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Slawomir Rupinski[1], Zbigniew K. Brzozowski[1, 2] and Malgorzata Uliasz[3]

STUDY ON THE APPLICATION OF STARCH DERIVATIVES AS THE REGULATORS OF POTASSIUM DRILLING FLUIDS FILTRATION

[1] Warsaw University of Technology, Faculty of Chemistry, 75 Koszykowa str., 00-662 Warsaw, Poland, zbigbi@ch.pw.edu.pl
[2] Central Institute for Labour Protection, National Research Institute, 16 Czerniakowska str., 00-701 Warsaw, Poland
[3] The Oil and Gas Institute Krosno Branch, 3 Armii Krajowej str., 38-400 Krosno, Poland
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Abstract. Derivatives of starch, such as graft copolymer of acrylamide onto starch, carbamoylethylated starch, carbamoylethyl-dihydroxypropylated starch, and dihydroxypropylated starch have been tested for their properties as components of drilling fluids used for clay inhibition and for the regulation of their rheology. The influence of modified starch and their blends with tylose as protective agents in the filtration of drilling fluids, as well as replacement of tylose, by modified starch were investigated. The viscosity, flow limit, filtration, pH, and dispersion as factors of the properties of potassium drilling fluids with the addition of starch derivatives were determined.

Keywords: starch, starch derivatives, filtration, inhibition, drilling fluid.

1. Introduction

Starch is usually used in the technology of drilling fluids in modified forms due to its solubility in water. Starch materials are predominantly used as effective protective colloids decreasing the filtration of practically all kinds of water dispersing drilling fluids with the impact on the kind of used salt and its amount salt and additionally increasing the viscosity of drilling fluids. This starch action is caused by its swelling and increasing of its volume due to free water absorption. At the same time we can observe the decrease of filtration and the increase of rheological properties of drilling fluids. Swelled starch becomes a component of filtrating deposit to form polymer-clayey mixture. This mixture decreases the permeability of this deposit and reduces negative action of filtrate on sectors of borehole without drill pipe. There is a possibility of controlling the permeability of filtration deposit by proper utilization of starch constituents and their mixture with bentonite and other polymers. It is the best method of filtration regulation [1].

Starch constituents are characterized by high chemical activity in the system of drilling fluid forming dispersion centre. They are typical protective colloids in fact. Generally hydrophilic colloids and starch constituenrs are characterized by the following properties [2]:
– easy solubility in dispersion centre;
– increased viscosity of prepared solutions due to linking big volumes of water by the particles of dispersion phase;
– gelatinizing caused by spontaneous transformation of sol into gel;
– swelling as the result of solid phase volume increasing caused by the adsorption of dispersion centre;
– interaction of dispersion phase particles with the dispersion centre.

Drilling fluids introduced in 1887 and used in the period 1887–1901 were basic mixtures of clays and water that had no impact on the surrounding environment. However, they have now become a complex mixture of fluids, suspended or dissolved solids, polymers and chemicals, and thus require an engineered approach to fulfill their technical performance without having any impact on the surrounding environment, ecosystems and habitats, as well as to ensure the occupational health and safety of drilling-fluid testing and handling staff. Environmental problems associated with complex drilling fluids in general, and oil-based mud in particular, are among the major concerns of world communities. For this reason, the US Environmental Protection Agency and other regulatory bodies are imposing increasingly stringent regulations to ensure the use of environmentally friendly muds and mud additives [3-6].

Organic polymers are commonly used to control the rheology and filtrate loss required for water-based drilling fluids. An ecologically-friendly water-based drilling fluid was developed by studying the rheological behavior of tamarind gum and polyanionic cellulose on bentonite water suspensions [7].

The newest trends are application of sulphonated and chlorosulphonated polymers [8]. This tendency is observed also in Poland especially in Oil and Gas Institute in Cracow [9]. The leader of the research on drilling fluids in the above mentioned Institute is Dr. M. Uliasz, co-author of our publication [10-13].

The goal of the presented investigation was the evaluation of the possibility of application of our newly-elaborated starch derivatives [14-17]: St-Aam (graft copolymer of acrylamide onto starch) [14], CrES (carbamoylethylated starch) [18-20], CrE-DHPS (carbamoylethyl-dihydroxypropylated starch) [21], DHPS (dihydroxypropylated starch) [22] as the inhibitors of the argillaceous rock hydration and regulators of the filtration when applied in the mud drilling fluids. Newly obtained starch derivatives were also generally tested [15, 23-25].

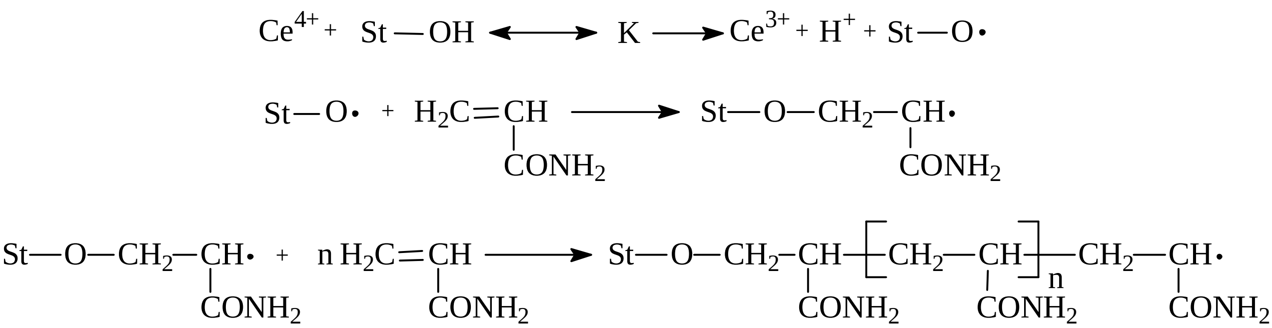
2. Experimental

2.1. Materials

- Bentopol (drilling clay) was purchased from Zaklady Gorniczo-Metalowe, Zebiec, Poland
- Potassium hydroxide, potassium chlorine, barium sulfate (baryt), lignosulfonate without chromium was purchased from Best Drilling Chemicals Poland Sp. z o.o., Lubicz, Poland.
- 1-octanol, Polskie Odczynniki Chemiczne POCh S.A., Gliwice, Poland
- Tylose were purchased from Clariant Polska Sp z o.o., Warszawa, Poland
- lignit K

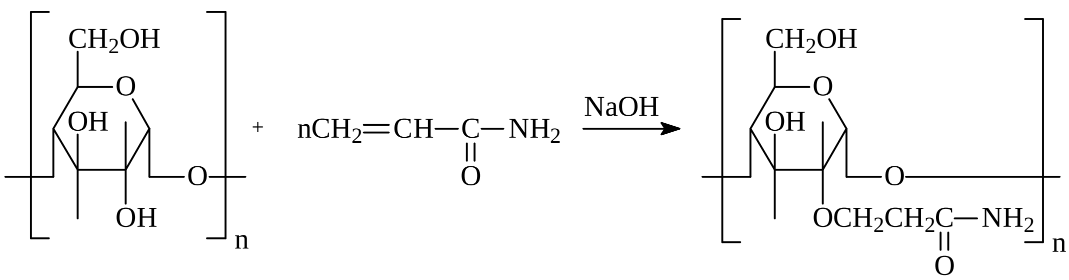
Starch derivatives:

1) St-Aam ((graft copolymer of acrylamide onto starch), obtained by the description [14]:

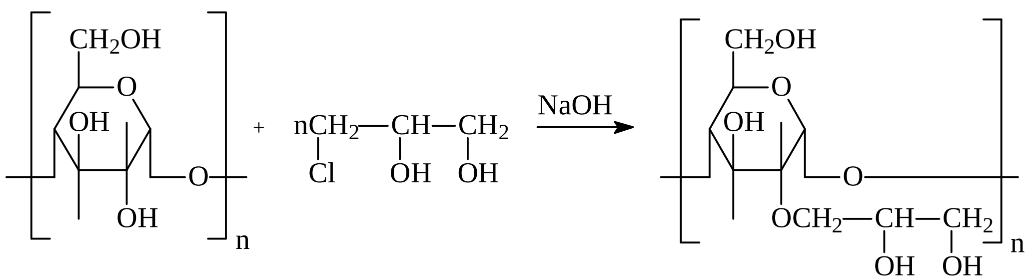


where: K — is starch (St—OH)—cerium (Ce) complex

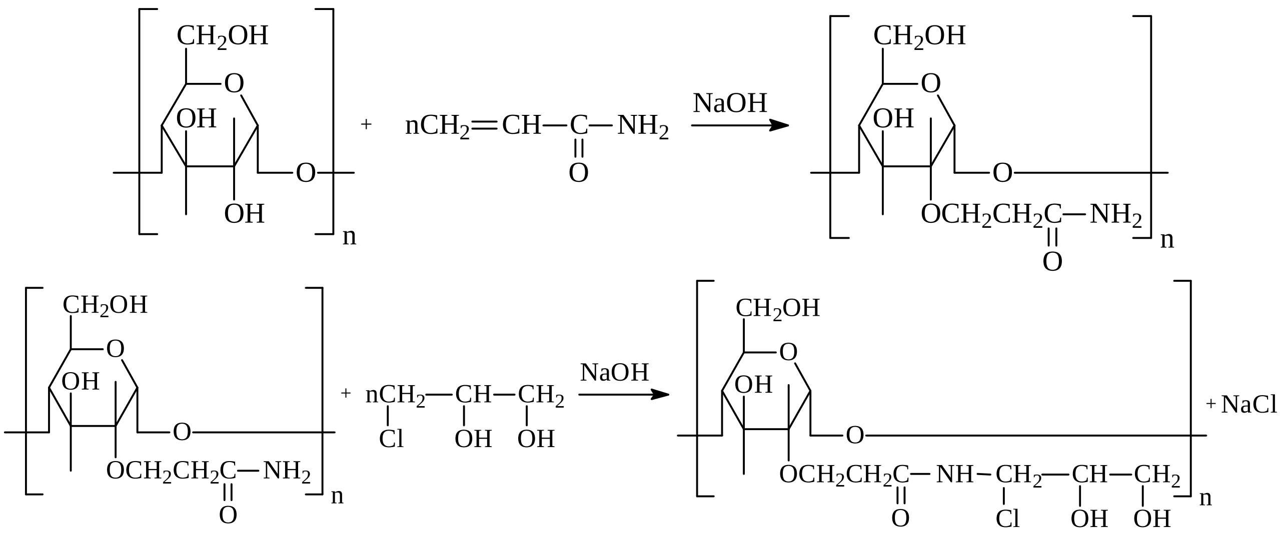
2) CrES (carbamoylethylated starch), obtained by the description [18]:



3) DHPS (dihydroxypropylated starch), obtained by the description [22]



4) CrE-DHPS (carbamoylethyl-dihydroxypropy-lated starch), obtained by the description [21]



All the chemicals obtained were used without further purification.

2.2. Rheological Experiment

The rheological experiments for modified starches were conducted by using Mettler RM 180 rheometer at the temperature of 298 K for different shear rates. The measurements were carried out in the coaxial cylinders. Before measuring, all samples were mixed in 298 K for 60 min and thermostated for 10 min.

2.3. Mud Rheology Test

All the drilling mud composition was made. Prior to rheology test, this drilling mud composition was aged for 24 h at room temperature. The required quantity of modified starch was added to the drilling mud composition and stirred at high speed for 15 min. Then, the rheological property of the treated drilling mud composition was measured using a FANN model 35 type rotating viscosimeter. The rheological parameters such as apparent viscosity (h_a), plastic viscosity (h_p) and frontier flow (t_y) can be determined as described in [26-28].

2.4. Preparation of Drilling Fluid

A sample drilling fluid was prepared in the mechanical mixer. 700 cm^3 of water were poured into the miner and mixing started. The components indicated in Tables 2 and 3 (in wt %) were added and all ingredients were mixed for 90 min. After the mixing 300 cm^3 of water was added and mixing was continued for another 15 min. The obtained drilling fluid was transmitted through vibrating screen and the properties, which were influencing the drilling process, were tested. 1-Octanol was added to the initial drilling fluid as the anti-foaming agent.

3. Results and Discussion

Native starch is not dissolving in cold water and could not be used for chemical treatment of drilling fluid. So in our investigation modified starches were used. They are fairly soluble in water at room temperature. For each drilling fluid viscosity measurements of 5% solutions were carried out – they are shown in Table 1. The highest viscosity values were obtained for CrE-DHPS. Unlike other starch derivatives they have two different substituents in the starch chains – carbamoylethyl and di-hydroxypropyl.

The used starch derivatives are anionic macromolecular compounds and are hydrophilic. They were used as hydration inhibitors of argillaceous rocks and agents decreasing filtration of drilling fluids. The laboratory tests were carried out using potassium drilling fluid as an initial one. The obtained results were compared after the addition of definite amount of used starch derivative. 0.5 % of each polymer was added to the potassium drilling fluid. The main criteria of polymer suitability were dispersions, *e.g.* P_1 and P_2 quantities. These parameters determined inhibit action on the argillaceous rock. The results are presented in Table 2.

Table 2 shows the influence of starch derivatives on the diminishing of potassium drilling fluid filtration. The derivatives (starch-acrylamide copolymers, carbamoylethylated starch, carbamoylethyl-dihydroxypropylated starch) increase this filtration. The viscosity in the case

Table 1

Viscosity values for 5% water solutions of starch derivatives

Substance	Shear rate, s^{-1}							
	64.6	99.0	152.0	233.0	357.0	549.0	841.0	1291.0
	Viscosity, mPa·s							
$CrES_h$	-	-	0.040	0.037	0.035	0.032	0.029	0.026
CrES	-	-	0.039	0.035	0.033	0.030	0.028	0.025
CrE-DSPh	0.062	0.060	0.058	0.052	0.047	0.043	0.039	0.035
DHPS	-	0.047	0.044	0.042	0.039	0.035	0.032	0.030

Table 2

The results of potassium drilling fluid investigation with the addition of starch derivatives as regulators of filtration and inhibitors of argillaceous rock hydration

	Drilling composition, %		Viscosity, mPa·s		Frontier flow, Pa	Filtration, cm^3	pH	Dispersion, %	
			h_p	h_a	τ_y			P_1	P_2
1.	Drilling clay (Bentopol) KOH Lignit K KCl Tylose Lignosulfonate 1- Octanol	7.0 0.1 4.0 3.0 2.0 0.5 0.1	15.0	16.5	3.0	6.8	10.6	34	26
2.	Drilling fluid 1 + St-Aam	0.5	15.0	15.5	1.0	5.2	10.2	60	42
3.	Drilling fluid 1 + CrES	0.5	14.0	15.0	2.0	5.2	10.3	52	44
4.	Drilling fluid 1 + CrE-DHPS	0.5	13.0	14.5	3.0	5.6	10.3	50	42
5.	Drilling fluid 1 + DHPS	0.5	16.0	17.5	3.0	7.0	10.3	50	40

of dihydroxypropylated starch is caused by its higher viscosity in the comparison with that of the initial drilling fluid, as well as with drilling fluid containing other starch derivatives. The addition of starch derivatives slightly decreases pH of the systems. The reason of the pH decrease is probably hydrolysis of carbamoyl groups to carboxylic ones with the release of NH_3 (from starch derivatives) to environment.

The highest dispersions were obtained for drilling fluids with St-Aam and CrES. The above mentioned starch derivatives meet the demands for hydrophilic colloids. Absorbing water in the system of potassium drilling fluids evidently regulates its filtration as well as rheological and structural properties. In the case of high dispersion they exhibit proper inhibition. The addition of St-Aam and CrES increases the suspending properties of drilling fluids and essentially prevents water absorption by argillaceous rock containing bentopol. Mixing of tylose with the particular starch derivative may be treated as standard protective colloid. This colloid increases rheological and structural properties of drilling fluid due to presence of tylose and decreases filtration due to the presence of starch derivatives.

Salt-starch drilling fluids (in our case potassium starch drilling fluid) for low filtration obtaining should contain 2–4 % of starch component per 1 m^3 of drilling fluid. In our investigation medium values were used and 3 % of starch derivative were added in the second step instead of tylose (agent decreasing filtration). The results are shown in Table 3. The replacement of tylose by starch derivatives does not positively influence the filtration of drilling fluid. In all tested drilling fluids the filtration was higher in comparison with the filtration of drilling fluid containing tylose. In the case of using higher amounts of starch derivatives than tylose, the decrease of the viscosity and pH of the tested drilling fluid was observed. However by comparing the results from Table 3, where 3 % of starch derivatives were added, with the results from Table 2, where only 0.5 % of starch derivatives together with tylose were added, it can be concluded that the addition of small amount of starch derivative acts as protective colloid which regulates the filtration and slightly increases viscosity resulting in the decrease of filtration.

The flow limit increases in comparison with the initial drilling fluids (Table 3) despite the decrease of plastic viscosity of drilling fluids containing starch derivatives. This can be the result of high ability of drillings removal.

Table 3

The results of investigation of potassium drilling fluid with the addition of starch derivatives as the filtration regularity agents replacing tylose

	Drilling composition, %		Viscosity, mPa·s		Frontier flow, Pa	Filtration, cm^3	pH	Dispersion, %	
			h_p	h_a	τ_y			P_1	P_2
1.	Drilling clay (Bentopol) KOH Lignit K KCl Tylose Lignosulfonate 1- Octanol	7.0 0.1 4.0 3.0 2.0 0.5 0.1	15.0	16.5	3.0	6.8	10.6	34	26
2.	Drilling clay (Bentopol) KOH Lignit K KCl St-Aam Lignosulfonate	7.0 0.1 4.0 3.0 3.0 0.5	10.0	12.5	5.0	7.6	7.4	52	20
3.	Drilling clay (Bentopol) KOH Lignit K KCl CrES Lignosulfonate	7.0 0.1 4.0 3.0 3.0 0.5	11.0	14.0	6.0	10.8	7.2	36	22
4.	Drilling clay (Bentopol) KOH Lignit K KCl CrE-DHPS Lignosulfonate	7.0 0.1 4.0 3.0 3.0 0.5	11.0	15.5	9.0	16.0	7.2	46	22
5.	Drilling clay (Bentopol) KOH Lignit K KCl DHPS Lignosulfonate	7.0 0.1 4.0 3.0 3.0 0.5	10.0	12.5	5.0	10.6	7.2	38	20

Starch derivatives are easily soluble in the dispersive environment of drilling fluid. This phenomenon affects the creation of proper fibril structure. This structure with lower rheological properties is characterized by high dispersion, even higher than that in the initial drilling fluid. To achieve the possibility of total tylose replacement it is necessary to use starch derivatives with higher molecular weight than those has been obtained up to date.

4. Conclusions

Based on the result of the tests it may be concluded that starch derivatives described in the paper may be used as agents decreasing the filtration of drilling fluids oversalted by potassium chloride. The obtained drilling fluids were characterized by lower filtration in the comparison with the initial drilling fluid. They inhibited argillaceous rock. Among the tested polymers St-Aam and CrES acted as hydration inhibitors. The drilling fluids containing these polymers were characterized by good rheological properties and lower filtration compared with the initial drilling fluid. The application of starch derivatives as a single protective agent is not profitable in every case. However, mixture of starch derivatives with other celluloses (tylose) materials, especially taking into account such spectacular advantage as the possibility of their biodegradation occurring during the time of operation, may positively change the properties of a drilling fluid.

References

[1] Chatterji J. and Borchardt J.: Applications of water-soluble polymers in the oil field. JPT 1981.
[2] Basinski A.: Zarys fizykochemii koloidow. Polish Scientific Publishers, Warszawa 1957.

[3] Amanullah M.: Exploration & Production: Oil Gas Rev., 2007, **II**, 68.
[4] Amanullah M. and Yu L.: J. Petrol. Sci. Eng., 2005, **48**, 199.
[5] Amanullah M.: SPE/IADC Middle East Drilling Technology Conference and Exhibition, 12–14 September 2005, Dubai, UAE, SPE-97008-PP.
[6] Amanullah M. and Boyle R.: SPE Europec/EAGE Conference and Exhibition, Vienna, Austria 2006, 12–15 June, SPE-99410.
[7] Mahto V. and Sharma V.P: J. Petrol. Eng., 2004, **45**, 123.
[8] Mazard C., Guichard B. and Valenti A.: US Pat. Appl. 200802489975 – Class: 5072227 (USPTO), 2008.
[9] Bielewicz D., Wysocki S., Buczek-Kucharska Z., Wysoka M. and Witek E.: Wiertnictwo, Nafta, Gaz, 2008, **25**, 211.
[10] Uliasz M.: Nafta-Gaz, 2007, **63**, 223.
[11] Uliasz M.: Nafta-Gaz, 2004, **60**, 475.
[12] Uliasz M., Chudoba J. and Herman Z.: Prace Instytutu Nafty i Gazu, 2006, **139**, 72.
[13] Uliasz M.: Nafta-Gaz, 2004, **60**, 13.
[14] Brzozowski Z. and Noniewicz K.: Polimery, 1993, **38,** 8.
[15] Brzozowski Z. and Noniewcz K.: Conference "Indoor Climate of Buildings", Strabskie Pleso, Slowacja 1991.
[16] Rupinski S.: PhD thesis, Warsaw University of Technology, Warsaw 2005.
[17] Brzozowski Z.: Zywnosc. Technologia. Jakosc, 1996, **2**, 110.
[18] Rupinski S. and Brzozowski Z.: Polimery, 2003, **48**, 122.
[19] Brzozowski Z., Pietruszka N. and Rupinski S.: Conference proceedings APME'99, Williamsburg, USA, 1999, 19.
[20] Brzozowski Z. and Rupinski S.: World Polymer Congress IUPAC Macro'2000, Warszawa, 2000, 104.
[21] Rupinski S. and Brzozowski Z.: "Advanced Polymers via Macromolecular Engineering 2001", Gatlinburg TN, USA, 2000, 35.
[22] Eur. Pat. Appl. A2 0 266 759, Publ. May 11, 1988.
[23] Brzozowski Z., Pietruszka N., Galaev J. and Mattisson B.: Polimery, 2000, **45**, 687.
[24] Brzozowski Z., Pietruszka N., Galaev J. and Mattisson B.: *ibid*, 707.
[25] Rupinski S., Brzozowski Z., Staszczak S. and Hadam L.: Na pograniczu chemii i biologii, 2004, **XI**, 85.
[26] Raczkowski J. (ed.): Technologia pluczek wiertniczych. Slask, Katowice 1981.
[27] Zhang K. and Chen Y.: Drilling fluids. Petroleum Industry Press, Beijing 1988, 10.
[28] Zhang L., Tan Y. and Li Z.: Carbohydrate Polymers, 2001, **44**, 255.

ЗАСТОСУВАННЯ ПОХІДНИХ КРОХМАЛЮ ЯК РЕГУЛЯТОРІВ ДЛЯ ФІЛЬТРАЦІЇ КАЛІЄВИХ БУРОВИХ РОЗЧИНІВ

Анотація. *Вивчені властивості похідних крохмалю, а саме: прищепленого кополімеру акриламіду і крохмалю, карбамоїлетилового крохмалю і карбамоїлетилдигідрокси-пропілового крохмалю як компонентів бурових розчинів для інгібітування глин і впорядкування їх реології. Встановлено вплив модифікованого крохмалю та його сумішей з тилозою як захисних агентів на фільтрацію бурових розчинів, а також заміни тилози модифікованим крохмалем. Визначені в'язкість, обмеження текучості, фільтрацію, pH-середовище і дисперсію як чинники властивостей калієвих бурових розчинів з додатками похідних крохмалю.*

Ключові слова: *крохмаль, похідні крохмалю, фільтрація, інгібітування, буровий розчин.*