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## INVESTIGATION OF THE IMPACT OF SULFONATED REFINERY PRODUCTS ON THE PROPERTIES OF WATER-BASED DRILLING FLUIDS

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**The relevance** of the work stems from the need to develop requirements for sulfonated bitumen applied in the composition of water-based drilling fluids to control their quality when entering drilling enterprises.

Due to the presence of water-insoluble substances, sulfonated bitumens are considered to be hydrophobic bridging agents of clay rocks, though the proportion of water-soluble substances in their composition is much higher (~70 %). Nowadays the influence of the water-soluble component of sulfonated bitumen on clay rock in terms of inhibition and peptization is unknown. There are also no data on salt resistance and resistance to alkaline earth metals ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) of sulfonated bitumen. All this can lead to their irrational use. The study of these issues will help formulate requirements and select methods for assessing the quality of sulfonated bitumens, as well as improve the efficiency of their use in drilling fluids.

**The main aim** of the research is to experimentally determine the functional properties of sulfonated bitumen in the composition of water-based drilling fluids.

**The main objectives** of the research are to study the sulfonated bitumen effect on clay rocks and assess the sulfonated bitumen resistance to mineralization and divalent cations.

**Objects:** sulfonated bitumen samples of various brands and manufacturing plants.

**Methods.** The technological parameters of clay drilling fluids were determined by standard methods in accordance with SS 33213-2014 (ISO 10414-1:2008); the inhibitory and peptization properties of the research objects in relation to clay rocks were studied by the method of clay swelling when they were in the sample solution (on the Zhigach–Yarov tester) and by means of sedimentary analysis (on the Figurovsky weight scale); salt resistance of sulfonated bitumens was determined by the method of sedimentation while placing sulfonated bitumens in a mineralized environment.

**Results.** The authors have carried out the comparative analysis of six sulfonated bitumen samples to identify the physicochemical effect of this group reagents on clay rocks. By assessing the degree of swelling and particle-size determination of clay while its staying in the drilling fluids of the test samples, two groups of reagents of sulfonated bitumen were found, which are opposite in their functional effect on clay: 1) peptizing agents (deflocculants); 2) clay inhibitors. It was experimentally proved that all sulfonated bitumens contribute to the deterioration of the thixotropic, rheological, and filtration properties of fresh clay systems, while samples with inhibitory properties are more effective viscosity reducers; in a mineralized environment, the presence of divalent cations and sulfonated bitumens are conducive to a decrease in filtration properties, but are ineffective as viscosity reducers, and also, they are conducive to thickening due to their coagulation or solubility decrease. Experiments proved that for determining the functional purpose of high-molecular-weight sulfonated bitumens in the composition of water-based drilling fluids and controlling the quality of the samples, it is necessary to test them according to the following indicators: to determine the size of clay particles in water and in a solution of the test sample in order to identify its inhibitory or peptizing properties; to evaluate the thinning capacity and the effectiveness of reducing the filtration characteristics when adding a reagent to a fresh clay suspension.

### Key words:

drilling fluids, sulfonated bitumen, sulfonated asphalt, clay swelling inhibiting, clay dispersion, coagulation.

### Introduction

Many types of drilling problems which mostly depend on the composition and properties of the drilling fluid may occur during the well drilling. One of the types of such drilling problems is a damage of wellbore integrity, manifested in the form of screens and ground caving or swelling of clay-containing rocks.

During the drilling in areas where low-permeable mudstones and clay shales are located, the drilling fluid

filtrate, penetrating into the pores of the formation, sharply increases the pore pressure, which leads to rock fracturing and subsequently to screens and ground caving [1, 2].

To prevent this phenomenon, the use of bridging agents is effective. They clog the pore space inside the rock at the well-formation system, thus ending the process of filtrate invasion of the drilling fluid deep into the formation [3–6].

Recently, sulfonated bitumen or asphalts have been gaining wide popularity as bridging agents, which, when ingested into the pores and clay shales microfractures and mudstones, due to the water-insoluble component, concurrently physically clog and hydrophobize the pores, thereby avoiding the increasing of interior pressure, and quickly stop fracture spreading [7–9].

However, the presence of a water-soluble component and sulfogroups that impart anionic properties to these reagents, as well as their adsorbability on the clay's surface, predetermine the study of them as stabilizers of water-based drilling fluids. In addition, some researchers position these reagents as viscosity reducers [10]. Other researchers, on the contrary, note the thickening of drilling fluids when using these reagents [11, 12]. Understanding the effects of sulfonated bitumen impact on the operating properties of drilling fluids can extend the range and their effective implementation, as well as solve the issue of quality control of the sulfonated bitumen supplied to drilling enterprises. Therefore, this research paper presents the results of the study of effect of sulfonated bitumen

from different manufacturers on the filtration, rheological, and inhibitory properties of water-based drilling fluids, which are described from the point of view of their mechanism of action on clay.

#### Rationale for choosing research objects

Sulfonated bitumen (asphalt) is the sulfonated product of natural or petroleum bitumen neutralized by alkaline agents or ammonia, most of which are soluble in water [13–16].

Nowadays, sulfonated bitumen is produced by many foreign companies, primarily in China and India, as well as some Russian companies, such as CJSC «Khimpartners», LLC «Khimprom» and LLC «Arkhim». It is clear that each manufacturer produces its own individual product, the physical/chemical properties of which differ from others. Consequently, every individual product will have a different impact on drilling fluids.

During the research work, six samples of sulfonated bitumen from various brands and manufacturing plants were selected. The data are presented in Table 1.

**Table 1.** Samples of sulfonated bitumen tested and their physico-chemical properties

**Таблица 1.** Образцы сульфированных битумов, подвергшихся испытанию, и их физико-химические свойства

Sample number № образца	Sample Образец	Manufacturer Производитель	Physico-chemical properties Физико-химические свойства		
			Solubility in white spirit, % Растворимость в уайт-спирите, %	Solubility in water, % Растворимость в воде, %	pH of 1 % solution, units pH 1 %-го раствора, ед.
1	Sulfonated bitumen «AM» Сульфированный битум AM	LLC «Arkhim» ООО «Архим»	16,1	70,7	8,95
2	Sulfonated sodium asphalt «FT-1A» Сульфированный Na асфальт «FT-1A»	LLC « Unified Trading System» ООО «Единая торговая система»	9,8	72,6	8,52
3	Sulfonated sodium bitumen Сульфированный натриевый битум		14,9	67,4	8,67
4	Sulfonated sodium asphalt «FT-35» Сульфированный Na асфальт «FT-35»		11,0	69,3	8,60
5	Sulfonated bitumen Сульфированный битум	CJSC «Khimpartners» ЗАО «Химпартнеры»	20,4	72,3	8,64
6	«Asfasol» «Асфасол»	LLC «Khimprom» ООО «Химпром»	16,2	69,1	8,60

The samples were selected based on the prevalence of their use by various oil and service companies: some of them are produced in China (ООО «Unified Trading System»), and some are produced in the Russian Federation (LLC «Khimprom», CJSC «Khimpartners» and LLC «Arkhim»).

#### Behavioral study of sulfonated bitumen in fresh water systems

The results of the study of the sulfonated bitumen capacity to inhibit the swelling of clay, conducted by a number of researchers [17–19], have proved to be contradictory. Therefore, in order to understand the mechanism of the physico-chemical effect of the objects of study on clay, first of all, their inhibitory properties were studied. For this purpose, a clay sample weighing 10 g was placed in a cell of the Zhigach–Yarov tester,

into which water or 1 % solution with a sample of sulfonated bitumen was poured; the change in the volume of the clay sample in dynamics was recorded by an indicating gage. The dependence diagrams in Fig. 1 shows a significant decline of the clay swelling with all the test samples compared to water, reflecting the binding of water molecules by the hydrophilic part of sulfonated bitumen. At the same time, additives 1–3 suppress the clay swelling to a less extent than additives 4–6: in the first case, the increase in the height of the clay sample is 30,82–33,56 %, in the second case – 23,49–23,94 %.

The results are explained well by the sedimentation analysis data, that demonstrate the particle size of untreated bentonite in water and in solutions of sulfonated bitumen. The results are presented in Table 2.

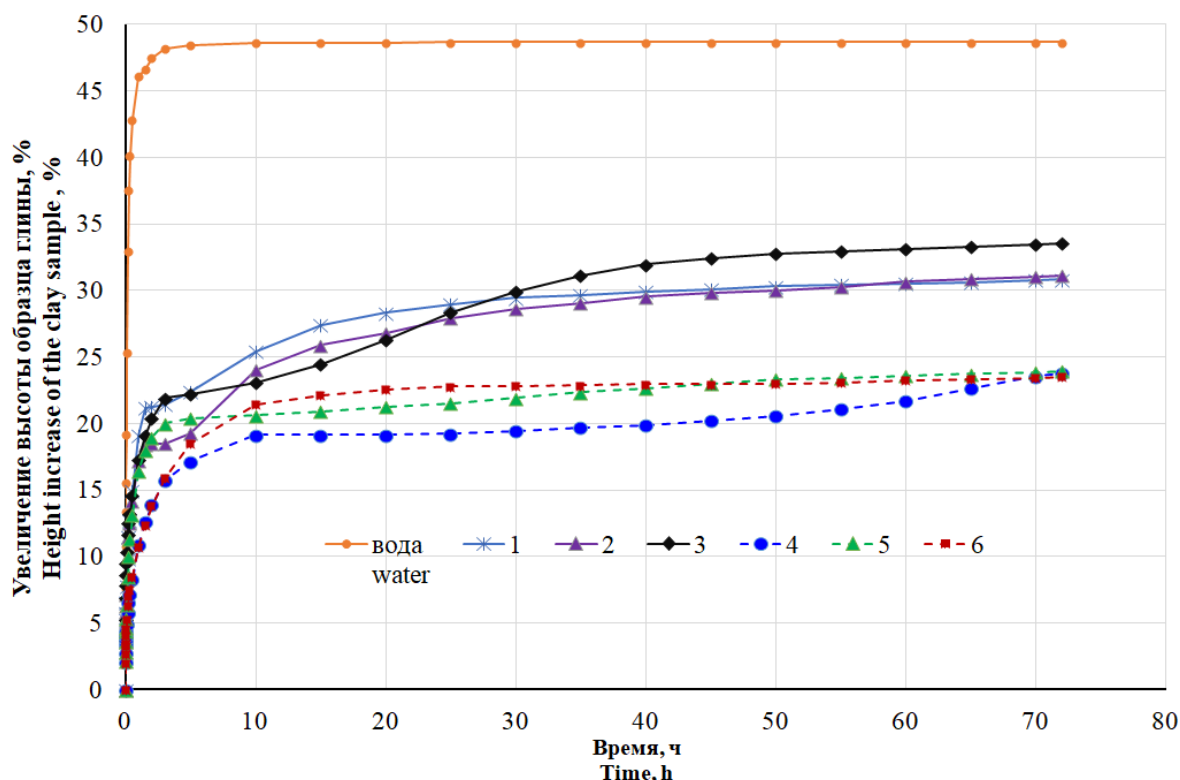


Fig. 1. Height change dynamics of clay sample when it is in water and in 1 % solutions of sulfonated bitumen tested

Рис. 1. Динамика изменения высоты образца глины при нахождении его в воде и в 1%-х растворах исследуемых сульфированных битумов

Table 2. Size distribution of clay particles in water and in 1 % solutions of sulfonated bitumen determined by sedimentation analysis on the Figurovsky weight scale

Таблица 2. Распределение частиц глины по размерам в воде и 1%-х растворах сульфированных битумов, определенных методом седиментационного анализа на приборе Фигуровского

Solution composition/Состав раствора	D50	D10-D90
	μm/мкм	
Water/Вода	8,88	6,88–19,02
Water + sample no. 1/Вода + образец № 1	8,4	5,1–11,5
Water + sample no. 2/Вода + образец № 2	5,8	4,2–8,4
Water + sample no. 3/Вода + образец № 3	8,5	6,8–10,2
Water + sample no. 4/Вода + образец № 4	15,32	11,52–20,88
Water + sample no. 5/Вода + образец № 5	15,01	9,7–28,0
Water + sample no. 6/Вода + образец № 6	17,1	9,8–32,0

D10, D50 and D90 are the sizes below which 10, 50 and 90 % of clay particles are contained.

D10, D50 и D90 обозначают размер, ниже которого содержится, соответственно, 10, 50 и 90 % частиц глины.

Table 2 shows that, samples 1–3 reduce the size of clay particles compared with their initial size – sulfonated bitumen molecules, adsorbed on the surface of clay particles, increase their hydrophilicity, resulting in the expansion of the inter-pack layers and the clay swelling; samples 4–6, on the contrary, increase the size of clay particles, which indicates the presence of coagulating components in the test additives, preventing water penetration into the interlayer space. That’s why the clay swells less.

In this way, the test samples can be divided into two groups:

- Group I – peptizing agents (deflocculants) of clays (samples 1–3);
- Group II – clay inhibitors (samples 4–6).

The mechanism of action of sulfonated bitumen samples of peptising orientation is as follows. The presence of electronegative sulfogroup –  $\text{SO}_3\text{H}$  – in the structure of hydrophilic macromolecules of sulfonated bitumen allows them to be adsorbed on positively charged corners and edges of clay particles. Due to this, the negative charge increases and the clay hydrophilizes, which results in the expansion of clay plates with the creation of new surfaces and the formation of hydrophilic shell on each of them.

In the case of using inhibitory orientation samples, clay particles, on the contrary, will stick together under the influence of coagulating components, and the effect of hydrophilic macromolecules will be limited only by hydrophilization of the outer surface of clay particles (coagulating components will hold clay plates together and suppress peptization).

Diphilic macromolecules of sulfonated bitumen are capable of hydrophobizing the clay surface – adsorbed by sulfonated hydrophilic sites on positively charged corners and edges of clay plates; they orient themselves with a hydrophobic part into the dispersion medium and prevent water penetration to the clay [20].

Analysis of sulfonated bitumen solubility in organic solvent and water (Table 1) shows that total oil and water solubility is less than 100 % and averages 85 % for sam-

ples of both groups. Consequently, at least 15 % of the sulfonated bitumen components do not dissolve either in organic solvents or in water. These microparticles should be colmatants of the filtration crust.

The significant impact of samples of both sulfonated bitumen groups on clay suggests their significant influence on the rheological and filtration properties of clay drilling fluids. The formation of labile hydrophilic and hydrophobic shells on the clay surface should reduce contact interactions and friction between solid particles and contribute to the reduction of rheological parameters. Due to the binding of free water by the hydrophilic part, the deposition of hydrophobized clay particles in the filtration crust and additional colmatation of its insoluble microparticles, sulfonated bitumen should help reduce the filtration performance of clay drilling fluids.

In this regard, there was studied the influence of the sulfonated bitumen samples on the technological properties of a clay suspension containing 35 % by weight of untreated bentonite and 0,2 % by weight of NaOH. To do this, a suspension of untreated bentonite was dissolved in tap water, to which NaOH was previously added, and kept in a heating furnace in a hermetically sealed container (pressure cooker) at 80 °C for 3 days. After 3 days, by adding tap water in portions, followed by stirring on a stirrer for 30 minutes, the clay suspension was diluted to an effective viscosity of 25–30 mPa·s; by adding 1 n NaOH, the pH was adjusted to 9,5–10,0 units. Thus, seven liters of solution were prepared.

The resulting solution was taken as the initial clay suspension (CS). 1000 ml of CS was taken, 1 % of the sulfonated bitumen sample was added, mixed for 15 minutes on a high-speed mixer (10000 rpm) and the prepared solution was left at room temperature in a hermetically sealed container for 16 hours. After the time elapsed, the solution was stirred for 15 minutes on a laboratory stirrer and the technological parameters were determined (Table 3) in accordance with SS 33213-2014 (ISO 10414-1:2008) [21]; the thixotropy coefficient  $K_t$  was calculated using a formula analogous to [22]:

$$K_t = \frac{\text{Gel 10 min} - \text{Gel 10 sec}}{10 \text{ min} - 10 \text{ sec}},$$

where Gel 10 min and Gel 10 sec are the static gel strengths for 10 min and 10 sec.

Since some researchers position sulfonated bitumen as effective viscosity reducing additives, the dilution capacity of the samples was additionally evaluated, which is defined as the percentage of reduction in the apparent viscosity of the CS after adding a sample of sulfonated bitumen to it:

$$\text{Dilution Capacity} = 100 - \frac{100 \cdot AV^s}{AV^{CS}},$$

where  $AV^s$  и  $AV^{CS}$  – apparent viscosity of the drilling fluid with the sample and the initial CS at the shear rate  $1021,38 \text{ s}^{-1}$ , mPa·s.

**Table 3.** Technological properties and dilution efficiency when adding 1 wt. % of sulfonated bitumen to CS

**Таблица 3.** Технологические свойства и эффективность разжижения при добавлении 1 % масс. сульфированного битума к глинистой суспензии (ГС)

Drilling fluid Раствор	Reagent type* Тип реагента	API fl. loss, ml/30 min Показатель фильтрации ПФ, мл/30 мин	pH	Plastic viscosity PV, mPa·s Пластическая вязкость ПВ, мПа·с	Yield point UP, lb/100ft <sup>2</sup> Динамическое напряжение сдвига ДНС, фунт/100 фут <sup>2</sup>	Gel, lb/100 ft <sup>2</sup> Статическое напряжение сдвига СНС, фунт/100 фут <sup>2</sup>		Thixotropy coefficient $K_t$ Коэффициент тиксотропии $K_t$	Apparent viscosity AV, mPa·s Эффективная вязкость $\eta_{эф}$ , мПа·с	Dilution capacity, % Разжижающая способность, %
						10 s/c	10 min мин			
CS ГС	–	14,4	9,68	4,3	50,9	74	118,1	4,5	29,7	–
CS+№ 1 ГС+№ 1	I group I группа	9,9	9,43	17,5	17,6	7,7	43,4	3,6	26,3	11,5
CS+№ 2 ГС+№ 2		13,7	9,18	8,2	29,7	36,8	77,7	4,2	23,0	22,5
CS+№ 3 ГС+№ 3		13,9	9,74	6,9	28,9	25,4	68,2	4,4	21,4	28,1
CS+№ 4 ГС+№ 4	II group II группа	12,8	9,42	17,8	7,4	3,8	24,7	2,1	21,5	27,6
CS+№ 5 ГС+№ 5		10,3	9,32	18,0	5,9	0,5	29,0	2,9	21,0	29,3
CS+№ 6 ГС+№ 6		9,9	9,64	21,0	4,7	5,9	28,4	2,3	23,3	21,5

\*I group – peptizers; II group – inhibitors.

\*I группа – пептизаторы; II группа – ингибиторы.

The data in Table 3 demonstrate, that all additives contribute to a decrease in the parameters of the Gel characterizing the thixotropic properties of the system, while drilling fluids with group I reagents (peptizers) have higher values of the thixotropy coefficient ( $K_t \geq 3,6$ ) compared to the values of group II ( $K_t < 3$ ), which indicates active structurization in the system in the presence of a peptizing orientation and suppression of this process in the presence of an inhibitory orientation of sulfonated bitumen. Lower yield value (YP), which characterizes the electrochemical interactions between particles of the dispersed phase during the flow of the drilling fluid, are observed in systems with samples of group II (inhibitors); on average the dilution capacity is higher in reagents of this group.

Low efficiency of reducing rheological parameters by group I reagents (peptizers) is apparently due to an increase in the degree of the clay phase dispersion and, accordingly, an increase in the surface area of clay on which sulfonated bitumen macromolecules can be adsorbed. The adsorption of macromolecules on new surfaces leads to a lack of them, as a result of which some clay particles do not have hydrophilic and hydrophobic shells that reduce contact interactions and friction between solid particles. Thus, effective viscosity reducing agents in fresh systems are samples of sulfonated bitumen with inhibitory properties.

The addition of sulfonated bitumen to the CS helps to reduce the filtration rate, but there is no significant difference between the samples of both groups.

#### Investigation of sulfonated bitumen behavior in mineralized systems

Often, drilling fluids with a high degree of mineralization or containing alkaline-earth metals ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) are used in drilling technology. In this case, the requirements for reagents to maintain their effectiveness in the presence of salts and bivalent cations increase. The research [23] shows high resistance to strong electrolytes ( $\text{KCl}$ ,  $\text{CaCl}_2$ ) of Na-salts of sulfonated humic acids. This gave us reason to assume that a similar salt resistance may be characteristic of sulfonated bitumen.

In this regard, clay solutions with samples of the tested sulfonated bitumen (1 wt. %), the description of the preparation of which is presented above, were polluted with highly mineralized reservoir water. To do this, 450 ml of the finished solution was taken, 50 ml of highly mineralized reservoir water was added, stirred for 15 minutes on a high-speed mixer (10000 rpm) and the prepared solution was left at room temperature in a hermetically sealed container for 16 hours. Similarly, the initial CS was polluted with reservoir water. After the time elapsed, the solution was stirred for 15 minutes on a laboratory stirrer and the technological parameters were determined (Table 4).

It can be seen that under conditions of high mineralization, samples of sulfonated bitumen of both groups (peptizers and inhibitors) provide lower values of the filtration index compared to the initial CS, but at the same time, the values of the Yield Point significantly increase and the thixotropic properties of the solutions deteriorate.

**Table 4.** Technological properties of CS containing 1 wt. % sulfonated bitumen, when adding 10 % vol. of highly mineralized reservoir water

**Таблица 4.** Технологические свойства ГС, содержащей по 1 % мас. образца испытуемого сульфированного битума, при добавлении 10 % об. высокоминерализованной пластовой воды

Drilling fluid Раствор	Reagent type* Тип реагента*	API fl. loss, ml/30 min, Показатель фильтрации ПФ, мл/30 мин	pH	Plastic viscosity PV, mPa·s Пластическая вязкость ПВ, мПа·с	Yield Point YP, lb/100 ft <sup>2</sup> Динамическое напряжение сдвига ДНС, фунт/100 фут <sup>2</sup>	Gel, lb/100 ft <sup>2</sup> Статическое напряжение сдвига СНС, фунт/100 фут <sup>2</sup>		Thixotropy coefficient K <sub>t</sub> Коэффициент тиксотропии K <sub>t</sub>	Apparent viscosity AV, mPa·s Эффективная вязкость Пэф, мПа·с	Dilution capacity, % Разжижающая способность, %
						10 s/c	10 min мин			
CS ГС	–	44,6	7,86	4,4	8	11,4	14	0,26	8,4	–
CS+№ 1 ГС+№ 1	I group I группа	31,2	7,75	2,6	35,3	30,6	36,6	0,61	20,2	–139,9
CS+№ 2 ГС+№ 2		30,8	7,77	9,9	17,8	17,6	14,5	–0,32	18,8	–124,4
CS+№ 3 ГС+№ 3		40,5	7,86	3,4	20,3	19	17	–0,20	13,5	–61,1
CS+№ 4 ГС+№ 4	II group II группа	34,2	8,24	10,3	13,1	13,8	12	–0,18	16,8	–100,1
CS+№ 5 ГС+№ 5		35,0	8,03	0,4	30,2	27,6	26	–0,16	15,5	–84,6
CS+№ 6 ГС+№ 6		32,2	8,18	3,9	26,2	17,9	14,3	–0,37	17	–102,6

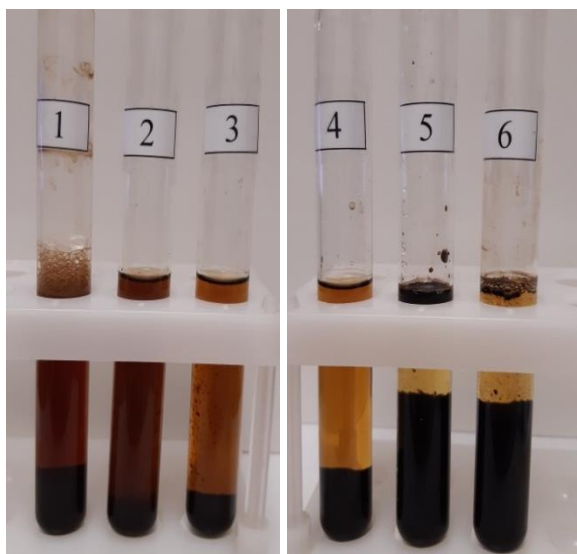
\*I group – peptizers; II group – inhibitors.

\*I группа – пептизаторы; II группа – ингибиторы.

When mixing equal volumes of pre-filtered 1 % solutions of sulfonated bitumen with saturated sodium chloride solution (26 wt. %) in a test tube, sedimentation was

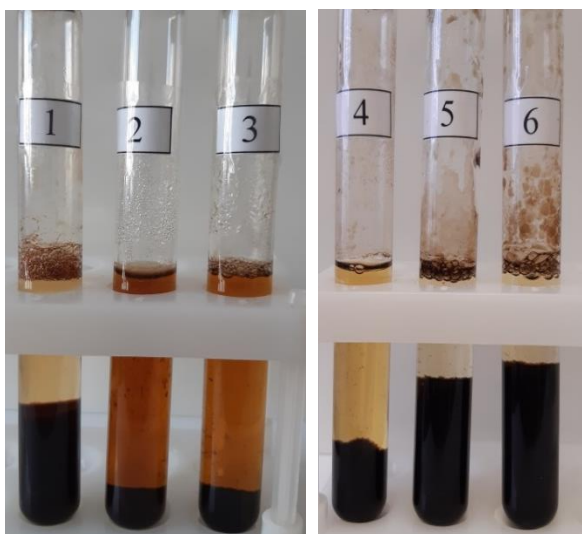
observed in all test samples (Fig. 2), which indicates coagulation or a decrease in the solubility of sulfonated samples in a mineralized environment. A similar pattern

was observed when equal volumes of 1 % solutions of sulfonated bitumen were mixed in a test tube with 0,5 % calcium chloride solution (Fig. 3); in terms of  $\text{Ca}^{2+}$  ions, this corresponds to 900 mg/l.



**Fig. 2.** Coagulation of sulfonated bitumens in the presence of NaCl (13 wt. %)

**Рис. 2.** Коагуляция сульфированных битумов с NaCl (13 % мас.)



**Fig. 3.** Coagulation of sulfonated bitumens in the presence of  $\text{CaCl}_2$  (900 mg/l  $\text{Ca}^{2+}$ )

**Рис. 3.** Коагуляция сульфированных битумов с  $\text{CaCl}_2$  (900 мг/л  $\text{Ca}^{2+}$ )

Thus, sulfonated bitumen is ineffective as a viscosity reducing agent in mineralized systems and in the presence of divalent cations, such as  $\text{Ca}^{2+}$ , due to their coagulation

or reduced solubility. But this property of sulfonated bitumen can have a positive effect on the exposing of water- and brine showing layers – when interacting with the reservoir fluid, they will coagulate to form sediment and clog the formation. Determining the threshold concentrations of salts and divalent cations with the presence of which they begin to coagulate is the task of future research.

#### Conclusions and recommendations

1. It was revealed that there are two groups of reagents of sulfonated bitumen (asphalt) opposite in effect on clay: 1) clay peptizers (deflocculants); 2) clay swelling inhibitors. It is shown that the samples of the second group to a greater extent prevent water penetration into the interlayer space of clays and have a better liquefying ability with simultaneous improvement of filtration properties of fresh clay systems.

The first group includes reagents of the following brands: sulfonated bitumen AM of LLC «Arkhim», sulfonated Na asphalt FT-1A and sulfonated sodium bitumen of OOO «Unified Trading System». The second group of reagents includes sulfonated Na asphalt FT-35 OOO «Unified Trading System», sulfonated bitumen CJSC «Khimpartners» and Asphasol LLC «Khimprom».

2. It has been experimentally proved that sulfonated bitumen of both groups does not have a resolving ability in the presence of salts (NaCl) and divalent cations ( $\text{Ca}^{2+}$ ) due to coagulation, but at the same time retains its effectiveness as filtration reducers.
3. Based on the complex of studies conducted, it was found that in order to control the quality and determine the scope of application of sulfonated additives in the composition of drilling fluids, it is necessary to test them according to the following indicators:

- determine the size of clay particles in water before and after adding the test sample to define the inhibitory properties of the reagent;
- evaluate the reagent dilution ability when it is added to a fresh clay suspension;
- determine the effectiveness of reducing filtration properties when adding a reagent to a fresh clay suspension;
- determine the effectiveness of reducing filtration properties when adding the test reagent to mineralized and divalent cation-containing systems.

Research in this direction should be continued. In the future, a more detailed study of the behavior of sulfonated bitumen in mineralized systems (type and concentration of electrolyte), as well as under the influence of elevated temperatures, is possible.

#### REFERENCES

1. Van Oort E., Pasturel C., Bryla J., Ditlevsen F. Improved wellbore stability in Tor/Ekofisk wells through shale-fluid compatibility optimization. *SPE/IADC Drilling Conference and Exhibition*. The Hague, The Netherlands, 2017. pp. 1-24.
2. Shirokov M.N. Exceptional wellbore stability: what to do when drilling mud weighting does not work? *Drilling and oil*, 2019, no. 9, pp. 46-49. In Rus.
3. Reid P.I., Santos H. Ultra-low invasion drilling fluids: a practical route to reduced wellbore instability, reduced mud losses, wellbore strengthening and improved well productivity. *SPE/IADC Indian Drilling Technology Conference and Exhibition*. Mumbai, India, 2006. pp. 1-12.

4. Stowe C. Dzh. II, Bland R. G., Clapper D., Syan T., Benaissa S. *Burovyye rastvory na vodnoy osnove s primeneniem lateksnykh dobavok* [Water-based drilling fluids using latex additives]. Patent RF, no. 010638B1, 2008.
5. Ramirez M. A., Bishop M. D. *Wellbore drilling compositions*. Cox. Patent 11078395B2 USA, 2021.
6. Ramirez M. A., Benaissa S., Ragnes G., Almaraz A. Aluminum-based HPWBM successfully replaces oil-based mud to drill exploratory well in the Magellan Strait, Argentina. *SPE/IADC Middle East Drilling Technology Conference and Exhibition*. Cairo, Egypt, 2007. pp. 1–11.
7. Kuzmin V. N., Trefilova T. V. Inhibition of drilling fluids with the goal of accident-free drilling of the interval of unstable clay rocks. *Online scientific publication «Neftyanaya provintsiya»*, 2020, no. 1 (21), pp. 73–82. In Rus.
8. Ryabtsev P. L. AKROS: innovative drilling fluid systems and effective drilling solutions. *Drilling and oil*, 2015, no. 3, pp. 36–38. In Rus.
9. Ishbaev G. G., Milezhko A. A., Ishbaev R. R., Petrov D. V., Mamaeva O. G., Mirsayapova R. M. *Termostoyky biopolimerny burovoy rastvor* [Heat-resistant biopolymer drilling mud]. Patent RF, no. 2711222, 2020.
10. Clampitt R. L., Russell J. A. *Sulfonated asphalt*. Cox. Patent 4514308A USA, 1985.
11. Arkhipovtsov A. A., Mayevskiy S. P., Kharitonov V. V. Import substitution of foreign reagents for drilling. Sulfonated asphalt of the Russian production. *Drilling and oil*, 2016, no. 2, pp. 48–50. In Rus.
12. Moysa Yu. N., Ivanov D. Y., Marusov M. A. Ingibiruyushchie i smazochnye dobavki dlya utyazhelennykh burovyykh rastvorov [The inhibiting and lubricant additives for the weighted drilling fluids]. *Bulatovskie chteniya* [Bulatov readings]. Krasnodar, Yug Publ. House, 2018. Vol. 3, pp. 196–205.
13. Stratton C. A. *Production of sulfonated asphalt*. Cox. Patent 3089842A USA, 1963.
14. Rooney P., Russell J. A., Brown T. D. *Production of sulfonated asphalt*. Cox. Patent 4741868A USA, 1988.
15. Prevedello A., Platone E., Donati E. *Process for preparing a sulfonated dispersant from petroleum asphalt fractions*. Cox. Patent 5322556A USA, 1994.
16. Shen Q., Xian T., Yu B. Research on the preparation of sodium asphalt sulfonate and its mechanism of fluid loss control for drilling fluids. *SPE International Symposium on Oilfield Chemistry*. San Antonio, Texas, 1995. pp. 1–21.
17. Marusov M. A., Moysa Yu. N. Lubricating and inhibiting additives for weighted drilling fluids. *Drilling and oil*, 2018, no. 11, pp. 48–50. In Rus.
18. Buyanova M. G. *Razrabotka tekhnologii primeniya i sovershenstvovanie sostavov modifitsirovannogo burovogo rastvora dlya povysheniya effektivnosti stroitelstva skvazhin*. Diss. Kand. nauk [Development of application technology and improvement of modified drilling mud compositions to improve the efficiency of well construction. Cand. Diss.]. Ufa, 2021. 190 p.
19. Clampitt R. L., Swanson B. L. *Process for making sulfonated uimtaite and well fluid additives including sulfonated uimtaite*. Cox. Patent 6514916B1 USA, 2003.
20. Huber J., Plank J., Heidlas J., Keilhofer G., Lange P. *Additive for drilling fluids*. Cox. Patent 7576039B2 USA, 2009.
21. GOST 33213-2014. *Kontrol parametrov burovyykh rastvorov v promyslovykh usloviyakh. Rastvory na vodnoy osnove* [State Standard 33213-2014 (ISO 10414-1:2008). Control of drilling fluid parameters in field conditions. Water based fluids]. Moscow, StandartInform Publ., 2015. 75 p.
22. Ryazanov Ya. A. *Entsiklopediya po burovym rastvoram* [Encyclopedia of drilling fluids]. Orenburg, Letopis Publ., 2005. 664 p.
23. Hilko S. L., Titov E. V., Fedoseeva A. A., Vliyanie silnykh elektrolitov na vodnye rastvory Na-soley nativnykh i sulfirovannykh guminovykh kislot [The effect of strong electrolytes on aqueous solutions of sodium salts of native and sulfonated humic acids]. *Kolloidny zhurnal*, 2001, vol. 63, no. 5, pp. 706–710.

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## ИССЛЕДОВАНИЕ ВЛИЯНИЯ СУЛЬФИРОВАННЫХ ПРОДУКТОВ НЕФТЕПЕРЕРАБОТКИ НА СВОЙСТВА БУРОВЫХ ПРОМЫВочНЫХ ЖИДКОСТЕЙ НА ВОДНОЙ ОСНОВЕ

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**Актуальность** исследования обусловлена необходимостью разработки требований к сульфированным битумам (асфальтам), применяемым в составе буровых растворов на водной основе, для контроля их качества при поступлении на буровые предприятия.

Вследствие наличия водонерастворимых веществ сульфированные битумы считаются гидрофобными кольматантами глинистых пород, хотя на самом деле доля водорастворимых веществ в их составе значительно выше (~70%). На сегодняшний день неизвестно влияние водорастворимой составляющей сульфированных битумов на глинистую породу с точки зрения ингибирования и пептизации. Также отсутствуют данные о солестойкости и устойчивости к щелочноземельным металлам ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) сульфированных битумов. Все это может привести к нерациональному их применению. Изучение этих вопросов поможет сформулировать требования и подобрать методы оценки качества сульфированных битумов, а также улучшить эффективность их использования в составе буровых растворов.

**Цель:** экспериментально определить функциональные свойства сульфированных битумов в составе буровых растворов на водной основе.

**Задачи:** изучить влияние сульфированных битумов на глины и оценить их устойчивость к минерализации и двухвалентным катионам.

**Объекты:** образцы сульфированных битумов различных марок и заводов-производителей.

**Методы.** Технологические параметры глинистых буровых растворов определялись стандартными методами в соответствии с ГОСТ 33213-2014 (ISO 10414-1:2008); ингибирующие и пептизирующие свойства объектов исследования по отношению к глинистой породе изучали методом набухания глины при нахождении ее в исследуемом растворе (на приборе Жигача–Ярова) и посредством седиментационного анализа (на весах Фишеровского); солестойкость сульфированных битумов определяли методом осадкообразования при нахождении их в минерализованной среде.

**Результаты.** Проведен сравнительный анализ шести образцов сульфированных битумов для выявления физико-химического влияния реагентов данной группы на глинистую породу. Посредством оценки степени набухания и определения размера частиц глины при нахождении ее в растворах исследуемых образцов установлено, что существует две группы реагентов сульфированных битумов, противоположных по функциональному воздействию на глину: 1) пептизаторы (дефлокулянты); 2) ингибиторы набухания. Экспериментально доказано, что все сульфированные битумы способствуют ухудшению тиксотропных, реологических и фильтрационных свойств пресных глинистых систем, при этом более эффективными понизителями вязкости являются образцы, обладающие ингибирующими свойствами; в минерализованных средах и при наличии двухвалентных катионов сульфированные битумы также способствуют ухудшению фильтрационных свойств, но неэффективны как понизители вязкости, и даже наоборот, способствуют сильному загущению, что связано с их коагуляцией, или снижением растворимости. Установлено, что для определения функционального применения высокомолекулярных сульфированных битумов в составе буровых растворов на водной основе и контроля качества образцов необходимо испытывать их по следующим показателям: определять размер частиц глины в воде и в растворе испытуемого образца с целью выявления его ингибирующих или пептизирующих свойств; оценивать разжижающую способность и эффективность снижения фильтрационных свойств при добавлении реагента к пресной глинистой суспензии.

### Ключевые слова:

буровые растворы, сульфированный битум, сульфированный асфальт, ингибирование набухания глин, пептизация глин, коагуляция.

### СПИСОК ЛИТЕРАТУРЫ

1. Improved wellbore stability in Tor/Ekofisk wells through shale-fluid compatibility optimization / E. Van Oort, C. Pasturel, J. Bryla, F. Ditlevsen // SPE/IADC Drilling Conference and Exhibition. – The Hague, The Netherlands, 2017. – P. 1–24.
2. Широков М.Н. Исключительная стабильность ствола скважины: что делать, когда не работает повышение плотности бурового раствора? // Бурение и нефть. – 2019. – № 9. – С. 46–49.
3. Reid P.I., Santos H. Ultra-low invasion drilling fluids: a practical route to reduced wellbore instability, reduced mud losses, wellbore



- strengthening and improved well productivity // SPE/IADC Indian Drilling Technology Conference and Exhibition. – Mumbai, India, 2006. – P. 1–12.
4. Буровые растворы на водной основе с применением латексных добавок: Евразийская патентная организация, № 010638: заявл. 02.08.2004; опублик. 30.10.2008. – 20 с.
  5. Wellbore drilling compositions: Patent 11078395 B2 USA. Fil. 18.06.2019; Publ. 03.08.2021.
  6. Aluminum-based HPWBM successfully replaces oil-based mud to drill exploratory well in the Magellan Strait, Argentina / M.A. Ramirez, S. Benaissa, G. Ragnes, A. Almaraz // SPE/IADC Middle East Drilling Technology Conference and Exhibition. – Cairo, Egypt, 2007. – P. 1–11.
  7. Кузьмин В.Н., Трефилова Т.В. Ингибирование буровых растворов с целью безаварийной проходки интервалов неустойчивых глинистых пород // Сетевое научное издание «Нефтяная провинция». – 2020. – № 1 (21) – С. 73–82.
  8. Рябцев П.Л. Компания «АКРОС»: инновационные системы буровых растворов и эффективные решения для бурения // Бурение и нефть. – 2015. – № 3. – С. 36–38.
  9. Термостойкий биополимерный буровой раствор: пат. Рос. Федерация, № 2711222, заявл. 15.11.2018; опублик. 15.01.2020. Бюл. № 2. – 9 с.
  10. Sulfonated asphalt: Patent 4514308 A USA. Fil. 29.07.1983; Publ. 30.04.1985.
  11. Архиповцов А.А., Маевский С.П., Харитонов В.В. Импортное замещение зарубежных реагентов для бурения. Сульфированный асфальт российского производства // Бурение и нефть. – 2016. – № 2. – С. 48–50.
  12. Мойса Ю.Н., Иванов Д.Ю., Марусов М.А. Ингибирующие и смазочные добавки для утяжеленных буровых растворов // Булатовские чтения: материалы II Международной научно-практической конференции. – Краснодар: ИД «Юг», 2018. – Т. 3. – С. 196–205.
  13. Production of sulfonated asphalt: Patent 3089842 A USA, Fil. 14.12.1959; Publ. 14.05.1963.
  14. Production of sulfonated asphalt: Patent 4741868 A USA, Fil. 04.03.1985; Publ. 03.05.1988.
  15. Process for preparing a sulfonated dispersant from petroleum asphalt fractions: Patent 5322556 A USA, Fil. 08.03.1993; Publ. 21.06.1994.
  16. Shen Q., Xian T., Yu B. Research on the preparation of sodium asphalt sulfonate and its mechanism of fluid loss control for drilling fluids // SPE International Symposium on Oilfield Chemistry. – San Antonio, Texas, 1995. – P. 1–21.
  17. Марусов М.А., Мойса Ю.Н. Смазочные и ингибирующие добавки для утяжеленных буровых растворов // Бурение и нефть. – 2018. – № 11. – С. 48–50.
  18. Буянова М.Г. Разработка технологии применения и совершенствование составов модифицированного бурового раствора для повышения эффективности строительства скважин: дисс. ... канд. техн. наук. – Уфа, 2021. – 190 с.
  19. Process for making sulfonated uitaite and well fluid additives including sulfonated uitaite: Patent 6514916 B1 USA, Fil. 12.09.2000; Publ. 04.02.2003.
  20. Additive for drilling fluids: Patent 7576039 B2 USA, Fil. 26.01.2005; Publ. 18.08.2009.
  21. ГОСТ 33213-2014. Контроль параметров буровых растворов в промысловых условиях. Растворы на водной основе. – М.: Стандартинформ, 2015. – 75 с.
  22. Рязанов Я.А. Энциклопедия по буровым растворам. – Оренбург: Летопись, 2005. – 664 с.
  23. Хилько С.Л., Титов Е.В., Федосеева А.А. Влияние сильных электролитов на водные растворы Na-солей нативных и сульфированных гуминовых кислот // Коллоидный журнал. – 2001. – № 5. – С. 706–710.

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