ЕКОЛОГІЯ ТА РЕСУРСОЗБЕРЕЖЕННЯ

UDK 628. 168. 3

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EVALUATION OF THE EFFICACY OF ALKYLIMIDAZOLINES IN REDUCING THE CORROSION AGGRESSIVENESS OF OIL-CONTAINING WATERS

The subject of the study is the study of corrosion processes of non-alloy steel St 3 in water-oil mixtures to create effective compositions of corrosion inhibitors for oil and oil refining industries. Corrosion aggressiveness of commodity and formation waters, waters present in crude oil, due to their high mineralization, the presence of various sulfur compounds, as well as acidification due to the formation of carboxylic acids and other acidic compounds. High corrosion activity of water-oil mixtures causes rapid destruction of equipment and pipelines. This not only significantly affects the economic performance of production due to the cost of replacing metal structures, but also causes great environmental damage due to environmental pollution by both petroleum products and highly mineralized waters.

Therefore, one of the most important tasks is the protection of metal structures from corrosion in mineralized waters and water-oil mixtures.

Given the prospects for the use of corrosion inhibitors of non-alloy steel, the effectiveness of alkylimidazolines (C_{15}-C_{20}) in water-oil mixtures depending on the characteristics of aquatic environments and the parameters of corrosion processes was studied. Given that the real formation waters of Ukraine's oil fields differ significantly in chemical composition and are difficult to model in the laboratory, a 3 % solution of sodium chloride with acetic acid, sulfite and sodium metabisulfite was used. Aqueous solutions were mixed with oil in a ratio of 140:10–180:10. The concentration of sodium chloride solution (3 %) is due to the high corrosion activity of this solution to ferrous metals, including solutions with a high level of mineralization. The choice of alkylimidazolines is due to the fact that they are promising inhibitors in both aqueous media in the presence of oil and in oil in the presence of mineralized waters in a wide range of temperatures.

There are almost no data in the literature on the effect of pH, petroleum products, sulfites on the corrosion activity of mineralized media against non-alloy steel. There are no data on the effect of these parameters on the effectiveness of imidazoline corrosion inhibitors of steel.

The processes of corrosion of steel St3 in 3 % solution of sodium chloride and its mixtures with oil at temperatures from 20 to 85 ^oC at pH change from 2.65 to 6.25 at concentrations of imidazolines from 2 to 50 mg/dm^3 were studied. The impact on the corrosion of sodium sulfite and bisulfite in the presence of alkylimidazolines was evaluated. The effectiveness of alkylimidazolines in the aqueous medium as bactericidal inhibitors under anaerobic conditions has been determined.

It is shown that corrosion aggressiveness in water-oil mixtures increases with decreasing medium pH and increasing temperature. A significant reduction in the corrosion rate was achieved with the use of alkylimidazolines. In some cases, the values of the degree of protection of steel against corrosion at the level of 80-90% at doses of inhibitor up to 50 mg/dm^3. The use of imidazolines in the composition with sodium sulfite helps to increase the effectiveness of steel protection against corrosion. Alkylimidazolines (C_{15}-C_{20}) provided a high level of protection of steel from biocorrosion under anaerobic conditions.

Keywords: *oil production, mineralized waters, water-oil mixtures, corrosion of metals, biocorrosion, corrosion inhibitor*

DOI: 10.20535/2617-9741.2.2022.260350

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Received 10 February 2022; Accepted 23 March 2022

Formulation of the problem. The problem of protecting metals from corrosion remains relevant. This is due to the widespread use of metal products and structures in the industry, both in the past and today. The problem of corrosion in the oil and gas, petrochemical, chemical and other industries is quite acute [1]. This is often due to the use or disposal of highly mineralized waters, which contain large amounts of impurities (sulfates, chlorides, carbonates and bicarbonates, cations of alkali and alkaline earth metals, organic and inorganic sulfur compounds) and are complex multicomponent systems [2, 3]. In addition, corrosion in oil-containing media is largely determined by the presence of dissolved and free water [4]. Corrosion of metals poses a great danger to the processes of extraction, primary processing, transportation and refining of oil [5, 6]. At the same time, corrosion processes cause direct economic losses associated with the repair and replacement of equipment, loss of valuable raw materials. They are the cause of serious accidents in both production and water and oil pipelines, leading to a sharp exacerbation of environmental problems associated with the degradation and destruction of natural ecosystems. Therefore, solving the problems of protection of metals from corrosion in water-oil mixtures, which are formed during the extraction and processing of oil, its transportation, is important in terms of both economic feasibility and environmental safety. One of the ways to solve this complex scientific and technical problem is to choose and justify the feasibility of using at different stages of production of petroleum products corrosion inhibitors of metals with high efficiency at low cost and low toxicity.

Analysis of previous research. One of the negative factors that significantly affects the processes of extraction, transportation and refining of oil is the corrosion of metals [5, 6]. In the oil industry due to the specific organo-mineral composition of media corrosion of metals is characterized by certain differences [7, 8]. Corrosion activity of oil-containing media is largely determined by the presence of dissolved and free water [4], the level of mineralization of aqueous phases, the presence of sulfur compounds, various acidic substances [9].

The high level of mineralization of mine oil waters causes a high level of their corrosion activity [2, 3] and a tendency to sediment [10]. Given the high level of mineralization of mine oil, high levels of concentrations of mineral and organic impurities, other pollutants, it is unrealistic to use different methods of air conditioning and purification. The main effective way to combat sludge deposition is the use of sludge inhibitors [10] and metal corrosion inhibitors [11, 12]. The most effective inhibitors of steel corrosion in water-oil mixtures are inhibitors based on nitrogen-containing heterocyclic compounds [13, 14]. These include amides, amidoamines, and amino acids, including five-membered heterocyclic compounds, including benzitriazoles, benzimidazoles, and imidosalines. The most universal and most common among them are imidazolines [15]. Imidazoline-based inhibitors are one of the best adsorption-type inhibitors, which are effective not only in protecting against electrochemical corrosion, but also in protecting against biological corrosion of metals. Thus, in bactericidal properties of inhibitors "INCORGAZ-11TD" and compositions of the series "AMDOR" are described in [16, 9]. The basis of these compositions are imidazolines derived from diethylenetriamine and naphthenic, ethylhexanoic or oleic carboxylic acids. The main disadvantage of these inhibitors is their high cost due to high prices for higher carboxylic acids and polyalkylene polyamines. But given the possibility of obtaining imidazolines from available and cheap carboxylic acid derivatives [17], they can be considered quite promising, especially in the oil industry. At this stage, it was important to evaluate the effectiveness of imidazolines as corrosion inhibitors in general, taking into account the effects of mineralization, pH, temperature of water-oil mixtures, their ability to inhibit biocorrosion under anaerobic conditions.

The object of these studies were complex water-oil mixtures and their corrosion activity against non-alloy steel, protection of metals from corrosion in these environments, depending on their characteristics and conditions of use.

When conducting research, it is necessary to take into account the need for transportation and refining of oil, as well as the return of aqueous fractions to underground horizons. In all cases, reliable protection of pipelines and equipment against corrosion must be ensured.

One of the ways to solve this problem is to choose such metal corrosion inhibitors that provide effective protection of metals in both aqueous and organic environments, given the high level of mineralization of aqueous fractions, the presence of aggressive impurities in them. Inhibitors should be non-toxic and low cost.

The aim of this work was to determine the influence of the characteristics of water-oil mixtures, pH, temperature on their corrosion activity, determine the effectiveness of alkylimidazolines in these conditions as inhibitors of electrochemical and biological corrosion of steel.

To achieve this goal it is necessary to solve the following tasks:

1. To evaluate the effectiveness of alkylimidazolines (C_{15}-C_{20}) as inhibitors of steel corrosion in water-oil mixtures under conditions of acidification of solutions in the temperature range 20–85 °C.

2. Determine the corrosion rate of steel St3 in aqueous solutions of sodium chloride during their acidification with acetic acid in the presence of oil. Evaluate the impact on the corrosion processes of steel sulfite and sodium bisulfite.

3. To determine the effectiveness of imidazolines as inhibitors of biological corrosion under anaerobic conditions.

Methods of work. In this work, the corrosion rate of steel St 3 was controlled by the massometric method in stationary media by the difference in the masses of the corroded samples in grams per 1 m^2 of sample surface area per hour of interaction. The experiments were performed at temperatures of 20, 75, 80, 85 ºC. The duration of experiments at 75–85 ºC was 4–6 hours, at a temperature of 20 ºC – 96–150 hours, and during the evaluation of biocorrosion processes the duration of experiments was 2976 hours.

As a corrosive medium, a 3 % solution of sodium chloride with an acetic acid concentration of 0.5 to 18.5 g/dm^3, a sodium sulfite concentration of 5 g/dm^3, and a sodium bisulfite concentration of 1–10 g/dm^3 was used. The concentration of alkylimidazolines varied from 2 to 50 mg/dm^3. Volume ratio of aqueous solutions and oil 140:10; 175:10; 180:5.

To study the processes of biocorrosion used a solution of C-1, similar in composition to the solution of Postgate "B" [16]. The solution contained the following substances: $MgSO_4$ – 2 g/dm^3, Na_2CO_3 – 0,2 g/dm^3, NH_4Cl – 1,0 g/dm^3, KH_2PO_4 – 0,5 g/dm^3, sugar – 2,6 g/dm^3, Na_2S – 0,2 g/dm^3, $FeSO_4$ (5 % solution in 1 % HCl) – 0,5 g/dm^3. Before using 1 dm^3 of this solution was mixed with 100 cm^3 of formation water from the Lelyakivsky oil field. During corrosion tests, samples immersed in a mixture of oil and prepared solution (volume ratio as 5:180) were placed in beakers that were tightly closed without air. The concentration of imidazolines in the samples ranged from 2 to 50 mg/dm^3. The exposure time was 2976 hours. The temperature corresponded to 20 ºC. At the end of the exposure, the samples were treated as in all other experiments of massometric determination of the corrosion rate. Massometric corrosion rate was calculated by the formula (W):

$$W = \frac{(m_1 - m_2)}{S \cdot \tau}, g/(m^2 \cdot hour) \tag{1}$$

where m_1 – the mass of the sample before the test, g;
m_2 – the mass of the sample after the test, g;
S – sample area, m^2;
τ – duration of the test, h.

The corrosion inhibition coefficient was determined on the basis of the obtained massometric indicators of the corrosion rate (j):

$$j = \frac{W}{W_i} \tag{2}$$

where W – massimetric corrosion rate without inhibitor, g/(m^2·h);
W_i – massimetric corrosion rate with inhibitor, g/(m^2·h).

Based on the corrosion inhibition coefficient (j), the degree of corrosion protection was calculated (Z):

$$Z = \left(1 - \frac{1}{j}\right) \cdot 100, \% \tag{3}$$

The degree of protection of the metal from corrosion was determined as a percentage.

Presenting main material. Most often, electrochemical corrosion of metals occurs by oxidizing them with oxygen (oxygen depolarization) or protons (hydrogen depolarization). In reality, in the conditions of oil production or refining, the oxygen content in water-oil environments is insignificant. Therefore, corrosion is mainly due to hydrogen depolarization. In real conditions, there are formation waters with a pH close to 5. Therefore, in the first stage, the effect of the reaction of the environment on the corrosion activity of 3 % sodium chloride solution in the presence of oil relative to steel St 3 and the effectiveness of imidazolines (C_{15}-C_{20}) conditions as corrosion inhibitors of steel. First of all, the dependence of the corrosion rate of steel in 3 % NaCl solution on the concentration of acetic acid without oil and at a ratio of volumes of aqueous solutions and oil as 140:10 was determined (Table 1).

Table 1 – The dependence of the corrosion rate of steel St 3 on the concentration of acetic acid, the pH of the medium in 3 % NaCl solution in the absence of oil (I) and its presence (II) in the ratio of water to oil 140:10

[$CH_3C(O)OH$], g/dm^3	pH	W, g/(m^2·h)			
		T=20 ºC		T=80 ºC	
		I	II	I	II
0.00	6.25	0.0567	0.0123	0.7920	0.2497
0.50	3.33	0.0882	0.0206	3.0496	1.7457
2.50	2.98	0.1039	0.0394	3.6530	1.7565
5.00	2.84	0.1245	0.0488	4.5690	2.3707

As can be seen from table 1, the corrosion rate increases significantly with decreasing pH (3% NaCl solution) from 6.25 to 2.84. The corrosion rate increases especially significantly with increasing temperature. However, in aqueous-petroleum mixtures, the corrosion rate is reduced by 2–4 times compared to aqueous solutions. Obviously, when the water surface is covered with a layer of oil, the diffusion of oxygen into the water is significantly reduced, and corrosion occurs due to hydrogen depolarization.

The reduction of the effect of oxygen depolarization on the corrosion of steel 3 in NaCl solution in the presence of oil can be judged from the results presented in table 2. In this case, the corrosion rate was determined in sealed beakers in which the aqueous solution was coated with oil.

Table 2 – The dependence of the corrosion rate of steel St 3 on the concentration of sodium bisulfite in 3% NaCl solution at a ratio of aqueous solution and oil as 180:5 at a temperature of 20 ºC in hermetically sealed beakers

[$NaHSO_3$], g/dm^3	-	-	1	3	5	10
pH	6.25	6.25	4.47	4.01	3.85	3.84
W, g/(m^2·h)	0.0272*	0.0222	0.0647	0.2523	0.3930	0.7039

*Note: * - the beaker is opened*

As can be seen from the table, as the concentration of sodium bisulfite increased and the pH decreased, the corrosion rate of steel increased. Increased mainly due to hydrogen depolarization. Oxygen could not get into the water in hermetically sealed glasses. In addition, sulfite and sodium bisulfite bind oxygen efficiently. Therefore, even traces of oxygen in these conditions are absent. It should be noted that in the control experiment in the open and closed glass corrosion rates differed little. Obviously, in this case, to reduce the diffusion of oxygen in the water, it is enough to cover the water surface with a layer of oil. In addition to reducing the diffusion of oxygen into water, the addition of oil contributes to the hydrophobicity of the surface of metal samples. However, this does not prevent corrosion in acidic solutions.

When the pH decreases from 6.25 to 2.84 at a temperature of 20 ºC, the corrosion rate of steel in the presence of oil increases almost 4 times, and at a temperature of 80 ºC – 9.5 times (Table 1). This is due both to the acceleration of the reaction of iron with protons with increasing concentration and temperature, and with the destruction of the oil film on the surface of metal samples at high temperatures. Alkylimidazolines help reduce the rate of corrosion of steel St 3. The effectiveness of inhibitors at a temperature of 20 ºC can be judged from the data shown in Fig. 1–3.

As can be seen from Fig. 1, in neutral 3 % NaCl solution at a temperature of 20 ºC imidazolines reduce the corrosion rate of steel to 0.0060 g/(m^2·h). This is a much lower corrosion rate than in distilled or fresh water. It is obvious that alkylimidazolines contribute to the formation of a hydrophobic film of petroleum products on the steel surface due to good adsorption of nitrogen-containing fragments on the metal surface and due to sorption of oil on hydrophobic radicals.

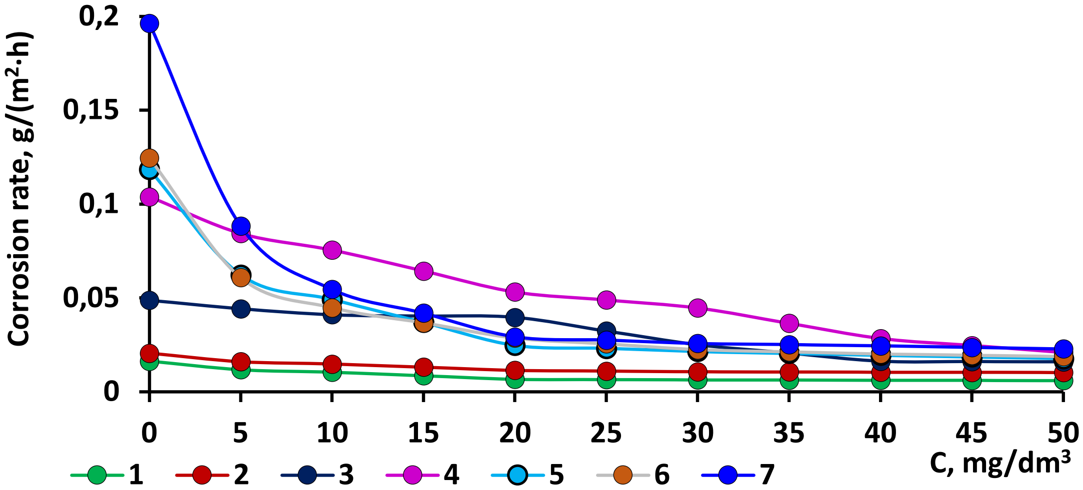

Fig. 1 – Dependence of the corrosion rate of steel St 3 (1; 2; 3; 4; 5; 6; 7) on the dose of alkylimidazolines (C_{15}-C_{20}) at a temperature of 20 ºC at a concentration of acetic acid, g/dm^3: 0.00 (1) ; 0.50 (2); 2.50 (3); 5.00 (4); 6.25 (5); 12.50 (6); 18.75 (7) in 3 % NaCl solution at a ratio of aqueous solution and oil 140:10

At the same time, even at an acetic acid concentration of 18.75 g/dm³ at an inhibitor dose of 50 mg/dm³, the corrosion rate is reduced to 0.0229 g/(m²·h).

As can be seen from Figures 2 and 3, the degree of protection of steel against corrosion by inhibitors with increasing concentration of acetic acid not only does not decrease, but, conversely, increases.

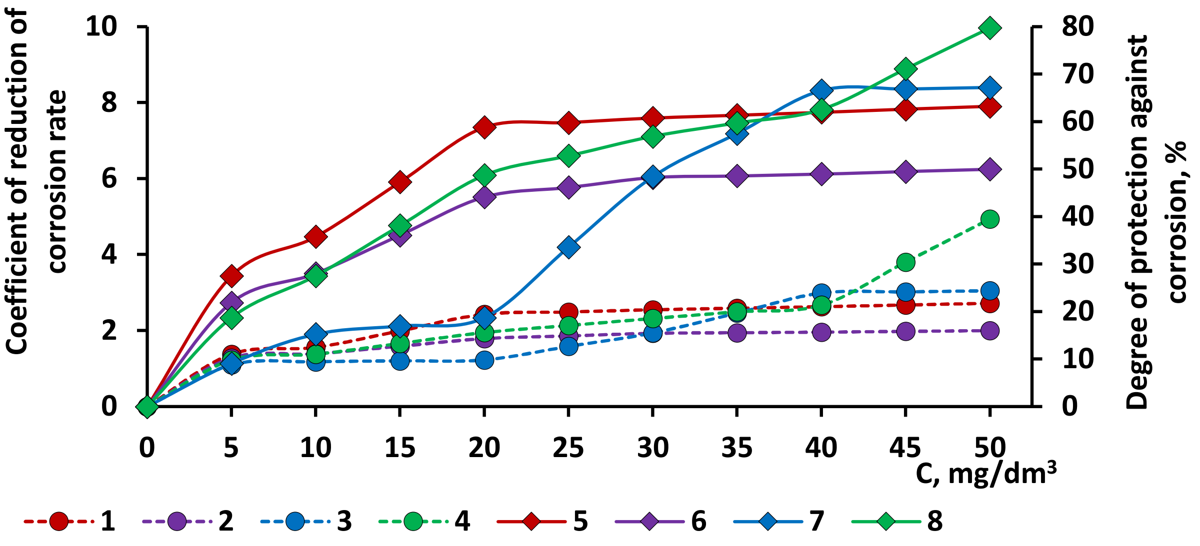

Fig. 2 – Dependence of the coefficient of reduction of corrosion rate (1; 2; 3; 4) and the degree of protection against corrosion of steel St 3 (5; 6; 7; 8) on the dose of alkylimidazolines (C_{15}-C_{20}) at a temperature of 20 °C at acetic acid concentration, g/dm³: 0.0 (1; 5); 0.5 (2; 6); 2.5 (3; 7); 5.0 (4; 8) in 3 % NaCl solution at a ratio of aqueous solution and oil 140:10

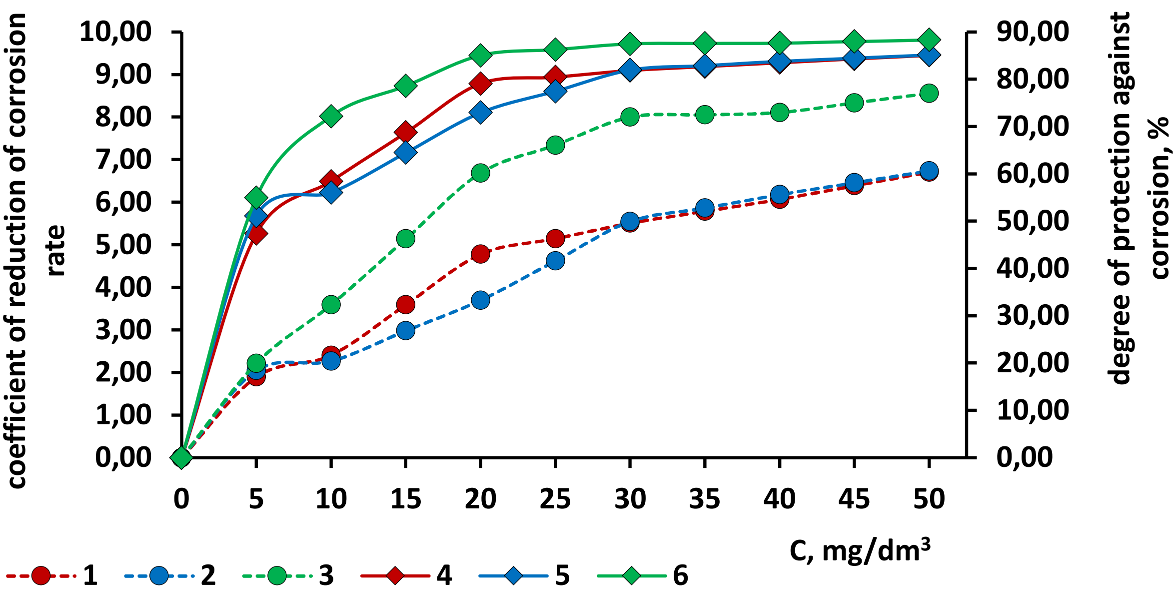

Fig. 3 – Dependence of the coefficient of reduction of corrosion rate (1; 2; 3; 4) and the degree of protection against corrosion of steel St 3 (5; 6; 7; 8) on the dose of alkylimidazolines (C_{15}-C_{20}) at a temperature of 20 °C at acetic acid concentration, g/dm³: 0.00 (1; 5); 6.25 (2; 6); 12.5 (3; 7); 18.75 (4; 8) in 3 % NaCl solution at a ratio of aqueous solution and oil 140:10

This is due to a significant increase in the rate of corrosion of the metal with increasing acidity of the solution in the absence of inhibitor. In addition, at a temperature of 20 °C in the presence of the inhibitor, a strong hydrophobic film is formed on the metal surface, which significantly reduces the rate of diffusion of water molecules and protons to the steel surface. Under these conditions, the degree of protection of steel reaches 50–60 % at an acid concentration of 0.5–5.0 g/dm^3 and 80–88 % at an acid concentration of 6.25–18.75 g/dm^3. The protective effect of the inhibitor increases with increasing concentrations from 2 to 50 mg/dm^3. Significant efficiency in reducing the corrosion rate was observed at concentrations of 10–50 mg/dm^3.

The efficiency of alkylimidazolines in protecting against corrosion of steel St 3 in water-oil media at a temperature of 80 °C was lower (Table 3).

Table 3 – The dependence of the effectiveness of corrosion inhibitors steel St 3 (alkylimidazolines C_{15}-C_{20}) on the characteristics of the aquatic environment at a ratio of 3 % NaCl solution and oil as 140:10 at a temperature 80 °C

$[CH_3C(O)OH]$, g/dm^3	$[Na_2SO_3]$, g/dm^3	pH	D_i, mg/dm^3	W, g/(m^2·h)	j	Z, %
0.0	0.0	6.25	0	0.2899	–	–
			10	0.1957	1.48	32.43
			20	0.1242	2.33	57.08
			50	0.0995	2.91	65.63
0.5	0.0	3.35	0	1.5872	–	–
			10	0.9755	1.62	38.27
			20	0.8012	1.98	49.49
			50	0.7901	2.00	50.00
2.5	0.0	2.96	0	1.7565	–	–
			10	1.0704	1.64	39.02
			20	0.8441	2.08	51.92
			50	0.7759	2.26	55.76
2.5	5.0	3.01	0	1.7901	–	–
			10	0.6430	2.78	64.08
			20	0.6358	2.82	64.53
			50	0.5711	3.13	68.05
4.0	0.0	2.90	0	2.4083	–	–
			10	1.7424	1.38	27.54
			20	1.6236	1.48	32.43
			50	1.0776	2.23	55.15
4.0	5.0	2.95	0	2.3525	–	–
			10	0.9411	2.45	59.18
			20	0.7292	3.16	68.35
			50	0.6861	3.36	70.24
5.0	0.0	2.81	0	2.5805	–	–
			10	1.6846	1.41	29.07
			20	1.5230	1.56	35.90
			50	0.9447	2.52	60.31
10.0	0.0	2.77	0	4.7414	–	–
			10	2.4533	1.91	47.64
			20	1.6128	2.94	66.00
			50	1.3542	3.50	71.42
12.0	0.0	2.70	0	4.9405	–	–
			10	3.1861	1.55	46.80
			20	2.4713	2.00	50.00
			50	1.2141	4.67	75.42

As can be seen from the table, in neutral NaCl solutions in the presence of oil at a temperature of 80 °C, the corrosion rate of steel St 3 reached 0.2899 g/(m^2·h). When the pH was reduced to 2.70, the corrosion rate increased to 4.9905 g/(m^2·h) (~ 5 mm/year). When using alkylimidazolines in concentrations of 10–50 mg/dm^3, a decrease in the corrosion rate by 2–4 times was observed. The degree of protection in some cases reached 70–75 %. A slight increase in the degree of protection was achieved by adding sodium sulfite to aqueous solutions at a concentration of 5 g/dm^3. The effect was negligible because sodium sulfite effectively reduces the rate of corrosion that occurs with oxygen depolarization. But in the presence of oil, the diffusion of oxygen into water is insignificant, so the effect of the use of Na_2SO_3 was insignificant.

If we evaluate alkylimidazoline-based inhibitors in terms of their effectiveness on the acidity of NaCl solutions in the presence of oil at 80 °C (Table 3), we can note an increase in the degree of protection of steel against corrosion with increasing acidity of solutions with increasing inhibitor dose. However, the lowest values of corrosion rate – 0.0995 g/(m^2·h) were achieved in a neutral environment at a dose of inhibitor 50 mg/dm^3. In acidic environments, the minimum corrosion rate at an inhibitor dose of 50 mg/dm^3 increases from 0.7901 g/(m^2·h) at an acetic acid concentration of 0.5 g/dm^3 to 1.3542 g/(m^2·h) at an acid concentration of 10 g/dm^3. Therefore, in General, we can expect a positive effect when using alkylimidazolines (C_{15}-C_{20}) in weakly acidic media of water-oil mixtures.

Based on the fact that in real formation waters the pH of oil production is almost never lower than 5.0, we evaluated the imidazoline inhibitor at pH = 5.0 (Table 4). Despite the fact that the degree of protection of steel against corrosion in this case did not exceed 57 %, the rate of corrosion of steel was reduced to 0.2371 g/(m^2·h) at a dose of inhibitor of only 2 mg/dm^3.

Table 4 – The dependence of the effectiveness of corrosion inhibitors steel St 3 (alkylimidazolines C_{15}-C_{20}) in 3 % NaCl solution (pH = 5.0) at a temperature of 80 °C by the ratio of the volume of aqueous solution and oil as 140:10

D_i, mg/dm^3	W, g/(m^2·h)	j	Z, %
0	0.3514	–	–
0	0.2497*	–	–
2	0.2371	1.47	31.97
5	0.2263	1.55	35.48
10	0.2083	1.68	40.48
20	0.1904	1.84	45.65
50	0.1511	2.31	56.71

*Note: * – at pH 6,41*

This rate of corrosion of steel St 3 is lower than the corresponding value in a neutral solution of 3 % NaCl in a mixture with oil, where the corrosion rate reaches 0.2497 g/(m^2·h). The effectiveness of alkylimidazoline-based inhibitors at temperatures of 75 °C and 85 °C was determined in the study of corrosion processes in weakly acidic media (Fig. 4–6).

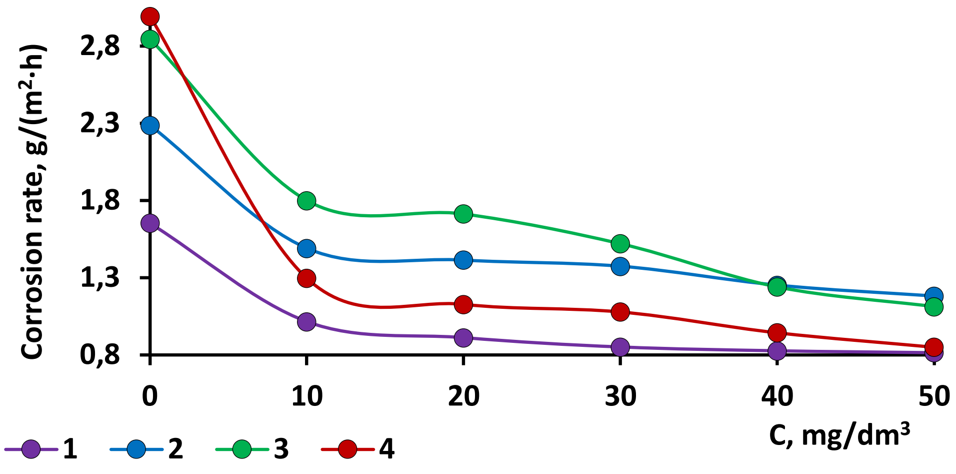

Fig. 4 – Dependence of the effectiveness of alkylimidazolines (C_{15}-C_{20}) as inhibitors of steel St 3 corrosion inhibitors on their concentration in 3 % NaCl solution at the expense of acetic acid, g/dm^3: 2.5 (1); 4.0 (2); 6.0 (3); 8.0 (4) and sodium sulfite 5 g/dm^3 (4) at temperatures of 75 °C (1, 2) and 85 °C (3, 4) at a ratio of aqueous solution and oil as 140:10

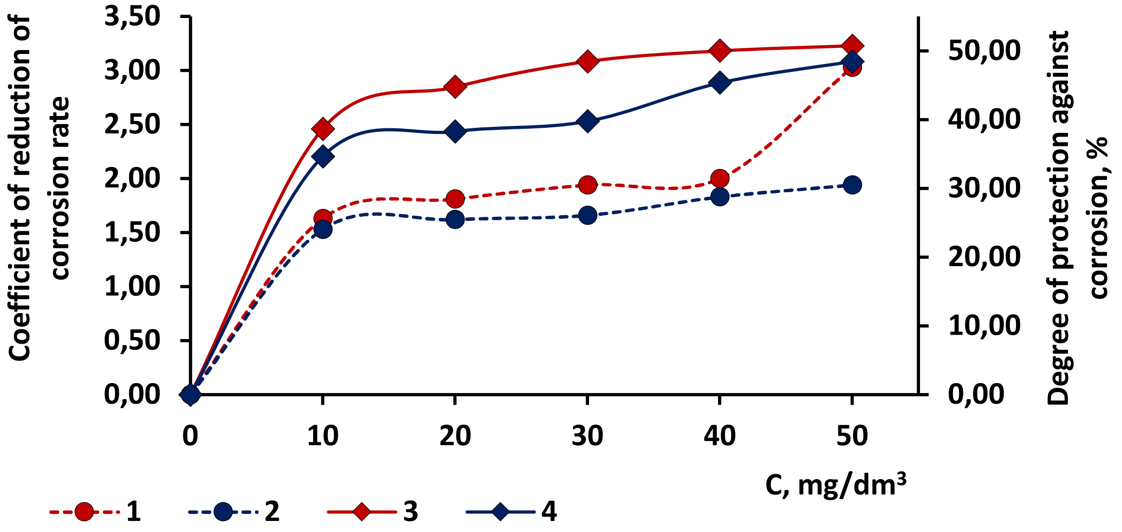

Fig. 5 – Dependence of the coefficient of reduction of corrosion rate (1, 2) and the degree of protection against corrosion of steel St 3 (3, 4) on the dose of alkylimidazolines (C_{15}-C_{20}) at a temperature of 75 °C at acetic acid concentration, g/dm^3: 2.5 1, 3) and 4.0 (2, 4) in 3 % NaCl solution at a ratio of aqueous solution and oil 140:10

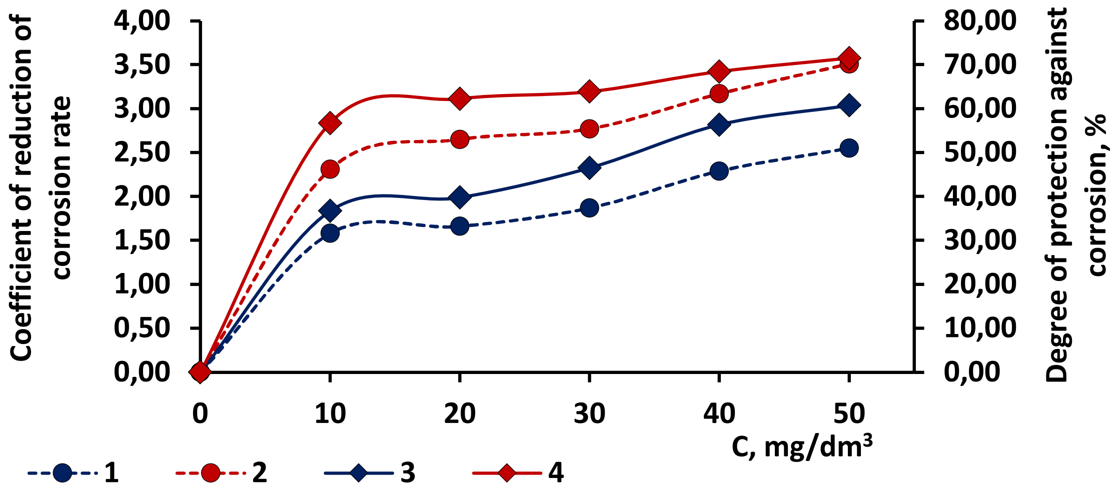

Fig. 6 – Dependence of the coefficient of reduction of corrosion rate (1, 2) and the degree of protection against corrosion of steel St 3 (3, 4) on the dose of alkylimidazolines (C_{15}-C_{20}) at a temperature of 85 °C at an acetic acid concentration of 6.0 g/dm^3 (1, 2, 3, 4) and Na_2SO_3 concentration of 5 g/dm^3 (2, 4) in 3 % NaCl solution at a ratio of volumes of water solution and oil 140:10

As can be seen from the figures, the effectiveness of inhibitors at these temperatures is almost no different from their effectiveness at a temperature of 80 °C. However, with an increase in temperature from 75 °C to 80 °C, an increase in the degree of corrosion protection from 48–50 % to 60–70 %.

This is due to the increase in the corrosion rate of steel in control experiments with decreasing pH and increasing temperature. There was also some increase in the degree of protection against corrosion when using alkylimidazolines in the presence of sodium sulfite.

Interesting results were obtained when using alkylimidazolines to protect against corrosion of steel under anaerobic conditions. To obtain media suitable for the development of sulfate-reducing microorganisms, used a solution similar in composition to the medium of Postgate "B" [16]. As a medium where anaerobic microorganisms capable of sulfate reduction are present, formation water from an oil field was used. Since the content of anaerobic microorganisms in such waters significantly decreased during water transportation, for their recovery and reproduction, the duration of the experiments was increased to 2976 hours. The results are shown in table 5.

In this case, in a control experiment where the inhibitor was not used, the corrosion rate reached 0.0047 g/(m^2·h). At inhibitor doses (C_{15}-C_{20} alkylimidazolines) from 2 mg/dm^3 to 50 mg/dm^3, the corrosion rate decreased from 0.033 g/(m^2·h) to 0.0007 g/(m^2·h), respectively. The degree of protection increased from 29.89 % to 85.16 %. This is due to the bactericidal properties of alkylimidazolines [15, 16]. Of course, biocorrosion in highly mineralized waters at high temperatures is almost impossible on large surfaces of metals.

However, bacterial corrosion can occur at pH from 1 to 10.5 and temperatures from 6 ºC to 40 ºC in the presence of various organic and inorganic substances in local areas. In this case, microorganisms can create favorable conditions for development. Under the layer of rust (corrosion product) creates anaerobic conditions for the development of sulfite-reducing bacteria [18].

Table 5 – The dependence of the corrosion rate of steel St 3, the coefficient of reduction of corrosion rate and the degree of protection against corrosion from the dose of alkylimidazolines (C_{15}-C_{20}) in medium C-1 at a temperature of 25 ºC in hermetically sealed containers (water solution and oil 180: 10), test time 2976 hours

D_i, mg/dm^3	W, g/(m^2·h)	j	Z, %
0	0.0047	–	–
2	0.0033	1.4264	29.89
5	0.0021	2.2373	55.30
10	0.0011	4.3264	76.89
20	0.0009	4.9869	79.95
30	0.0008	5.8750	82.98
40	0.00075	6.2667	84.04
50	0.00070	6.7349	85.16

Therefore, based on the results shown in table 5, we can say that alkylimidazolines are multifunctional inhibitors that effectively protect unalloyed steels from both electrochemical, chemical corrosion and biological corrosion.

Conclusions. As a result of studies to study the effectiveness of alkylimidazolines in reducing the corrosion aggressiveness of oil-containing

- it is shown that in 3 % NaCl solution the corrosion rate increases with decreasing pH and increasing temperature. In water-oil mixtures, the trend continues, although in the presence of oil, the corrosion rate is reduced by 2–4 times due to a decrease in the rate of diffusion of oxygen into water.
- it is shown that the inhibitor based on alkylimidazolines (C_{15}-C_{20}) provides a significant reduction in the rate of corrosion of steel in both neutral and weakly acidic environments in aqueous-petroleum mixtures at temperatures of 20–80 ºC. The use of sodium sulfite with alkylimidazoline increases the degree of protection of steel from corrosion by 5–10 %.
- it was found that alkylimidazolines provide effective protection of steel St 3 from biocorrosion under anaerobic conditions. At imidazoline concentrations of 2–50 mg/dm^3, the degree of corrosion protection reached 30–85 %.

Prospects for further research. Alkylimidazoline-based inhibitors are effective at all stages of oil production and refining. They are effective in both crude oil and formation waters, regardless of the level of their mineralization in neutral and slightly acidic environments. Alkylimidazolines are surfactants that are sufficiently soluble in both organic and aqueous media. They are well adsorbed on the surface of metals, promoting the formation of hydrophobic films by improving the sorption of petroleum products on the surface of metals, which helps protect them from aggressive aquatic environments. Alkylimidazolines are stable substances in a wide range of temperatures. Therefore, they provide protection of metals from corrosion both in the extraction and primary refining of oil, its transportation, and in the thermal refining of oil.

Imidazolines are obtained by condensation of polyethylene polyamines and higher carboxylic acids or their derivatives. The high cost of raw materials and energy consumption in production cause the high cost of inhibitors of this type. These inhibitors are not produced in Ukraine.

Laboratory studies have confirmed the possibility of obtaining alkylimidazolines from vegetable fats and animal fat wastes. This opens the prospect of their production and sale in Ukraine at relatively low prices. These inhibitors are promising not only in oil production, but also in gas production, as well as in reducing the corrosion activity of mineralized mine waters in other extractive industries.

Given that most alkylimidazolines are solids or viscous liquids at low temperatures, they should be used as 40–50 % solutions in isopropanol, methanol or kerosene.

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ОЦІНКА ЕФЕКТИВНОСТІ АЛКІЛІМІДАЗОЛІНІВ ПРИ ЗНИЖЕННІ КОРОЗІЙНОЇ АГРЕСИВНОСТІ НАФТОВМІСНИХ ВОД

Предметом дослідження є вивчення процесів корозії нелегованої сталі Ст 3 у водно-нафтових сумішах для створення ефективних композицій інгібіторів корозії для підприємств нафтодобувної та нафтопереробної промисловості. Корозійна агресивність підтоварних та пластових вод, вод, що присутні у сирій нафті, обумовлена їх високою мінералізацією, наявністю різних сірчистих сполук, а також підкисленням за рахунок утворення карбонових кислот та інших кислих сполук. За високої корозійної активності водно-нафтових сумішей відбувається швидке руйнування обладнання та трубопроводів. Це не лише суттєво впливає на економічні показники виробництв за рахунок витрат на заміну металевих конструкцій, але й спричиняє великі екологічні збитки, які обувлені забрудненням довкілля як нафтопродуктами, так і високомінералізованими водами.

Тому одним із найважливіших завдань є захист металевих конструкцій від корозії у мінералізованих водах та водно-нафтових сумішах.

Враховуючи перспективність застосування інгібіторів корозії нелегованої сталі, було вивчено ефективність алкілімідазолінів (C_{15}-C_{20}) у водно-нафтових сумішах в залежності від характеристик водних середовищ та параметрів процесів корозії. Враховуючи те, що реальні пластові води нафтових родовищ України суттєво відрізняються за хімічним складом і змоделювати у лабораторних умовах їх важко, було використано, головним чином, 3%-й розчин хлориду натрію із домішками оцтової кислоти, сульфіту та метабісульфіту натрію. Водні розчини змішувалися із нафтою у співвідношенні 140:10–180:10. Концентрація розчину хлориду натрію (3 %) обумовлена високою корозійною активністю даного розчину до чорних металів, включаючи і розчини з високим рівнем мінералізації. Вибір алкілімідазолінів обумовлений тим, що вони є перспективними інгібіторами як у водному середовищі у присутності нафти, так і у нафті в присутності мінералізованих вод у широкому діапазоні температур.

У літературі практично відсутні дані про вплив pH, нафтопродуктів, сульфітів на корозійну активність мінералізованих середовищ щодо нелегованої сталі. Відсутні дані й про вплив згаданих параметрів на ефективність імідазолінових інгібіторів корозії сталі.

У роботі вивчено процеси корозії сталі Ст 3 у 3-%-му розчині хлориду натрію та його сумішах із нафтою при температурах від 20 до 85 ^{o}C при зміні pH від 2,65 до 6,25 за концентрацій імідазолінів від 2 до 50 мг/дм^3. Проведено оцінку впливу на процеси корозії сульфіту та бісульфіту натрію у присутності алкілімідазолінів. Визначено ефективність алкілімідазолінів у водному середовищі як інгібіторів-бактерецидів в анаеробних умовах.

Показано, що корозійна агресивність у водно-нафтових сумішах зростає зі зниженням pH середовища та підвищенням температури. Суттєвого зниження швидкості корозії досягнуто при використанні алкілімідазолінів. В окремих випадках досягнуто значень ступеню захисту сталі від корозії на рівні 80–90 % при дозах інгібітора до 50 мг/дм^3. Використання імідазолінів у композиції із сульфітом натрію сприяє підвищенню ефективності захисту сталі від корозії. Алкілімідазоліни (C_{15}-C_{20}) забезпечили високий рівень захисту сталі від біокорозії в анаеробних умовах.

Ключові слова: *нафтодобування, мінералізовані води, водно-нафтові суміші, корозія металів, біокорозія, інгібітор корозії.*

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