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RESEARCH OF A NEW MULTIFUNCTIONAL COMPOSITION AGAINST THE CORROSION OF THE INTERNAL SURFACE OF OIL PIPELINES IN THE MINE SHAFT

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For the first time, a chloroprene reagent (named as Z-1) has been used against corrosion in various aggressive environments under laboratory conditions. The corrosion protection properties of the reagent Z-1 have been studied in formation waters taken from oil wells No. 2646, 33151, 4012, 31193 and 33016 in operation at Balakhani Oil OGED. Samples made of Ct3 and P-105 brand steels with dimensions of $42\times15\times5$ mm have been used during the tests. Experiments have been performed under dynamic conditions at room temperature for six and twenty-four hours, and the corrosion rate has been determined by gravimetric method. During the experiments, concentrations of 10, 15, 20 and 25 mg/l of Z-1 composition were used. The analysis of results from numerous experiments conducted with both types of steel revealed that the optimal concentration of the composition is 25 mg/l. The protection efficiency of the composition Z-1 in the formation waters of the abovementioned oil wells during the six-hour experiment was as follows: for Ct3 samples, it ranged from 75% to 94%, 75% to 97%, 76% to 98%, 72% to 94%, and 68% to 87%, respectively, while for P-105 steel samples, it ranged from 76% to 96%, 72% to 92%, 73% to 85%, 70% to 90%, and 72% to 96%, respectively. During 24-hour corrosion tests, the protection efficiency of the composition Z-1 was 73–92%, 74–96%, 75–97%, 70–92%, and 66–85% for Ct3 steel samples and 75–94%, 70–91%, 72–83%, 68–89%, and 71–95% for P-105 steel samples, respectively.

Keywords: penetration coefficient, corrosion rate, inhibitor, concentration, formation water, protection effect.

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Introduction

Currently, the rapid development of the oil industry requires increasing the operational efficiency of wells in oil extraction. For this reason, in order to stabilize oil production and increase the operational efficiency of wells, the protection of the internal surface of mine pipelines from electrochemical corrosion processes caused by an aggressive environment remains an urgent issue. It is known that in most cases, in order to stabilize and increase oil production, many technical and technological methods, including injecting water and gas into the reservoir, changing the type of operation of the wells, in particular, switching to rod pump and depth pump methods, thermalizing the layer, injecting chemical reagents

and the like measures are implemented. As a result of such measures, oil fields are enriched with substances that create an aggressive environment, the amount of oxygen, carbon and hydrogen-sulfide gases increases significantly, which in turn causes the acceleration of the corrosion process inside the pipes $[1-7]$.

The results of the conducted microbiological analysis confirm the presence of microbiological groups, including sulfate-reducing bacteria (SRB), iron bacteria (IB), hydrocarbon-oxidizing bacteria (HOB) and thion bacteria (TB) in the reservoir waters produced together with oil. Mainly sulfate-reducing bacteria cause severe corrosion of the inner surface of underground pipelines. It should be noted that in recent years their amount reaches 10⁷ per 1 ml of some production well

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products. In general, the use of irrigation in the oil production process leads to enrichment of productive oil reservoirs with bacteria. Some studies show that 80% of equipment failures in the oil industry are due to corrosion caused by microorganisms.

An effective way to protect the inner surface of underground pipelines from corrosion is the application of inhibitors. The main function of inhibitors is to reduce the corrosion aggressiveness of the fluid produced from the well. Without studying the mechanism of action of inhibitors, it is impossible to select an effective inhibitor for any specific condition. Thus, the inhibitor shows different effects depending on the environment, because the temperature of the aggressive environment, the speed of movement of the liquid, its aggressiveness and many other factors affect the effectiveness of the inhibitor. One of the effective measures applied in the protection of oil from corrosion in internal transport systems of the mine is the preparation of multi-functional bactericidal-inhibitory compounds $[6,8-11]$.

Analysis of the reagents used in the oil fields of Azerbaijan showed that cost-effective corrosion inhibitors were used mainly in the production of hydrogen-sulfide (acidic medium) and sulfur-free (neutral medium) cases. An inhibitor that is effective in an acidic environment is less effective in a neutral environment, and conversely, an inhibitor that is effective in a neutral environment may be less effective in an acidic environment. In addition, using the same reagent for a long time is not very effective. Thus, although some reagents have a very strong bactericidal effect on most microbiological groups at the beginning of their use, with prolonged use of that reagent, some groups of microorganisms adapt to that environment. Some reagent that previously had a bactericidal effect on that group wanes over time, and eventually that group of microorganisms may use those reagents as nutrient components. From this point of view, it is more appropriate to alternate the application of bactericides in oil fields in a planned manner. Each newly developed reagent should be tested in a mixture of sea water and formation waters with products produced from all horizons of the field; and its bactericidal property, its effect on corrosion of relevant metal equipment, pH of the environment, as well as its interaction with chemical reagents that can be applied in the case of salt deposition in that environment, paraffin deposition and other complications in wells should be studied.

Long-term exploitation of oil fields caused their watering, which increased the aggressiveness of corrosion. Depending on the aggressiveness of the medium, the process of electrochemical and biological

corrosion, sometimes the transition of biological corrosion to electrochemical corrosion, as well as the reverse process became characteristic. Under such difficult conditions, the use of inhibitors unilaterally slowing down the corrosion process does not give the desired economic results. From this point of view, there was a need to investigate bactericide inhibitors of complex action for the protection of oilfield equipment against electrochemical and biological corrosion. Although these inhibitors consist of several components, each of which separately has certain effectiveness, their mixture slows down various corrosive effects and has a complex effect by creating a synergistic effect [12–14].

The work objective is to develop and study the properties of a complex effective new multi-functional composition for corrosion protection of the inner surface of oil mine pipelines.

Experimental

Chloroprene reagent was used to protect the inner surface from corrosion. Its chemical formula is $CH₂=CCI–CH=CH₂;$ it is a colorless liquid with a boiling point of 59.40C. Its molar mass is 88.5365 g/mol and its density is 960 kg/m³.

Chloroprene as a corrosion inhibitor was first studied under laboratory conditions in reservoir waters taken from various wells at the «Balakhani Oil» Oil Gas Extraction Department. For this, the steel plates taken for testing were cleaned of dirt and rust, polished, and then wiped with a solvent (alcohol) and dried. Laboratory tests were conducted in accordance with the state standard SS 9.506-87 in a U-shaped device at a temperature of 20°C for 6 hours. In an aggressive environment, the consumption amount of the composition was in the range of $10-30$ mg/l. In the tests, a mechanical mixer that circulates water 500 times per minute was used, which allows the oxygen flow, which acts as a depolarizer, to be fully ensured.

To carry out the tests, the surface of the steel samples made of Ct3 and P-105 brand steels with dimensions of $42\times15\times5$ mm was pre-degreased with organic solvents, and when they were put to the test, their surfaces were wiped with a cloth swab soaked in ethyl alcohol (according to the state standard 5962-67), and then the samples were weighed on an analytical scale and their initial weight was determined. After the test, the corrosion products on the samples were cleaned in accordance with the state standard 9.907-83, then washed with technical water under the tap, rinsed in distilled water and dried through filter paper. The type of corrosion and the coverage area were determined by visual inspection of the samples removed from the test. Then they were reweighed on an analytical scale and the weight loss

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occurring in them during the test period was determined. Based on the determined weight loss, the corrosion rate of the metal was calculated.

Metal weight loss $(∆m)$ is calculated by the following equation:

$$
\Delta m = m_0 - m_1,\tag{1}
$$

where m_0 and m_1 are the weights of the samples before and after corrosion tests, respectively.

During the experiment, metal weight loss is calculated for three steel plates and the average weight is found. During gravimetric tests, the weight index of corrosion rate in both reagentless and reagent media is characterized by the corrosion rate $(K_m, g/(m^2 \cdot h))$ and is calculated by the following mathematical equation:

$$
K_m = \frac{\Delta m}{S \cdot \tau} \tag{2}
$$

where S is the average surface area calculated for three samples (m²); and τ is the duration of the test (hours).

Based on the corrosion rate, the penetration coefficient is determined as follows:

$$
K_{p} = \frac{8760 \cdot K_{m}}{\rho},\tag{3}
$$

where K_p is the penetration coefficient (mm/year); K_m is the corrosion rate (g/m²·h); ρ is the density of the studied metal (g/cm^2) ; and 8760 is a constant number of hours in a year.

The equation used to calculate the inhibition factor (γ) is as follows:

$$
\gamma = \frac{K_0}{K_{\text{inh}}},\tag{4}
$$

were K_0 is the rate of corrosion in the absence of a reagent; and K_{inh} is the corrosion rate in the presence of the reagent.

The protection effect of the reagent is calculated by the following equation:

$$
Z = \frac{K_0 - K}{K_0} \cdot 100\%,\qquad(5)
$$

where K_0 is the corrosion rate of the sample in a reagent-free environment (g/m²·h); and K_{inh} is the corrosion rate of the sample in reagent environment (g/m^2-h) .

The area of Ct3 and P-105 brand steel samples

with dimensions of $42\times15\times5$ mm is calculated according to the following formula:

$$
S_N = 2ah + 2bh + 2ab,
$$
 (6)

where S_N is the surface area of the steel sample (m²); a is the sample length (mm); b is the sample width (mm); and h is the height of the sample (mm).

Since $a=42$ mm, $b=15$ mm, and $h=5$ mm, the surface area of the steel sample taken for testing was S_N =2⋅42⋅5+2⋅4215+2⋅15⋅5=1830 mm²=0.00183 m².

Results and discussion

It is known that an increase in the amount of water in oil wells leads to an increase in the amount of elements with corrosion aggressiveness, including sulfur, oxygen compounds, hydrogen-sulfide and carbon dioxide, as well as mineral salts dissolved in formation waters and microorganisms that cause biological corrosion. The mentioned substances contained in formation water mainly increase the corrosion rate of the oil field equipment. For this reason, it is necessary to protect the inner surface of the pipelines that carry out the underground transportation of the oil well products delivered to the surface of the earth against electrochemical and microbiological corrosion.

First of all, in order to determine the optimal rate of consumption of reagents to be applied against aggressive environments, the aggressiveness of the operating environment and the concentration of the ions that create this aggressiveness should be determined. The experiments were carried out under the laboratory conditions in formation waters taken from the oil wells in operation at the «Balakhani Oil» OGED.

The laboratory analysis of formation waters showed that the amount of hydrogen sulfide gas in the formation waters of «Balakhani Oil» oil and gas extraction department varied from 16.7 mg/l to 101.6 mg/l. Since the oil wells of this OGED have been in operation for a long time, the amount of aggressive ions in the formation waters has increased significantly as the dilution reached the limit of 98%. It should be noted that when taking formation water samples from the production wells for the experiment, due to the low pressure, the solubility of carbon dioxide and hydrogen sulfide is relatively reduced and these gases can be separated from the water by evaporation. During packaging and research, a certain amount of gases is lost due to the fact that the hermeticity of the system is not fully ensured. This causes a change in pH, which is an indicator of hydrogen in the environment.

Under laboratory conditions, the effect of chloroprene on the corrosion rate of P-105 and Ct3 steel samples in aggressive formation waters was studied. The experiments were carried out for 6 hours in formation waters taken from active wells at

«Balakhani Oil» oil and gas extraction department. The consumption amount of chloroprene in the corrosion environment was 10–30 mg/l. The obtained results are given in Tables 1–5.

Table 1

Effect of chloroprene on the rate of corrosion in formation water taken from well No. 2646 of «Balakhani Oil» oil and gas extraction department (6-hours tests)

C_{inh} , g/t	K_0 , g/m^2 ·h	K_{komp} , g/m ² ·h		K_p , mm/year	$Z, \%$		
Ct ₃ steel samples							
$^{(1)}$	2.4318						
10		0.6323	3.84	0.708	74		
20		0.2918	8.33	0.326	88		
30		0.1459	16.6	0.163	94		
P-105 steel samples							
$^{(1)}$	2.0304				$_{0}$		
10		0.4873	4.16	0.545	76		
20		0.2030	10.0	0.227	90		
30		0.0812	25.0	0.090	96		

Table 2

Effect of chloroprene on the rate of corrosion in formation water taken from well No. 33151 of «Balakhani Oil» oil and gas extraction department (6-hours tests)

Table 3

Effect of chloroprene on the rate of corrosion in formation water taken from well No. 4012 of «Balakhani Oil» oil and gas extraction department (6-hours tests)

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Table 4

Effect of chloroprene on the rate of corrosion in formation water taken from well No. 31193 «Balakhani Oil» oil and gas extraction department (6-hours tests)

Table 5

Effect of chloroprene on the rate of corrosion in formation water taken from well No. 33016 of «Balakhani Oil» oil and gas extraction department (6-hours tests)

C_{inh} , g/t	K_0 , g/m ² ·h	K_{komp} , g/m ² ·h		K_p , mm/year	$Z, \%$	
Ct ₃ steel samples						
$\bf{0}$	1.5928		U		0	
10		0.5096	3.12	0.570	68	
20		0.3822	4.16	0.428	76	
30		0.2070	7.69	0.231	87	
P-105 steel samples						
θ	2.5430		O	0	0	
10		0.7120	3.57	0.797	72	
20		0.3051	8.33	0.341	88	
30		0.1017	25.0	0.113	96	

Tables $1-5$ show that the P-105 steel is subjected to relatively sharper corrosion effects in the environment of formation water mixture than Ct3 steel. In addition to general corrosion, pitting corrosion is assumed to occur in the steel samples in the environment. During the 6-hour tests, the corrosion rate of Ct3 and P-105 brand samples at concentrations of 10–30 mg/l of the reagent in the formation waters taken from wells No. 2646, 33151, 4012, 31193, and 33016 of «Balakhani Oil» oil and gas extraction department was 0.6323–0.1459, 0.4873–0.0812, 0.3816–0.0456, 0.9593–0.2741, 0.3380–0.0275, $0.6174-0.1143, 0.3497-0.0749, 1.002-0.3342,$ 0.5096–0.2070, and 0.7120–0.1017 $g/m²·h$, respectively. The protection effect of chloroprene ranges between 74–94%, 76–96%, 75–97%, 72–92%, 76–98%, 73–95%, 72–94%, 70–90%, 68–87%, and 72–96%, respectively.

In addition, studies were carried out for 24 hours in the formation waters taken from wells in operation

at «Balakhani Oil» oil and gas extraction department, and the obtained results are given in Tables 6–10.

It can be seen from Tables $6-10$ that during the 24-hour test, the corrosion rate of Ct3 and P-105 steel samples at the concentrations of 10–30 mg/l of the reagent Z1 in the formation waters taken from the wells No. 2646, 33151. 4012, 31193, and 33016 is 0.1172–0.0347, 0.0830–0.0234, 0.0708–0.0109, $0.1861-0.0558$, $0.0640-0.0073$, $0.1199-0.0299$. 0.0669–0.0200, 0.2056–0.0707, 0.0966–0.0426, and $0.1418 - 0.0244$ g/m² \cdot h, respectively. The respective protection effect of chloroprene ranges between 73–92%, 75–94%, 74–96%, 70–91%, 74–97%, 72–93%, 70–91%, 68–89%, 66–85%, and 71–95%.

Thus, the chloroprene reagent has a significant effect on the rate of the electrochemical corrosion process occurring in the hydrogen sulfide formation water taken from different wells, showing a high protective effect.

Table 6

Effect of chloroprene on the rate of corrosion in formation water taken from well No. 2646 of «Balakhani Oil» oil and gas extraction department (24-hours tests)

Table 7

Effect of chloroprene on the rate of corrosion in formation water taken from well No. 33151 of «Balakhani Oil» oil and gas extraction department (24-hours tests)

Table 8

Effect of chloroprene on the rate of corrosion in formation water taken from well No. 4012 of «Balakhani Oil» oil and gas extraction department (24-hours tests)

Conclusions

1. The effect of chloroprene reagent on the corrosion rate of the hydrogen sulfide formation water taken from wells No. 2646, 33151, 4012, 31193 and 33016 of «Balakhani Oil» OGED was studied for the first time, samples made of Ct3 and P-105 steels being used in the experiment lasting 6 and 24 hours. The consumption rate of chloroprene reagent was up to 30 mg/l.

2. The protective effect of chloroprene at concentrations of 10–30 mg/l of the reagent for Ct3 and P-105 steel samples in the formation waters taken

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Table 9

C_{inh} , g/t	K_0 , g/m ² ·h	K_{inh} , g/m ² ·h		K_p , mm/year	$Z, \%$		
Ct ₃ steel samples							
	0.2230			0			
10		0.0669	3.33	0.074	70		
20		0.0289	7.71	0.032	87		
30		0.0200	11.15	0.022	91		
P-105 steel samples							
	0.6428			0			
10		0.2056	3.12	0.230	68		
20		0.1478	4.35	0.165	77		
30		0.0707	9.09	0.079	89		

Effect of chloroprene on the rate of corrosion in formation water taken from well No. 31193 of «Balakhani Oil» oil and gas extraction department (24-hours tests)

Table 10

Effect of chloroprene on the rate of corrosion in formation water taken from well No. 33016 of «Balakhani Oil» oil and gas extraction department (24-hours tests)

C_{inh} , g/t	K_0 , g/m ² ·h	K_{inh} , g/m ² ·h	γ	K_p , mm/year	$Z, \%$		
Ct ₃ steel samples							
0	0.2844	U					
10		0.0966	2.94	0.108	66		
20		0.0739	3.84	0.082	74		
30		0.0426	6.67	0.047	85		
P-105 steel samples							
θ	0.4890						
10		0.1418	3.44	0.158	71		
20		0.0684	7.15	0.076	86		
30		0.0244	20.0	0.027	95		

from wells No. 2646, 33151, 4012, 31193, and 33016 of «Balakhani Oil» OGED for 6 hours tests varied between 74–94%, 76–96%, 75–97%, 72–92%, 76–98%, 73–95%, 72–94%, 70–90%, 68–87%, and 72-96%.

3. It was determined that during the 24-hours tests, chloroprene effect (10–30 mg/l) for Ct3 and P-105 samples in the formation waters taken from wells No. 2646, 33151, 4012, 31193, and 33016 of «Balakhani Oil» OGED varied between 73–92%, 75–94%, 74–96%, 70–91%, 74–97%, 72–93%, 70–91%, 68–89%, 66–85%, and 71–95%.

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ДОСЛІДЖЕННЯ НОВОЇ БАГАТОФУНКЦІОНАЛЬНОЇ КОМПОЗИЦІЇ ДЛЯ ЗАХИСТУ ВНУТРІШНЬОЇ ПОВЕРХНІ НАФТОПРОВОДІВ У ШАХТІ

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Вперше хлоропреновий реагент (під назвою Z-1) був використаний для захисту від корозії в різних агресивних середовищах у лабораторних умовах. Захисні корозійні властивості реагенту Z-1 були вивчені у пластових водах, взятих з нафтових свердловин № 2646, 33151, 4012, 31193 та 33016, що працюють на Балаханському нафтовому ОГДЕГ. Під час випробувань використовували зразки зі сталей марок Ст3 та Р-105 з розмірами 42г15г5 мм. Експерименти проводилися в динамічних умовах при кімнатній температурі протягом шести та двадцяти чотирьох годин, а швидкість корозії визначалася гравіметричним методом. Під час експериментів використовувалися концентрації Z-1 10, 15, 20 та 25 мг/л. З аналізу результатів численних експериментів, проведених з обома типами сталей, було виявлено, що оптимальна концентрація складу становить 25 мг/л. Ефективність захисту композиції Z-1 у пластових водах зазначених вище нафтових свердловин під час шестигодинного експерименту була наступною: для зразків Ст3 вона коливалася від 75% до 94%, від 75% до 97%, від 76% до 98%, від 72% до 94% та від 68% до 87%, відповідно, толі як для зразків сталі P-105 вона коливалася від 76% до 96%, від 72% до 92%, від 73% до 85%, від 70% до 90% та від 72% до 96%, відповідно. Під час 24-годинних випробувань на корозію ефективність захисту складу Z-1 була 73–92%, 74–96%, 75–97%, 70–92% та 66–85% для зразків сталі Ст3 і 75–94%, 70–91%, 72–83%, 68–89% та 71–95% для зразків сталі Р-105, відповідно.

Ключові слова: коефіцієнт проникнення, швидкість корозії, інгібітор, концентрація, пластова вода, ефект захисту,

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For the first time, a chloroprene reagent (named as Z-1) has been used against corrosion in various aggressive environments under laboratory conditions. The corrosion protection properties of the reagent Z-1 have been studied in formation waters taken from oil wells No. 2646, 33151, 4012, 31193 and 33016 in operation at Balakhani Oil OGED. Samples made of Ct3 and P-105 brand steels with dimensions of 42r15r5 mm have been used during the tests. Experiments have been performed under dynamic conditions at room temperature for six and twentyfour hours, and the corrosion rate has been determined by gravimetric method. During the experiments, concentrations of 10, 15, 20 and 25 mg/l of Z-1 composition were used. The analysis of results from numerous experiments conducted with both types of steel revealed that the optimal concentration of the composition is 25 mg/l. The protection efficiency of the composition Z-1 in the formation waters of the abovementioned oil wells during the six-hour experiment was as follows: for Ct3 samples, it ranged from 75% to 94%, 75% to 97%, 76% to 98%, 72% to 94%, and 68% to 87%, respectively, while for P-105 steel samples, it ranged from 76% to 96%, 72% to 92%, 73% to 85%, 70% to 90%, and 72% to 96%, respectively. During 24-hour corrosion tests, the protection efficiency of the composition Z-1 was 73–92%, 74–96%, 75–97%, 70–92%, and 66–85% for Ct3 steel samples and 75–94%, 70–91%, 72–83%, 68–89%, and 71–95% for P-105 steel samples, respectively.

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