce the rheological parameters of drilling muds. The ability of enzymes and oxidants to decompose colloids used in the composition of drilling muds was determined on the basis of measurements of their rheological parameters and the influence of oxidants and enzymes on the properties of filter cakes. The final effect of the presented research was the development of a drilling mud treatment method before the cementing procedure and the development of washer fluids containing enzymatic or oxidizing agents to be used to prepare the borehole for the cementing procedure. The drilling muds selected for the research contained starch and cellulose polymer colloids, which allowed for the selection of appropriate agents depending on the type of polymer set used in the drilling mud. Positive results were obtained regarding the possibility of thinning the drilling mud immediately before cementing, as well as the possibility of using oxidants and enzymes in the composition of washer fluids.

Keywords: drilling mud; oxidants; enzymes; filter cake

#### 1. Introduction

In order to improve the quality of cementing of casing, the drilling mud is treated to lower its rheological parameters. Obtaining low rheological parameters of the drilling mud facilitates displacement of the drilling mud solidified at the wall of the borehole and partial leaching of the clay cake that hinders the contact of the cement grout with the rock. The treatment of drilling muds with thinning agents changes the rheological parameters without significantly changing the properties of the drilling mud [1,2].

The filter cake on the borehole wall is formed by filtering the water phase from the drilling mud. It is a mixture of a polymer solution, weighting agent and finely drilled solid phase. The filter cake produced during drilling increases the stability of the borehole walls and reduces the permeability of the porous layers, therefore there are no major losses of the water phase from the drilling mud, which can significantly reduce the strength of the rocks. When drilling cracked rocks, the filter cake is also deposited in the crevices, binding individual rock fragments, and increasing their strength. In addition, the filter cake contributes to an even distribution of hydrostatic pressure on the borehole wall, which prevents its damage. In weakly compact rocks, the filter cake protects the borehole wall against the erosive impact of the drilling mud stream and ensures a good technological process until the casing is inserted into the borehole [3–6].

The use of agents which decompose colloids, which are components of the drilling mud, thins the drilling mud and removes clay deposits stuck by these colloids. Polymers can be decomposed in several ways, by biological, mechanical, chemical or radiation decomposition [7,8].



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Water-soluble polysaccharides used as components of drilling muds have unique, stable rheological properties in drilling operations, but their structure and properties also have a decisive influence on the formation of a polymer film on the surface of the borehole walls, which in combination with the solid phase becomes difficult to remove from the walls of the borehole. Polysaccharides contain many glycosidic bonds (acetals). Glycoside bonds are sensitive to hydrolysis which leads to degradation of the polymer. The chemical decomposition process of the polymer must be properly designed for specific borehole conditions: temperature, pH, salinity, and exposure time. On the basis of laboratory tests, the most optimal and balanced conditions for polymer decomposition should be determined. Chemical degradation of polymers can be carried out by the action of oxidants and enzymes [3,7,9,10].

Oxidizing agents decompose the polymers contained in the filter cake. Oxidation processes take place as a result of the exchange of electrons between the oxidizing substance and the reducing substance, as a result of which the atoms of the elements taking part in the reaction change their oxidation state. According to the electron interpretation of oxidation-reduction processes, oxidants are atoms, ions, or molecules capable of accepting electrons, i.e., receiving them from other atoms or groups of atoms, thus causing their oxidation. Thus, oxidants are themselves reduced by oxidizing other substances. The most popular oxidants are the most electronegative elements, i.e., fluorine  $F_2$ , chlorine  $Cl_2$ , bromine  $Br_2$  and oxygen  $O_2$ . Among chemical compounds, oxidants are those with certain elements in the highest oxidation states, e.g., potassium permanganate KMnO<sub>4</sub>, potassium dichromate  $K_2Cr_2O_7$ , hydrogen peroxide  $H_2O_2$ , potassium nitrate KNO<sub>3</sub>, nitric acid HNO<sub>3</sub> and others [11–14].

The principle action of oxidants is based on the gradual interaction of compounds with high electronegativity on the main polymer chains, breaking them into smaller fragments and, consequently, a decrease in the molecular weight of the polymer. The advantage of oxidants is their wide range of action at a pH of 3 to 14. Oxidizers react quickly with the polymer at high temperatures. Oxidizers cannot be used in an acidic environment as it is possible to oxidize H<sub>2</sub>S to elemental sulfur and clog the pores of reservoir rock [12].

Enzymes are another type of agent used to decompose the filter cake. Enzymes are biological catalysts, classified as proteins, which accelerate specific chemical reactions as a result of lowering their activation energy. Due to their protein nature, the activity of enzymes depends on the physical and chemical parameters of the environment, i.e., temperature, pH. The rate of enzymatic reactions rises with increasing temperature. After exceeding the optimal temperature, the thermal denaturation of enzymes progresses, and their activity drops sharply. Most enzymes also have an optimal operating pH. The pH optimum, next to the temperature optimum, is the second most important environmental parameter characterizing the activity of enzymes. Enzymes are most active in their optimal pH range and the activity declines with increasing or decreasing pH beyond this range. In most cases, the effects of enzymes heavily depend on their substrates [15–20].

In the case of using an invert drilling mud [21], a different approach should be applied to the problem of filter cake removal prior to cementing. The main task of the washer fluid is to remove the hydrophobic sediment and make the borehole wall hydrophilic, which requires the use of specially selected surfactants, which can possibly be combined with enzymes.

Enzymes such as cellulase can also be used to modify the properties of cellulose without decomposing it, for example to increase the amount of the crystalline phase in it [22], which may find application in the design of nanocomposites containing cellulose fillers.

The article presents the results of research carried out at the Oil and Gas Institute—National Research Institute, which aim to improve the quality of casing cementing. Due to insufficient quality of cementation manifested by the occurrence of gas exhalation, research is being carried out on the development of a methodology for the use of oxidants and enzymatic agents that break down polymers used in the composition of drilling muds. These results can be used in the preparation of the borehole prior to cementing to remove filter cake which contribute to reducing the bond between the cement stone and the borehole wall. Most of the research carried out in various research centers concerns the use of enzymes or oxidants in treatment fluids, the purpose of which is to remove drilling mud residues from rock pores in order to reduce damage to rock permeability. The authors [8–11,15,20] use enzymatic agents in their research to remove mud sediments from the pore space of rocks. For the same purpose, ultrasound was used in [13]. Part of the work carried out [15,16,19] concerns the evaluation of enzyme activity under various conditions of temperature, pH, and salt content (chlorides, bromides, formates). The activity of the enzymes was assessed on the basis of the degree of their degradation. The paper [18] presents the results of research on the efficiency of filter cake removal with fluids containing enzymatic, oxidizing, and chelating agents depending on the used weighting agent.

#### 2. Materials and Methods

#### 2.1. Raw Materials

In the laboratory tests, natural and semi-synthetic polymers used in the drilling mud technology as well as enzymes and chemical compounds with an oxidizing effect were used. The chemicals and drilling mud materials used in the tests were:

- Biopolymer (xanthan), obtained in the process of fermentation of polysaccharides with microorganisms (Xanthomonas campestris bacteria). It is used to increase the viscosity of drilling muds of various degrees of salinity and to hold the weighting agents in suspension.
- Gelatinized starch, a natural starch that has been modified by thermal gelatinization to render it water-soluble and to form a colloidal solution.
- Carboxymethylcellulose, a semi-synthetic anionic polymer adsorbing on clay minerals. It is one of the most active agents in reducing filtration. It is formed by treating cellulose activated with sodium hydroxide with monochloroacetic acid.
- The partially hydrolyzed polyacrylamide (PHPA) forms a thin layer on the borehole wall and cuttings, which acts as a barrier to the migration of filtrate from the drilling mud to the rock.
- Carbonate blocker (CaCO<sub>3</sub>), a weighting agent obtained as a result of the mechanical processing of marble. Due to its solubility in acids, it is used primarily for weighting drilling muds and workover fluids used in opening the deposit and in workover works in boreholes [23,24].
- Chemical compounds with an oxidizing effect: calcium hypochlorite, urea peroxide, sodium persulfate.
- Enzymes: amylase, cellulase.

#### 2.2. Research Methodology

The research was carried out on muds with different density, salinity, and a set of colloids and polymers used for their preparation. To determine the efficiency of oxidants and enzymes in the drilling mud environment, three fluid compositions were selected for drilling holes in the Carpathian Foredeep and the Polish Lowlands. The efficiency of oxidizing agents and enzymes was assessed on the basis of changes in rheological parameters, filtrate volume, and changes in the pH value.

The drilling muds prepared according to the compositions used by the drilling mud services were used for the tests. The drilling muds marked as A and B correspond to the compositions of the drilling muds used in the Carpathian Foredeep. These drilling muds differ in the type of polymers used for their preparation. Drilling mud A contains a starch agent and a biopolymer, drilling mud B contains a cellulose agent, a biopolymer and a PHPA encapsulating polymer. The drilling muds marked with symbols A and B also differed in densities, which were, respectively, 1130 kg/m<sup>3</sup> and 1330 kg/m<sup>3</sup>. The drilling mud marked as C corresponded to the compositions of drilling muds in the area of the Polish Lowlands, therefore it contained NaCl in its composition in the amount corresponding to the concentration of the saturated solution. A biopolymer, a cellulose

agent and a PHPA polymer were used to prepare drilling mud C. Drilling mud C has a density of 1535 kg/m<sup>3</sup>. All drilling muds used in the test (A, B, C) additionally comprised of milled Miocene shale imitating cuttings, selected muds contained barite as a material for adjusting the density, and chemical contamination in the form of calcium and magnesium chlorides was additionally introduced into drilling mud C.

The efficiency of polymer decomposition by particular agents (oxidants and enzymes) in the drilling mud environment was assessed on the basis of changes in the rheological parameters of the drilling muds after the introduction of a given oxidant or enzyme. The tests were carried out in various temperature conditions enabling the assessment of the efficiency of the tested agents in borehole conditions. The efficiency of the enzymes was tested at the temperatures of 20 °C, 40 °C, 60 °C and 80 °C due to the decrease in their activity at temperatures above 65 °C. The optimal temperature for the application of the tested enzymes is determined in the range of 50–65 °C.

The efficiency of the filter cake removal was determined by the percentage loss of the filter cake due to the treatment fluid used, which differed in the type of the measures used. Filter cakes were formed on ceramic filter discs (OFITE No. 170–530) with a defined pore size of 50  $\mu$ m and a fixed permeability of 15 D using a dynamic High Temperature High Pressure (HTHP) filter press. The weight method was used to assess the efficiency of cake removal.

# 2.2.1. Weight Method of the Efficiency of Removing Filter Cake from Ceramic Discs Cake Formation

For 15 min the ceramic disc was soaked in a salt solution corresponding to the salinity of the tested drilling mud. The soaked ceramic disc was weighed, and its mass was determined as  $W_1$ . Then, the drilling mud filtration was measured on a dynamic HPHT filter press on a previously soaked ceramic disc, at a pressure of 0.7 MPa of N<sub>2</sub> gas, a set temperature, and the speed of the stirrer in the filtration chamber at 200 rpm. After reaching the set temperature, the drilling mud filtration and formation of the cake were measured for a period of 1 h.

#### Removal of Cake with Fluids of Various Compositions

After cooling, the measuring chamber was disassembled and the ceramic disk with the cake was carefully removed and washed with water. Then the disc with the cake was weighed and the mass was recorded as  $W_2$ . The previously prepared treatment fluid was slowly poured into the filtration chamber and the ceramic disc with the cake was placed back in the filtration chamber. At the pressure of 0.7 MPa, the set temperature was achieved and the stirrer's rotation in the filtration chamber was set to 500 rpm. Then, the filtration of the treatment fluid was measured for a period of 30 min. After cooling, the ceramic disc was removed and, after washing with water, weighed and the mass was determined as  $W_3$ . The efficiency of filter cake removal was calculated from the following formula:

$$E_{U} = \frac{W_2 - W_3}{W_2 - W_1} \cdot 100 \ (\%) \tag{1}$$

where:

 $E_U$ —efficiency of filter cake removal

 $W_1$ —the weight of a ceramic disc soaked with a salt solution corresponding to the salinity of the tested drilling mud (g)

 $W_2$ —the weight of the ceramic disc with the generated filter cake (g)

 $W_3$ —the weight of the ceramic disk after the effect of the treatment fluid (g).

#### 3. Results and Discussion

#### 3.1. Influence of Oxidants and Enzymes on the Properties of Potassium-Polymer Drilling Mud A

A biopolymer and gelatinized starch were used to prepare potassium-polymer drilling mud A. The drilling mud was salted with 5% KCl and a 7% carbonate blocker was added

to it. Then the drilling mud was weighted with barite to a density of  $1100 \text{ kg/m}^3$  and contaminated with ground Miocene clay simulating cuttings. The drilling mud prepared in this way had a density of  $1130 \text{ g/cm}^3$  and a plastic viscosity of 18 mPa·s, an apparent viscosity of 28.5 mPa·s and a yield point of 10 Pa.

The research on the influence of oxidants and the enzyme on the properties of drilling mud A are presented in Tables 1 and 2 and in Figures 1–4. Various amounts of oxidants and enzymes were added to the drilling mud in order to select the optimal dose at which the greatest thinning effect of the drilling mud can be achieved.

Table 1. The properties of potassium-polymer drilling mud A with the addition of oxidizing agents and amylase.

No.	Drilling Mud Composition (%)			Readi	ng on tl (F	he Visco Pa)	meter		Viscosity η <sub>pl</sub> η <sub>s</sub>		Yield Point <sub>Ty</sub>	Filtration	pН
			600	300	200	100	6	3	(mPa·s)		(Pa)	(cm <sup>3</sup> )	-
1	XCD Gelatinized starch KCl Carbonate blocker Barite up to 1.1 g/cm3 Cuttings (miocene)	0.2 3.0 3.0 7.0 5.0	29.1	19.9	15.8	10.7	2.6	1.5	18	28.5	10.0	2.4	9.0
2	Drilling mud No. 1 + calcium hypochlorite	0.3 0.5 1.0	27.1 27.1 19.4	19.4 19.4 13.3	16.3 16.3 11.7	11.7 11.7 8.7	3.6 3.6 2.0	3.1 3.1 1.5	15 15 12	26.5 26.5 19	11.0 11.0 6.7	2.2 2.4 3.2	8.5 8.3 8.0
3	Drilling mud No. 1 + sodium persulfate	0.3 0.5 1.0	23.5 21.4 23.5	16.9 15.3 16.9	13.8 12.3 13.8	10.2 8.7 9.7	3.1 3.1 3.1	2.6 2.0 2.6	13 12 13	23 21 23	9.6 8.6 9.6	2.4 2.8 3.0	8.8 8.5 8.2
4	Drilling mud No. 1 + urea peroxide	0.3 0.5 1.0	28.1 21.4 19.9	20.4 14.3 13.8	17.4 11.7 11.2	13.3 8.2 8.2	4.6 2.0 2.0	4.1 1.5 1.5	15 14 12	27.5 21 19.5	12.0 6.7 7.2	2.2 2.4 2.8	8.5 8.3 8.1
5	Drilling mud No. 1 + amylase	0.3	11.2	7.1	6.1	4.6	1.5	1.0	8	11	2.9	34	8.7

**Table 2.** The rheological parameters of potassium-polymer drilling mud A with thinning additives at various temperature values.

Type of Added	Pla	stic Visco	osity (mP	a∙s)	App	arent Vis	cosity (m	Pa∙s)	Yield Point (Pa)			
Agent	20 °C	40 °C	60 °C	80 °C	20 °C	40 °C	60 °C	80 °C	20 °C	40 °C	60 °C	80 °C
+ 1.0% calcium hypochlorite	12	8	7	5	19	14	11.5	8.5	6.7	5.7	4.3	3.4
+1.0% urea peroxide	12	9	9	5	19.5	15	14.5	10.5	7.2	5.7	5.3	5.3
+ 1.0% sodium persulfate	13	13	12	13	23	19.5	18.5	17	9.6	6.2	6.2	3.8
+0.3% amylase	8	6	5	4	11	9	7.5	6.5	2.9	2.9	2.4	2.4



**Figure 1.** Flow curves of drilling mud A with 1.0% calcium hypochlorite: (**a**) at a temperature of 20 °C, (**b**) at a temperature of 40 °C, (**c**) at a temperature of 60 °C, (**d**) at a temperature of 80 °C.



**Figure 2.** Flow curves of drilling mud A with the addition of 1.0% urea peroxide: (a) at 20 °C, (b) at 40 °C, (c) at 60 °C, (d) at 80 °C.



**Figure 3.** Flow curves of drilling mud A with 1.0% sodium persulfate: (**a**) at 20 °C, (**b**) at 40 °C, (**c**) at 60 °C, (**d**) at 80 °C.



**Figure 4.** Flow curves of drilling mud A with the addition of 0.3% amylase: (**a**) at 20  $^{\circ}$ C, (**b**) at 40  $^{\circ}$ C, (**c**) at 60  $^{\circ}$ C, (**d**) at 80  $^{\circ}$ C.

Potassium-polymer drilling mud A at 20 °C was resistant to the action of oxidants, the addition of 10 g/dm<sup>3</sup> of calcium hypochlorite to the drilling mud caused its plastic viscosity to decrease from 18 to 12 mPa·s, the yield point from 10 to 6.7 Pa, and increased its filtration from 2.4 to 3.2 cm<sup>3</sup> (Table 1). The rate of the oxidation reaction at 20 °C did

not change significantly over time (Figure 1), the greatest decrease in the viscosity of the drilling mud took place after about 1 h, and the further influence of calcium hypochlorite did not significantly affect a further decrease in rheological parameters. Increasing the temperature to 40 °C accelerated the process of decomposition of polymers contained in the drilling mud, the oxidation process was much faster, and the maximum thinning of the drilling mud took place after about 30 min of the effects of calcium hypochlorite. At the temperature of 80 °C, the process of decomposition of the polymers contained in the drilling mud was turbulent, after about 5 min the drilling mud thinned as a result of the oxidant and the further extension of the time of the oxidant did not significantly change the rheological parameters.

The effect of a 1% addition of urea peroxide on the properties of drilling mud A was marked by a reduction in the plastic viscosity down to 12 mPa·s and the yield point down to 7.2 Pa. The time required for the process of thinning the drilling mud at room temperature is about 24 h, and at the temperature of 40 °C the decomposition of the polymers contained in the drilling mud took place after about 30 min. However, at the temperature of 80 °C, the same thinning effect of the drilling mud was achieved after about 5 min.

Sodium persulfate showed a much weaker effect than urea peroxide and calcium hypochlorite. For the effective oxidation of the drilling mud with sodium persulfate, it was necessary to increase the temperature to about 60 °C. The drilling mud decomposition process at 60 °C was much faster and more effective. After the effect of 15 min of sodium persulfate, the plastic viscosity of the drilling mud decreased to 12 mPa·s, and the yield point to 6.7 Pa.

The action of amylase addition on the properties of the potassium-polymer drilling mud A is shown in Table 1. The decomposition of the polymers contained in the drilling mud A by means of amylase at a temperature of 20 °C was very fast, after about 5 min there was almost complete decomposition of the starch component of the drilling mud, which resulted in the reduction of the rheological parameters of the drilling mud. Extending the time of the enzyme's action and increasing the temperature did not significantly increase the decomposition effect of the drilling mud.

#### 3.2. Influence of Oxidants and Enzymes on the Properties of Potassium-Polymer Drilling Mud B

Drilling mud B XCD on the biopolymer matrix and the cellulose polymer colloid weighted with barite to a density of  $1330 \text{ kg/m}^3$  has a plastic viscosity of  $41 \text{ mPa} \cdot \text{s}$ , a yield point of 18.2 Pa and a filtration of  $4.4 \text{ cm}^3$ . The influence of oxidants on the rheological parameters of potassium-polymer drilling mud B at 20 °C is shown in Tables 3 and 4.

The highest degree of thinning of the drilling mud with calcium hypochlorite was obtained by using its addition in the amount of  $10 \text{ g/dm}^3$ . With such a concentration of calcium hypochlorite in the drilling mud, the plastic viscosity decreased from 41 to 20 mPa·s, and the yield point from 18.2 to 8.1 Pa. The drilling mud filtration increased from 4.4 to 6.2 cm<sup>3</sup>, and the pH value decreased to a value of 7.5. Under the conditions of elevated temperature, i.e., 40 and 60 °C, the oxidation process took place to a greater extent. The best results of the drilling mud thinning were obtained by carrying out the oxidation process at 80 °C for 15 min (Figure 5). The plastic viscosity of the drilling mud decreased to 6 mPa·s and the yield point up to 3.3 Pa (Table 4).

The most effective oxidizing action in relation to drilling mud B at the temperature of 20 °C was shown by urea peroxide (Figure 6), which, with the addition of 10 g/dm<sup>3</sup> after an exposure time of 24 h caused the reduction of its plastic viscosity to 13 mPa·s and the yield point to 5.7 Pa. Increasing the temperature improved the efficiency of the agent in relation to oxidation carried out at room temperature.

No.	Drilling Mud Composition (%)		I	Reading	; on the	Viscom	eter (Pa	a)	Viscosity Yield η <sub>pl</sub> η <sub>s</sub>		Yield Point <sub>Ty</sub>	Filtration	pН
			600	300	200	100	6	3	(mPa·s)		(Pa)	(cm <sup>3</sup> )	-
	XCD	0.2											
	CMC	2.0											
	KCl	5.0	61.3	40.3		20.4	4.1	3.1					
1	PHPA	0.2			34.2				41	60	18.2	4.4	9.6
	Carbonate blocker	7.0											
	Barite up to												
	$1.3 \mathrm{g/cm^3}$												
	Cuttings (miocene)	5.0											
2	Drilling mud No. 1 + calcium hypochlorite	0.3	46.5	30.1	23.5	15.3	3.6	2.6	32	45.5	12.9	4.4	8.0
		0.5	38.3	25.0	19.4	12.3	2.6	2.0	26	37.5	11.0	4.8	7.7
		1.0	29.1	18.9	14.8	9.7	2.6	2.0	20	28.5	8.1	6.2	7.5
	Drilling mud No. 1	0.3	43.4	28.6	22.5	14.8	3.6	2.6	29	42.5	12.9	4.6	8.6
3	+ sodium	1.0	39.3	25.5	19.9	13.3	3.6	2.6	27	38.5	11.0	4.8	8.5
	persulfate	1.5	44.4	28.6	22.5	14.8	3.6	2.6	31	43.5	12.0	5.0	7.8
		0.8	22.0	14.3	10.7	7.7	2.0	1.5	15	21.5	6.2	4.8	7.5
4	Drilling mud No. 1 + urea peroxide	1.0	19.4	12.8	9.7	6.6	1.5	1.0	13	19	5.7	5.2	8.2
	, and perconduce	1.5	14.3	9.2	7.7	5.1	1.5	1.0	10	14	3.8	5.8	8.1
5	Drilling mud No. 1 + cellulase + citric acid	0.3 0.1	19.4	12.8	10.2	6.6	1.7	1.4	13	19	5.7	8.4	8.7

Table 3. The properties of potassium-polymer drilling mud B with the addition of oxidizing agents and cellulase.

**Table 4.** The rheological parameters of potassium-polymer drilling mud B with thinning additives at various temperature values.

Type of Added	Pla	stic Visco	osity (mP	a∙s)	App	arent Vis	cosity (m	Pa∙s)	Yield Point (Pa)			
Agent	20 °C	40 °C	60 °C	80 °C	20 °C	40 °C	60 °C	80 °C	20 °C	40 °C	60 °C	80 °C
+ 1.0% calcium hypochlorite	20	14	11	6	28.5	21	13.5	9.5	8.1	6.7	2.4	3.3
+1.0% urea peroxide	13	9	8	6	19	13.5	12.5	10.5	5.7	4.3	4.3	4.3
+ 1.0% sodium persulfate	27	13	11	8	38.5	18	14.5	11.5	11.0	4.8	3.3	3.3
+0.3% cellulase	13	8	7	8	19	13.5	12	12	5.7	5.3	4.8	3.8



**Figure 5.** Flow curves of drilling mud B with 1.0% calcium hypochlorite: (**a**) at a temperature of 20 °C, (**b**) at a temperature of 40 °C, (**c**) at a temperature of 60 °C, (**d**) at a temperature of 80 °C.



**Figure 6.** Flow curves of drilling mud B with the addition of 1.0% urea peroxide: (**a**) at 20 °C, (**b**) at 40 °C, (**c**) at 60 °C, (**d**) at 80 °C.

The process of oxidating the drilling mud at 20  $^{\circ}$ C with sodium persulfate does not significantly change its rheological parameters (Figure 7). The introduction of 10 g/dm<sup>3</sup>

of sodium persulfate at 20  $^{\circ}$ C reduces the plastic viscosity of the drilling mud from 41 to 27 mPa·s and the yield point from 18.2 to 11 Pa (Table 3).

The action of cellulase on the drilling mud only partially thins it by decomposing cellulose compounds (Figure 8). The addition of 0.3 vol.% of the enzyme reduces the plastic viscosity from 41 to 13 mPa s and the yield point from 18.2 to 5.7 Pa (Table 3).



Figure 7. Flow curves of drilling mud B with 1.0% sodium persulfate: (a) at 20 °C, (b) at 40 °C, (c) at 60 °C, (d) at 80 °C.



**Figure 8.** Flow curves of drilling mud B with the addition of 0.3% cellulase: (**a**) at 20  $^{\circ}$ C, (**b**) at 40  $^{\circ}$ C, (**c**) at 60  $^{\circ}$ C, (**d**) at 80  $^{\circ}$ C.

### 3.3. The Influence of Oxidants and Enzymes on the Properties of Salt-Barite Drilling Mud C

Salt-barite drilling mud C based on the XCD biopolymer and cellulose colloid was salted with 33% of NaCl, weighted with barite to a weight of 1500 kg/m<sup>3</sup> and contaminated with calcium and magnesium ions. The prepared drilling mud has a plastic viscosity of 57 mPa·s and a yield point of 23 Pa. The influence of polymer degrading agents on the rheological parameters of the drilling mud at 20 °C is shown in Tables 5 and 6.

**Table 5.** The properties of salt-barite drilling mud C, density 1530 kg/m<sup>3</sup>, with the addition of oxidizing agents and cellulase enzyme.

No	Drilling Mud			Readi	ng on tl	ne Visco	meter		Visc η <sub>pl</sub>	osity η <sub>s</sub>	Yield Point τ <sub>y</sub>	Filtration	рН
110.	Composition (%	osition (%)		300	200	100	6	3	(mPa·s)		(Pa)	(cm <sup>3</sup> )	<b>r</b>
1	NaCl XCD CMC PHPA Carbonate blocker Barite up to 15 g/cm <sup>3</sup>	33.0 0.2 2.0 0.2 7.0	82.7	53.6	41.4	26.6	5.1	3.6	57	81	23.0	1.6	9.2
	Cuttings (miocene) CaCl2 MgCl2	5.0 1.0 0.5											
2	Drilling mud No. 1	0.3	44.4	27.6	20.9	12.8	2.6	2.0	33	43.5	10.1	1.6	9.0
	+ calcium hypochlorite	0.5	39.8	25.0	18.9	11.7	2.6	1.5	29	39	9.6	1.6	7.1
		1.0	34.2	20.9	15.8	9.7	2.0	1.5	26	33.5	7.2	2.4	6.9
	Drilling mud No. 1	0.3	46.5	29.6	22.5	14.3	3.1	2.0	33	45.5	12.0	1.8	7.6
3	+ sodium	0.5	45.5	28.6	22.0	13.8	3.1	2.0	33	43.5	11.0	2.0	6.5
	persulfate	1.0	44.9	27.6	21.4	12.8	3.1	2.0	34	44	9.6	2.2	6.3
	Drilling mud No. 1	0.5	23.0	14.8	11.2	8.7	1.5	1.0	16	22.5	6.2	32	7.2
4	+ urea	0.8	18.4	11.7	9.2	5.1	1.0	1.0	13	17	4.8	58	6.9
	peroxide	1.0	14.8	9.7	6.6	3.1	1.0	0.5	10	14.5	4.3	66	6.3
5	Drilling mud No. 1 + cellulase	0.3	37.3	23.5	17.9	11.2	2.3	1.8	27	36.5	9.1	4.2	9.1
6	Drilling mud No. 1 + cellulase + citric acid	0.3 0.1	32.2	20.9	15.8	9.7	2.0	1.5	22	31.5	9.1	6.4	8.3

Table 6. The rheological parameters of salt-barite drilling mud C with thinning additives at various temperature values.

Type of Added	Pla	stic Visco	osity (mP	a∙s)	App	arent Vis	cosity (m	Pa·s)	Yield Point (Pa)			
Agent	20 °C	40 °C	60 °C	80 °C	20 °C	40 °C	60 °C	80 °C	20 °C	40 °C	60 °C	80 °C
+ 1.0% calcium hypochlorite	26	15	13	14	33.5	19.5	17	18	7.2	4.3	3.8	3.8
+1.0% urea peroxide	10	9	8	5	14.5	11.5	9.5	6	4.3	2.4	1.4	1.0
+ 1.0% sodium persulfate	34	21	15	13	44	27.5	21	18	9.6	6.2	5.7	4.8
+1.0% cellulase	22	22	14	13	31.5	31	20	17.5	9.1	8.6	5.7	4.3

After adding calcium hypochlorite in an amount of 1.0 vol.% there is a significant decrease in the rheological parameters of the drilling mud. The plastic viscosity is reduced to 26 mPa·s and the yield point is reduced to 7.2 Pa. The filtration of the drilling mud increased to 2.4 cm<sup>3</sup> and the pH value decreased to 6.9. The oxidation reaction at an elevated temperature (Figure 9) is accompanied by a greater reduction in the drilling mud viscosity and the decomposition of polymers contained in the drilling mud occurs much faster than at 20 °C. Increasing the temperature of the reaction environment to 40 °C accelerates the process of decomposition of the drilling mud. At 60 °C, the oxidation process is similar, the maximum thinning of the drilling mud takes place after 15 min of the effect of calcium hypochlorite (Figure 9).



**Figure 9.** Flow curves of drilling mud C with 1.0% calcium hypochlorite: (**a**) at a temperature of 20 °C, (**b**) at a temperature of 40 °C, (**c**) at a temperature of 60 °C, (**d**) at a temperature of 80 °C.

The effectiveness of sodium persulfate in a salt-barite drilling mud at 20 °C is much lower than that of calcium hypochlorite. The addition of sodium persulfate to the drilling mud C in the amount of 10 g/dm<sup>3</sup> reduces the plastic viscosity of the drilling mud from 57 to 34 mPa·s and the yield point from 23 to 9.6 Pa (Table 5). The course of the oxidation reaction does not change significantly over time (Figure 10), the greatest decrease in the viscosity of the drilling mud takes place after approx. 1 h, and the further effect of sodium persulfate does not significantly affect a further decrease in rheological parameters. The use of sodium persulfate in the degradation of the polymers contained in drilling mud salt-barite C necessitates a treatment at 60 or 80 °C, the oxidation of the drilling mud at a temperature of 20 °C is inefficient and very slow (Figure 10).

An effective means for the distribution of polymers in salt-barite drilling mud C was urea peroxide, which with the addition of  $10 \text{ g/dm}^3$  to the drilling mud after approx. 30 min (Figure 11) causes almost complete decomposition of polymers, which lowers its rheological parameters: plastic viscosity from 57 to 10 mPa·s, and yield point from 20 to 4.3 Pa. Carrying out the process of decomposition of the drilling mud at higher temperatures slightly increases the effectiveness of its operation (Figure 11). However, the use of urea in the environment of full salinity does not require raising the temperature and extending the time of its effect. The process can be carried out at a temperature of about

20 °C. The disadvantage of thinning the drilling mud with urea peroxide is that it causes a significant increase in filtration. After the action of the agent on the drilling mud, it is completely degraded, thus the filtration value increases from 1.6 to 66 cm<sup>3</sup> (Table 5).



**Figure 10.** Flow curves of drilling mud C with the addition of 1.0% sodium persulfate: (**a**) at 20 °C, (**b**) at 40 °C, (**c**) at 60 °C, (**d**) at 80 °C.



**Figure 11.** Flow curves of drilling mud C with 1.0% urea peroxide: (**a**) at 20 °C, (**b**) at 40 °C, (**c**) at 60 °C, (**d**) at 80 °C.

The use of the enzyme to decompose salt-barite drilling mud C allows for partial thinning of the drilling mud (Figure 12), the addition of 0.3% cellulase enzyme at 20 °C reduces the plastic viscosity of the drilling mud to 27 mPa·s and the yield point to 9.1 Pa (Table 5). When the pH of the drilling mud drops below 9, the efficiency of the enzyme activity increases. After its action, the plastic viscosity drops to 22 mPa·s, and the apparent viscosity to 31.5 mPa·s.



**Figure 12.** Flow curves of drilling mud C with the addition of 0.3% cellulase: (**a**) at 20 °C, (**b**) at 40 °C, (**c**) at 60 °C, (**d**) at 80 °C.

The cake produced from the potassium-polymer drilling mud taken from the K-1 borehole was characterized by a density of 2.21 g/cm<sup>3</sup> and a hydration level of 52.88% (Figure 13a). Attempts were made to remove the cakes produced from the K-1 drilling mud with the fluids shown in Table 7. On the basis of the obtained results (Figure 14), it was found that the most effective agents in removing the cakes generated from the K-1 drilling mud were oxidants (urea, calcium hypochlorite). Eddy eroding at 50 °C and a differential pressure of 0.7 MPa with the help of fluid No. 2 with the addition of urea peroxide, it allowed to remove 86% of the cake (Figure 13c), while the efficiency of cake removal under the same conditions with fluid No. 1 with the addition of calcium hypochlorite allowed for the removal of 90% of the filter cake (Figure 13b).

**Table 7.** Selected fluid compositions for eroding filter cakes produced from drilling mud taken from the K-1 borehole.

Fluid 1	Fluid 2	Fluid 3
Water KCl—5%	Water KCl—5%	Water KCl—5%
calcium hypochlorite—1%	urea peroxide—1%	cellulase—1%



(c)

Figure 13. Filter cake produced from the drilling mud taken from the K-1 borehole: (a) before eroding, (b) eroded with fluid No. 1, (c) eroded with fluid No. 2, (d) eroded with fluid No. 3.



Figure 14. The efficiency of the removal of filter cakes produced from the drilling mud taken from the K-1 borehole, depending on the fluids used for eroding.

High efficiency of cake removal was achieved with fluid No. 3 with the addition of the enzyme, with this type of fluid 97% of the cake was removed (Figure 13d).

#### 4. Conclusions

The research concerned the recognition of the possibility of using enzymatic agents and oxidants for the decomposition of polymers used in drilling mud compositions. The obtained results of laboratory tests indicate the possibility of selecting, depending on the borehole conditions, the appropriate type of agents (enzymes or oxidants) that cause the decomposition of agents that impart viscosity to drilling muds. The effectiveness of selected enzymes and oxidants has been confirmed in the conducted tests, both in polymer solutions and drilling muds prepared according to the compositions used by the drilling services. Studies have shown that at low temperatures it is more advantageous to use enzyme agents, while oxidizing agents should be used at elevated temperatures.

Cellulase and amylase enzyme agents used in the research can be used to decompose colloids used in the composition of drilling muds. In the case of using enzymes in drilling muds at a pH level above 9.0 and with significant salinity, it may be necessary to increase the concentration of the enzyme or adjust the pH with citric acid. The presence of NaCl salt in the drilling muds in a concentration corresponding to a saturated solution, or calcium and magnesium chloride in the concentrations usually found in drilling muds, does not cause a significant reduction in enzyme activity at pH levels below 9. Among the oxidants used in the research, the most effective polymer decomposition was recorded in the case of calcium hypochlorite, urea peroxide and sodium persulfate. The effectiveness of the oxidizing agents in drilling muds does not depend on the pH value, and they show unchanged activity over a wide pH range. The increase in temperature and extension of the exposure time increases the effectiveness of the oxidants. For the decomposition of polymers in the composition of drilling muds, oxidizing agents and enzymes should be selected, on the basis of laboratory tests, according to the type of colloids and other polymers used in the drilling muds, and the most optimal conditions for their decomposition should be determined. The most effective thinning agent for salt-barite drilling muds is urea peroxide, which, regardless of the sodium chloride concentration in the drilling mud, showed the highest oxidizing efficiency. The oxidation reaction carried out in an environment of full salinity does not require increasing the temperature and extending the exposure time of urea peroxide. Calcium hypochlorite shows less efficiency as its effect depends on the sodium chloride content in the drilling mud, while sodium persulfate shows the weakest oxidizing effect. The use of cellulase and amylase enzyme solutions, as well as oxidant solutions (urea peroxide, sodium persulfate and calcium hypochlorite), as shown by the results of leaching of clay cakes in laboratory conditions, significantly facilitates the removal of filter cakes from drilling muds. The performed tests allowed for the development of methods of preparing the borehole for the cementing procedure with the use of oxidants or enzymes:

- Thinning of the drilling muds by the addition of enzymatic or oxidizing agents before cementing. Due to the application of such treatment, apart from thinning the drilling mud, the polymers contained in the solidified drilling mud at the borehole wall and clay cake are partially decomposed, which will contribute to better displacement of the drilling mud by the cement paste.
- Application of washer fluids in the form of 1% solutions of enzymes (cellulase) or oxidants (urea peroxide and calcium hypochlorite) prior to the cementing procedure in order to disassemble and then remove the remains of drilling mud and cake from the borehole walls.

In the holes where the expected temperature does not exceed 80 °C, it is recommended to use enzymatic agents (amylase, cellulase) to thin the drilling muds and remove cakes, while in the holes where the temperature exceeds 60 °C, oxidizing agents (urea peroxide, calcium hypochlorite) should be used.

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