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The research of multifunctional properties of the new composition named AZ-1

Badania wielofunkcyjnych właściwości nowej kompozycji o nazwie AZ-1

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ABSTRACT: This article presents the results of the study of multifunctional properties of a new composition, with the conventional name AZ-1, which was prepared from various reagents under laboratory conditions. For this purpose, the results of its effect on a number of rheological parameters of commodity oil and the corrosion rate in hydrogen sulphide formation water have been interpreted. Laboratory experiments were conducted using concentrations of 100, 300, 500, 700 and 900 g/t of the composition, all following established standard methods. For the research purposes, the oil sample was taken from Narimanov field of SOCAR, and the aggressive medium was hydrogen sulphide formation water taken from well No. 1082 of "Bibiheybatneft" OGPD. Numerous experiments have shown that the optimum consumption rate of AZ-1 composition is 700 g/t. AZ-1 composition reduces the freezing temperature from +14°C to –8°C by improving the fluidity of the studied oil sample at optimal viscosity. The value of the shear stress limit of the anomalous oil sample is also drastically reduced. During the experiments carried out using the "cold finger test" method, it was found that AZ-1 composition has a high effect on oil deposits. At the temperature of +5°C of the "cold finger test", its efficiency was 90% at the optimal consumption rate. During the effect of AZ-1 composition on the corrosion rate in hydrogen sulphide formation water, the protection effect increases at the concentration of 100–700 g/t and varies between 85–98%. At 900 g/t, the value of the protective effect is relatively reduced to 82%, and this is an indicator that the optimum consumption rate of AZ-1 composition is 700 g/t.

Key words: corrosion, protective effect, corrosion rate, freezing temperature, shear stress limit.

STRESZCZENIE: W niniejszym artykule przedstawiono wyniki badań wielofunkcyjnych właściwości nowej kompozycji, której nadano nazwę zwyczajową AZ-1, przygotowanej z użyciem różnych odczynników chemicznych w warunkach laboratoryjnych. W tym celu dokonano interpretacji wpływu tej kompozycji na szereg parametrów reologicznych wody złożowej zawierającej siarkowodór. Eksperymenty laboratoryjne przeprowadzono przy użyciu stężeń 100, 300, 500, 700 i 900 g/t mieszaniny, stosując określone standardowe metody. Próbka ropy naftowej do badań została pobrana ze złoża Narimanov, należącego do SOCAR, a czynnikiem korozyjnym była woda złożowa zawierająca siarkowodór, pobrana z odwiertu nr 1082 należącego do OGPD „Bibiheybatneft". Liczne eksperymenty wykazały, że optymalny dodatek kompozycji AZ-1 wynosi 700 g/t. Kompozycja AZ-1 obniża temperaturę krzepnięcia z +14°C do –8°C, zwiększając płynność badanej próbki ropy naftowej przy jej optymalnej lepkości. Wartość granicznego naprężenia ścinającego anomalnej próbki ropy również uległa znacznemu obniżeniu. Podczas badań przeprowadzonych metodą „cold finger test" stwierdzono, że kompozycja AZ-1 ma duży wpływ na wytrącanie osadów z ropy naftowej. W badaniu metodą „cold finger test" w temperaturze +5°C skuteczność wynosiła 90% przy optymalnym dodatku kompozycji. Podczas badania wpływu kompozycji AZ-1 na szybkość korozji w wodzie zawierającej siarkowodór, efekt ochronny wzrasta przy stężeniach 100-700 g/t, wynosząc 85-98%. Przy 900 g/t wskaźnik efektu ochronnego ulega względnemu obniżeniu do 82%, co wskazuje, że optymalny dodatek kompozycji AZ-1 wynosi 700 g/t.

Słowa kluczowe: korozja, efekt ochronny, szybkość korozji, temperatura krzepnięcia, graniczne naprężenie ścinające.

Introduction

Currently, the composition of the oil dispersion systems produced in countries with developed oil industry is characterised by a high proportion of components such as asphaltene, resin, and paraffin. These components significantly impact oil production, its preparation for extraction, and its transport through pipelines. Asphaltene-resin-paraffin compounds dispersed in oil increase rheological parameters values by imparting non-Newtonian properties to the oil as the temperature decreases. This, in turn, leads to complications in well-storage-transportation systems (Glushchenko, 2007; Khidr, 2011). The accumulation

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of asphaltene-resin-paraffin deposits separated from the volume of the dispersed oil system and deposit in pipes used in the process of oil production and transportation as well as on the internal surfaces of various oil field facilities, generally leads to the formation of technological complications, production decrease, and facilities failure. In some cases, the formed paraffin deposits can partially or completely limit the production and transportation of oil to economically unviable volumes. In such a situation, it is necessary to carry out various processes aimed at stopping oil production and transportation or cleaning asphaltene-resin-paraffin deposits (Tolokonsky et al., 2003). It should be noted that the amount of asphaltene-resin-paraffin components contained in oil affects both the process of preparing oil for transportation and its transportation itself. Thus, the increase in the amount of compounds such as asphaltene, resin, and paraffin in the produced oils leads to the formation of water-oil emulsions with aggregative and kinetic stability, and increases the viscosity and freezing temperature of oil (Jennings and Weispfennig, 2005). The formation of paraffin deposits on the internal surfaces of oilfield equipment and the measures to be taken to control them is currently one of the most important tasks facing oil research scientists. A variety of technological measures and methods are used to prevent paraffin deposition. However, in addition to the implementation of large-scale research works for the further improvement and economically efficient application of these methods, the clarification of the mechanism of influence on the transportation properties of oils characterised by a high amount of asphaltene-resin-paraffin components of both oil deposits and chemical reagents is a current issue arising from the demand of today (Bakhtizin et al., 2016; Matiyev et al., 2016).

Combatting paraffin deposition in the oil industry is essentially two-pronged. The first is to prevent the formation of paraffin deposits, and the second is to purify and bring to the surface paraffin that has already settled. Currently, mechanical, physical, chemical, and combined methods are used against asphaltene-resin-paraffin deposits that may form on the internal surfaces of oilfield facilities (Shadrina, 2015). Research indicates that the chemical method is considered the most effective among the mentioned methods in terms of economic and application technology. It should be noted that in the chemical method, various chemical reagents are applied to the internal surfaces of oilfield facilities (Tolokonsky et al., 2003; Mingalev et al., 2022). When selecting chemical reagents for application, the most important criteria are local production, cost-effectiveness, environmental friendliness, and their effective impact on paraffin deposits (Nurulayev et al., 2022). Also, it should be noted that the main advantages of chemical reagents used against oil deposits include the prevention of paraffin deposition through the injection of small doses, maintenance of long-term effects, simplicity of technology, and the potential for automation of technological processes. As already mentioned, the high content of asphaltene-resin-paraffin components in the oil not only makes it highly viscous but also causes the formation of stable water-oil emulsions. Another problem that occur during the production, storage, and transportation of this type of oil is the electrochemical corrosion of the internal surfaces of the facilities (Wilde, 2009; Shadrina, 2015). Research shows that the corrosion of the internal surfaces of oil-mining facilities is caused by the presence of aggressive elements in oil, including sulphur and oxygen compounds, hydrogen sulphide and carbon dioxide, as well as mineral salts dissolved in formation water. The effect of microbiological infections also intensifies this process and increases the corrosion of the internal surface of the facilities. As a result of internal surface corrosion, the oil industry suffers great economic and environmental damage. In such aggressive media, the presence of bacteria, particularly sulphate-reducing bacteria, exacerbates the damage caused by internal surface corrosion.

Due to the above-mentioned problems, the use of multifunctional compositions in the oil industry has recently become widespread. Considering these issues, the development of an effective, complex composition that addresses these problems simultaneously was set as a goal. For this reason, the effect of the AZ-1 composition, prepared by us under laboratory conditions, on paraffin deposition on the internal surfaces of oilfield facilities and its corrosion protection properties was studied under laboratory conditions for the first time (Khairov, 1996; Nurullayev et al., 2022).

The research objective is to investigate the multifunctional properties of AZ-1 composition under laboratory conditions.

Research methodology

The effect of the AZ-1 composition on the corrosion protection efficiency and rheological parameters of high-paraffin oils was studied under laboratory conditions. The composition with conventional name AZ-1 is a mixture of MARZA-1 + + ND-12 + BAF-1 in a 1:24:11 ratio. MARZA-1, which can be produced industrially from local raw materials, is a reagent of organic origin with triple bonds, the molecules of which are composed of carbon, hydrogen, halogen and oxygen element atoms. ND-12 demulsifier is a non-ionic surfactant produced in Azerbaijan and is currently used in oil dewatering and desalination under mining conditions. BAF-1 is a supramolecular nanostructured substance.

To determine the anticorrosive effectiveness of the AZ-1 composition, laboratory tests were carried out using formation water taken from the well No. 1802 of "Bibiheybatneft"

OGPD. The tests lasted for six hours and were carried out at a temperature of 25°C in a U-shaped apparatus following GOST-9506-87. The effect of different amounts of the composition on the corrosion rate was studied on samples made of Ct-3 steel with dimensions of 30 × 20 × 10 mm. The laboratory tests were carried out in the following order. First, the pre-purified steel samples were weighed on an analytical balance and placed in a four-necked flask equipped with a mechanical stirrer. The calculated amount of reservoir water and composition was then added to the flask. Stirring was performed continuously at 20 ±3°C, 800 rpm. After stirring for six hours, the system was left to stand for a certain period of time, then the steel samples were washed, cleaned, and dried with alcohol. These samples were then re-weighed on the analytical balance. To determine the effect of AZ-1 composition, verification experiments were conducted in the formation water environment without the presence of AZ-1. Based on the results of numerous experiments, the corrosion rate and protection efficiency of the composition were calculated using the gravimetric method. The experiments were carried out at the consumption rate of AZ-1 composition of 100, 300, 700, 900 g/t.

The effect of AZ-1 composition on the rheological parameters of high-paraffin oil was also investigated. A high-paraffin oil sample from the Narimanov oil field was used for this purpose. The effect of the composition on paraffin deposition was checked. The effectiveness of the composition was investigated using the "cold finger test" method. It should be noted that this method is much more suitable for mining conditions and allows to evaluate the effect of chemical reagents against paraffin deposition both qualitatively and quantitatively. Moreover, this method allows for the development of the application technology of the discovered ani-paraffin reagent. The tests carried out under laboratory conditions using the "cold finger test" method allow to study the effectiveness of the reagent on the basis of the change in the amount of paraffin accumulated in the cold finger due to the change in the freezing temperature of paraffin oils as a result of the action of chemical reagents. The apparatus shown in Figure 1 was used to carry out the experiments using this method.

The "cold finger test" method is carried out in the following order. First, a 1.5 litre sample of crude oil is poured into the vessel of the apparatus shown in Figure 1. Then, in order to eliminate the initial formation of paraffin crystals, the oil is heated to a temperature of 60°C and the temperature is kept constant in the thermostat by means of a contact thermometer. When the experiments are carried out, the stirrer in the Dewar vessel is started. The experiments are continued by lowering the temperature to 0°C in the second thermostat. The oil sample is kept under these conditions for 20 minutes, after which the amount of paraffin accumulated in the "cold finger" is determined by weighing it on an analytical balance. The experiments are then continued at temperatures of 5, 10, 15 and 20°C. Predetermined amounts of the AZ-1 composition are added to the oil samples and the experiments are carried out in the order indicated. Finally, the amount of paraffin crystals accumulated on the "cold finger" at different temperatures is determined by weighing on an analytical balance.

Results and discussion

The rheophysical and chemical properties of the crude and commodity oil samples used in the laboratory tests are given in Table 1.

First of all, the influence of the AZ-1 composition on a number of rheological parameters of the commodity form of oil the sample from the Narimanov field was studied in laboratory conditions. The process was carried out in the temperature range of 10–60°C. The amounts of 300, 500, 700 g/t of the composition were used. As a result of experimental and theo-

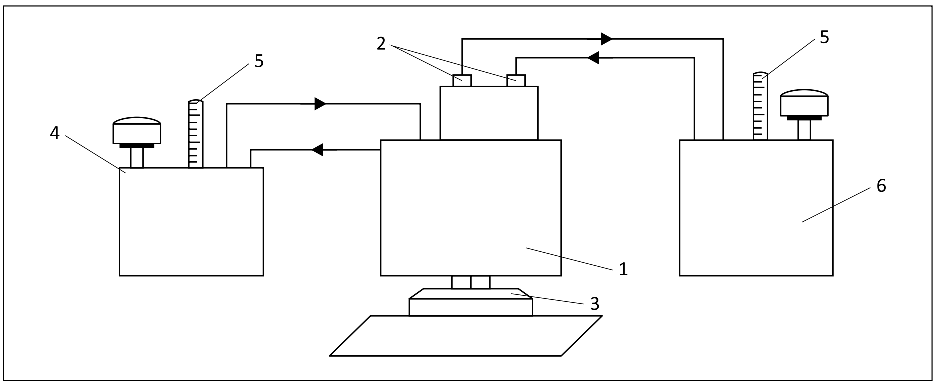

Figure 1. Schematic diagram of the special apparatus for the determination of paraffin deposition by the "cold finger test" method: 1 – Dewar vessel, 2 – "cold finger", 3 – mixer, 4 – heater, 5 – thermometer, 6 – refrigerator

Rysunek 1. Schemat zasady działania specjalnego urządzenia do oznaczania osadzania parafiny metodą „cold finger test": 1 – naczynie Dewara, 2 – „cold finger", 3 – mieszalnik, 4 – grzałka, 5 – termometr, 6 – lodówka

Table 1. Physical and chemical properties of the oil sample
Tabela 1. Fizyczne i chemiczne właściwości próbki ropy

Parameters	Quantity	Method of determination
Water content [%]	25	GOST 33700-2015
Density, ρ_4^{20} [kg/m^3]	899	GOST 3900-85
Paraffin content [%]	19.8	GOST 11851-85
Resin content [%]	23.3	GOST 11851-85
Asphaltene content [%]	2.65	GOST 11851-85
Freezing temperature [°C]	+14	GOST 20287-91
Melting temperature of paraffin [°C]	45	GOST 11858-83

retical calculations, the values of some rheological parameters for the studied oil sample at different temperatures and various layers of the composition are given in Table 2.

The results of the laboratory experiments given in Table 2 indicate that the AZ-1 composition has an effective impact on the fluidity of the oil sample studied. As can be seen from the table, the oil sample without the addition of the composition has poor fluidity, being a non-Newtonian fluid up to a temperature of 40°C, and starting from a temperature of 50°C, it becomes a Newtonian fluid. After the addition of the AZ-1 composition, this indicator drops to 30°C. At the same time, the value of the shear stress limit decreases sharply. From the results of the experiments conducted with different concentrations of the composition, it was found that the most effective amount is 700 g/t.

The mass of asphaltene-resin-paraffin deposits (ARDP) accumulated on the cold surface of the oil sample without reagent and with different amounts of reagent added was determined by the "cold finger test" method. The experimental procedure lasted for two hours, during which time the temperature of the "cold finger" was 0°C, 5°C, 10°C, 15°C, 20°C, 25°C, 30°C. At each temperature, the mass of paraffin deposits accumulated on the surface of the tube was measured at 0, 20, 40, 60, 80, 100, 120 minutes using an analytical balance. Table 3 shows the results of the "cold finger test" for the crude oil sample.

Table 2. Influence of AZ-1 composition on rheological parameters of the oil sample
Tabela 2. Wpływ kompozycji AZ-1 na parametry reologiczne próbki ropy

Composition quantity [g/t]	Temperature [°C]	Shear stress limit [Pa]		Data consistency [mPa · s]		Non-Newtonian exponent [n]	
		experiment	calculation	experiment	calculation	experiment	calculation
0.00	30	4.90	5.30	345.6	323.6	0.728	0.689
0.00	40	1.20	0.97	91.9	84.4	0.864	0.851
0.00	50	0	0	18.7	16.6	1.000	1.000
0.00	55	0	0	12.5	11.4	1.000	1.000
0.00	60	0	0	8.5	9.5	1.000	1.000
0.00	65	0	0	5.7	6.0	1.000	1.000
300	10	46.00	43.90	3349.4	3358.2	0.578	0.564
300	20	7.10	7.30	313.8	323.9	0.793	0.795
300	30	0	0	29.7	32.9	0.999	0.914
300	40	0	0	18.5	16.7	1.000	1.000
300	50	0	0	12.9	11.8	1.000	1.000
300	60	0	0	8.8	8.4	1.000	1.000
500	10	19.90	22.20	924.9	1040.0	1.000	1.000
500	20	1.20	0.99	112.2	114.4	0.918	0.848
500	30	0	0	29.3	27.8	1.000	1.000
500	40	0	0	17.9	16.2	1.000	1.000
500	50	0	0	12.7	12.9	1.000	1.000
500	60	0	0	8.7	9.2	1.000	1.000
700	10	29.40	31.74	1342.9	1347.2	0.683	0.649
700	20	3.96	4.27	148.6	144.8	0.877	0.845
700	30	0	0	29.3	27.4	1.000	1.000
700	40	0	0	19.3	16.9	1.000	1.000
700	50	0	0	12.9	11.3	1.000	1.000
700	60	0	0	0	8.7	7.900	1.000

Table 3. Amount of deposits accumulated on the surface of the "cold finger" from high paraffin oil
Tabela 3. Ilość osadów zgromadzonych na powierzchni „cold finger" z ropy o wysokiej zawartości parafiny

Time [minute]	Temperature of "cold finger"						
	0°C	5°C	10°C	15°C	20°C	25°C	30°C
	Mass of oil deposits [g]						
0	0.122	0.108	0.100	0.095	0.087	0.085	0.055
20	0.181	0.161	0.123	0.118	0.112	0.085	0.058
40	0.241	0.191	0.158	0.153	0.141	0.079	0.053
60	0.311	0.211	0.181	0.176	0.156	0.083	0.057
80	0.351	0.251	0.190	0.185	0.176	0.087	0.062
100	0.356	0.271	0.210	0.205	0.178	0.093	0.068
120	0.371	0.281	0.212	0.207	0.191	0.087	0.062

Experiments were carried out by adding 100, 300, 500, 700, 900 g/t of the AZ-1 composition to the oil samples studied, following the methodology mentioned above. After determining the amount of deposits accumulated on the cold surface at different temperatures by weighing, the efficiency of the composition was calculated according to the following mathematical dependence:

$$K = \frac{m_1 - m_2}{m_1} 100\%$$

where:
K – the efficiency of the composition,
m_1 – the mass of ARPD in a non-composite medium,
m_2 – he mass of ARPD in the medium containing the composition.

In Table 4, the values of the effectiveness of the AZ-1 composition against oil deposits are calculated at a temperature of 5°C of the "cold finger".

Using the values obtained based on the mathematical dependence presented in Table 4, a histogram of the effectiveness of the AZ-1 composition against oil deposits in the oil sample studied was constructed (Figure 2).

As can be seen from Figure 2, as the amount of AZ-1 composition increases from 100 g/t to 700 g/t, its efficiency increases and then decreases again at 900 g/t. The highest efficiency of the composition was 90% and was observed at a concentration of 700 g/t. This result in turn indicates that the optimum consumption rate of the AZ-1 composition is 700 g/t.

The effect of the new AZ-1 composition on the freezing temperature of the oil sample was also studied following RD-39-3-812-82 method. During the process, concentrations of 100, 300, 500, 700, 900 g/t of the composition were used, and the obtained results are shown in Figure 3.

As can be seen from Figure 3, the freezing temperature of the oil sample studied is +14°C. After adding the AZ-1 composition to the sample, there is a change in the freezing temperature value. Thus, the freezing temperature of oil added at 100 g/t is +10°C, +5°C at 300 g/t, +1°C at 500 g/t, –8°C at 700 g/t and +3°C at 900 g/t. It can be seen that the maximum

Table 4. Equations for calculating the effectiveness of the AZ-1 composition
Tabela 4. Równania do obliczania efektywności kompozycji AZ-1

Composition quantity [g/t]	Efficiency equation	Effect of composition [%]
100	$K = \frac{m_1 - m_2}{m_1} 100\%$	$K = \frac{0.281 - 0.1686}{0.281} 100\%$
300		$K = \frac{0.281 - 0.1124}{0.281} 100\%$
500		$K = \frac{0.281 - 0.07025}{0.281} 100\%$
700		$K = \frac{0.281 - 0.0281}{0.281} 100\%$
900		$K = \frac{0.281 - 0.10116}{0.281} 100\%$

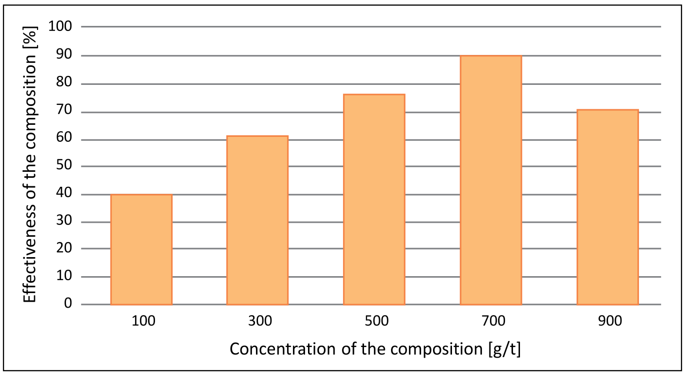

Figure 2. Effectiveness of the AZ-1 composition against oil deposits

Rysunek 2. Efektywność kompozycji AZ-1 względem osadów wytrącanych z ropy

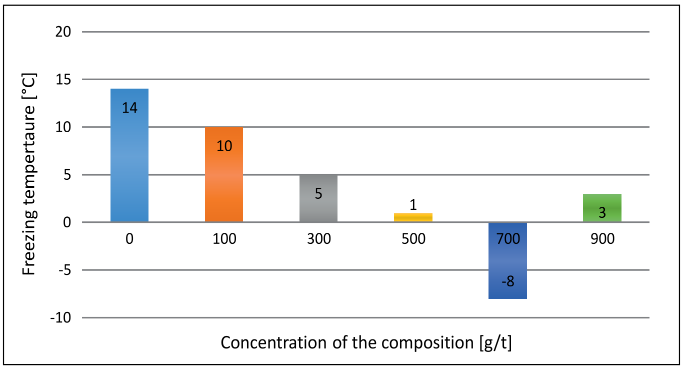

Figure 3. Effect of AZ-1 composition on oil freezing temperature

Rysunek 3. Wpływ składu AZ-1 na temperaturę krzepnięcia ropy

effect of the composition occurs at a concentration of 700 g/t, and the concentration decreases sharply at 900 g/t. This result once again suggests that the optimum concentration of the AZ-1 composition is 700 g/t.

Under laboratory conditions, the electrochemical corrosion protection efficiency of AZ-1 composition was studied following GOST-9506-87 standard. Formation water sample taken from well No. 1082 of SOCAR "Bibiheybatneft" OGPD was used as an aggressive medium. The analysed results of numerous experiments are given in Table 5.

As can be seen from the results in Table 5, the multifunctional composition AZ-1 shows a high efficiency in corrosion protection. The protective effect increases in the range of 100–700 g/t of composition concentration and varies between 85–98%. At 900 g/t, the value of the protective effect is relatively reduced to 82%, which indicates that the optimum consumption rate of the AZ-1 composition is 700 g/t.

Thus, the effect of the composition prepared using various reagents, designated AZ-1, on the rheological parameters of the commodity oil sample, the freezing temperature, the demulsification of the crude oil sample at dilution rate of 25%, and the corrosion rate in the formation water with hydrogen sulphide was studied for the first time, and the new composition was found to have multifunctional properties with effective impact.

Conclusion

1. The effect of the composition with conventional name AZ-1, prepared using different purpose reagents, on some rheological parameters of the commodity form of an anomalous oil sample and on the rate of electrochemical corrosion in hydrogen sulphide formation water has been studied for the first time and it has been found to have multifunctional properties with effective impact.
2. In numerous tests under laboratory conditions, using AZ-1 composition at concentrations of 100, 300, 500, 700 and 900 g/t, its optimum consumption rate was determined to be 700 g/t.
3. It has been found that the AZ-1 composition at the optimum rate of consumption greatly reduces the value of the shear stress limit of the oil sample and the amount of asphaltene-resin-paraffin deposits accumulated on the surface of the "cold finger".
4. As for the effect of AZ-1 composition on the freezing temperature of the oil sample taken for the research, the change in concentration in the range of 100–700 g/t results

Table 5. Protective effects of AZ-1 composition in hydrogen-sulphide formation water

Tabela 5. Efekty ochronne kompozycji AZ-1 w wodzie z zawartością siarkowodoru

Composition	C_{inh} [mg/l]	K [g/m² · hour]		Delay coefficient, γ	Penetration coefficient, P_k [mm/year]	Protective effect, Z [%]
		without inhibitor	with inhibitor			
AZ-1	0.0	1.3260	–	–	–	–
	100		0.19890	6.67	0.222768	85
	300		0.13260	10.00	0.148512	90
	500		0.03978	33.26	0.044554	97
	700		0.02652	50.00	0.029702	98
	900		1.08732	1.22	1.217798	82

in a change in the value of the freezing temperature of the oil between +14 and –8°C.

5. The composition has an effect on the rate of corrosion in hydrogen sulphide formation water. Thus, the protective effect increases in the range of 100–700 g/t of composition concentration and varies between 85–98%. At 900 g/t, the value of the protection effect is relatively reduced to 82%, which indicates that the optimal consumption rate of AZ-1 composition is 700 g/t.
6. The effective results obtained during numerous laboratory tests suggest that the AZ-1 composition prepared from various purpose reagents should be widely used in mining conditions in the oil industry.

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