UDC 620.197.3;628.168.3
https://doi.org/10.15407/kataliz2022.33.066

Chemical means of equipment protection during oil and gas fields operation

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In this article the problems associated with the corrosion processes of equipment in oil and gas production are analyzed. The basic anticorrosive methods and means used in modern conditions are considered. Taking into account the mechanism and conditions of corrosion processes in the extraction and transportation of oil-containing products and gas condensate, the chemical method of protection of the equipment was chosen for research. Both known inhibitors based on phosphonic acids and synthesized substances based on sulfonates, imidazolines, and diamines were used as chemicals in the research. As a result of the research, the effectiveness of protection of metals from corrosion depending on the composition of highly mineralized medium, metal type, inhibitor type, and its concentration was evaluated and the effectiveness of the developed scale stabilizer (sodium dimethylsulfonate phosphinate) was evaluated in comparison with known reagents. It is shown that the effectiveness of protection of metals from corrosion in aqueous-petroleum mixtures with alkylimidazoline inhibitors (derivatives of 4,5-dihydro-1,3-diazole or 4,5-dihydroimidazole) and inhibitors developed on the basis of sunflower oil and diethylenetriamine (AC-1), ethylenediamine (AC-2) reaches 90% in doses of 5 - 50 mg/dm^3. In addition, corrosion processes are often accompanied by processes of deposition of hardness salts on the surface of the equipment, which leads to a significant complication in the operation of the equipment. Therefore, studies of the anti-scale properties of these reagents under harsh conditions were performed. Real concomitant gas production waters were used as the medium. It was found that sodium dimethylsulfonate phosphinate is a very effective stabilizer of scale formation and is not inferior in effectiveness to known antiscalants. The proposed reagents can be used to stabilize water-oil mixtures and associated formation waters formed during the production and transportation of oil and gas.

Keywords: corrosion, inhibitor, oil-water mixtures, corrosion protection, scale stabilizer

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Introduction

One of the significant factors that negatively affect the operation of oilfield equipment is internal corrosion. Corrosion is a great danger for tanks, pipelines, and other equipment in the system of extraction, transportation, and storage of oil and petroleum products [1, 2]. Hydrocarbons, which are part of oil and motor fuels in pure form, in the absence of water are corrosive inactive in relation to metals. They become dangerous in terms of corrosion in the presence of sulfur compounds (mercaptans, hydrogen sulfide, sulfur dioxide, etc.) [3], which is due to increased aggressiveness of the environment.

In addition, the corrosion of metals in oil-containing media has its own specific features and is largely determined by the presence of dissolved and free water [4]. Storage, transportation and use of petroleum products is accompanied by constant saturation with water and condensation of water on metal surfaces. The water content in petroleum products can vary widely from 0.001 to 0.01%. It depends on the operating conditions of the technical equipment and the climatic conditions. The main source of water accumulation in petroleum products is atmospheric moisture, which condenses on metal surfaces when the temperature of petroleum products and tank walls changes.

In the vast majority of cases, corrosion of industrial equipment occurs by electrochemical mechanism in contact of metal with aqueous mineralized medium, so it is advisable to use inhibitory protection of equipment from corrosion. It is known that corrosion inhibitors are substances whose introduction in relatively small quantities into aggressive environments causes a marked slowdown in the corrosion of metals. It is essentially a substance that inhibits corrosion due to competitive adsorption with activator particles and the formation of protective adsorption or phase films on the metal surface, sometimes with barrier properties. Corrosion inhibitors affect the kinetics of electrode processes that take place during corrosion, and are also characterized by the ability to form oxide, hydroxide or other films on the metal and convert the metal into a passive state.

Prolonged use of carbon steel in corrosive environments in the production and use of oil and gas requires the use of effective corrosion inhibitors. At the same time to corrosion inhibitors certain requirements are put forward. They must provide the necessary protective effect when tested in model systems both under conditions of high pressures and temperatures, and under normal conditions: temperature +40°C, pressure 1 atm.; as well as under conditions of high flow velocities and the presence of abrasive particles [5, 6].

The inhibitor must have a low pour point (at least 50°C), good solubility in corrosive environments and high adsorption capacity, and must not affect the stabilization of water-oil emulsions.

According to the mechanism of action, inhibitors are divided into adsorption and passivation.

Passivation inhibitors promote the formation of a protective film on the metal surface and the transition of the metal into a passive state. Passivators are most widely used to combat corrosion in neutral or close environments, where corrosion occurs mainly with oxygen depolarization. The mechanism of action of such inhibitors is mainly determined by their chemical composition and structure. Among inorganic oxidizing substances they are represented by nitrites, molybdates, chromates. There are passivators that form sparingly soluble compounds with corroding metal ions - polyphosphates, silicates, alkali metal carbonates. A separate group consists of organic compounds that are not oxidants, but promote the adsorption of dissolved oxygen on the metal, which leads to its passivation. The inhibitory effect of most organic compounds is determined by their adsorption capacity on contact with the metal surface. As a rule, this ability is quite high due to the presence of atoms or functional groups in the molecules that provide active adsorption interaction of the inhibitor with the metal. Such active groups can be nitrogen-, sulfur-, oxygen- and phosphorus-containing groups, which are adsorbed on metals by donor-acceptor and hydrogen bonds.

The most common are inhibitors based on nitrogen-containing compounds [7]. Protective effect is shown by aliphatic amines and their salts, amino alcohols, amino acids, azomethines, anilines, hydrazides, imides, acrylonitriles, imines, nitrogen-containing five-membered (imidazolines, benzotriazoles, benzimidosols, etc.) and six-membered heterocycles. Phenols, cyclic and linear esters, esters of allyl alcohols, benzaldehydes and benzoic acids, alcohols, dioxanes and others have been used.

After corrosion, salt deposition is the second most important problem associated with the inflow of associated water. Salt deposition occurs in all methods of well operation, but the most negative consequences of salt deposition occur in oil production by rod submersible pumps and installations of electric submersible centrifugal pumps. Crystalline formations of inorganic salts on the working parts of submersible pumps lead to their increased wear, jamming and damage to the shafts of submersible centrifugal pumps and the like. In addition, as a result of increasing the water content of well products, salt deposits are formed in the surface equipment of group, metering units, oil reservoirs and oil treatment systems (degassing, stabilization, dehydration, desalination).

The main way to solve the problem of formation of salt deposits is stabilization treatment with the help of salt deposits stabilizers [8, 9]. The most common stabilizing reagents are complexes containing phosphate ions, phosphonate ions, phosphinate ions, carboxylate ions, sulfonate ions [10, 11].

However, the reagents used do not always provide a sufficiently high protective effect. Even in the conditions of one oil production enterprise or field on different sites this indicator can differ essentially. This is due to the solubility of the inhibitor in formation fluids, low level of its compatibility with formation waters, incorrect selection of the reagent for specific conditions. Usually, this problem is solved by increasing the dosage of the reagent, but this method does not always give a satisfactory effect. Therefore, at the present stage it is necessary to create new inhibitors of corrosion and scale formation, which would provide a high protective effect in a wide range of application conditions, or improve the quality of existing protective compositions.

The aim of this work was to conduct research to assess the effectiveness of protection of metals from corrosion depending on the composition of the highly mineralized environment, the type of metal, the type of inhibitor and its concentration; determining the effectiveness of the developed scale stabilizer for highly mineralized waters in comparison with known reagents.

Experiment

The following substances were used as corrosion inhibitors and stabilizers of salt deposition during the research:

- alkylimidazoline (is a derivative of 4,5-dihydro-1,3-diazole or 4,5-dihydroimidazole);
- inhibitors derived from sunflower oil and diethylenetriamine (AC-1), ethylenediamine (AC-2);
- oxyethylene diphosphonic acid (HEDP, $CH_3C(OH)(H_2PO_3)_2$);
- nitrilotrimethylphosphonic acid (ATMP, $N(CH_2PO_3H_2)_3$);
- sodium dimethylsulfonate phosphinate (SDP, $(NaSO_3CH_2)_2P(O)ONa^+$).

The main factor influencing the corrosive activity of aggressive environments is the ratio of oil and water. As the water content in the binary water-oil emulsion increases, the latter stratifies with the release of water as a separate phase. Reservoir water in contact with oil is quite mineralized. It may contain mineral dispersed particles (clay, sand, etc.); dissolved chlorides, carbonates, bicarbonates, sulfates of calcium, magnesium, sodium, potassium and iron; gaseous impurities: H_2S, CO_2, O_2, hydrocarbon gases. The mineralized aqueous phase belongs to the sodium chloride type, which is dominated by sodium and calcium chlorides, calcium bicarbonates; contains a small number of sulfates in almost neutral reaction medium (potential of hydrogen 6.5 ÷ 7.5).

Therefore, to study the corrosion processes in oil solutions, it was decided to use the following composition of the model solution: 140 cm^3 NaCl (30 g/dm^3), 10 cm^3 oil, 0.75 and 1.5 cm^3 acetic acid.

Samples of copper (C2), brass (B62) and steel (St3 and steel 20) were used as corrosive materials in the study.

The degree of corrosion was determined by masseteric method. Metal samples in the form of rectangular plates were prepared for testing. Before the test, the samples were ground by hand, then polished with a mechanically thin abrasive material to completely remove the marks remaining from grinding, marked. Degreasing was performed with ethyl alcohol, then weighed on analytical balances with an accuracy of ± 0.0001 g. After completion of the tests, the corrosion products were removed from the metal, the plates were washed, dried, and weighed again.

The corrosion rate (W) was determined by the formula:

$$W = \frac{(Mn - Mk)}{S \cdot \tau},\ g/(m^2 \cdot h) \qquad (1)$$

where Mn – initial mass of the sample, g;

Mk – a mass of the sample after the study, g;

S – sample area, m^2;

τ – duration of research, hours.

The coefficient of the corrosion rate reduction (J) was calculated by the formula:

$$j = \frac{W_x}{W_i}, \qquad (2)$$

where W_i – corrosion rate in the presence of inhibitor, $g/(m^2 \cdot h)$;

W_x – idle corrosion rate, $g/(m^2 \cdot h)$.

The degree of protection of the metal against corrosion (Z) was calculated based on the coefficient of the corrosion rate reduction, according to the formula:

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

where j – the coefficient of the corrosion rate reduction.

Environments for studying stabilization processes

During the production of oil, condensate and gas, together with the target product, the so-called concomitant formation waters rise to the surface. Concomitant formation waters (CFW) are a complex natural mixture consisting of formation waters of the production horizon, condensation, contour, and groundwater.

Ukraine produces about 2.1 million tons of oil annually, so it is estimated that on average, together with petroleum products, about 15 million tons of associated water are produced annually. This water increases the cost of oil production and can lead to a number of negative environmental consequences. The impact of CFW on the environment is characterized by salinization of fertile soils and pollution of aquifers used for drinking and domestic water supply. The penetration of associated water into these horizons leads to the need for mandatory groundwater treatment or the search for new sources of water supply.

Physic-chemical properties of SPV generally correspond to the properties of reservoir water of productive horizons (Table 1). When pumping gas or oil, this water is also contaminated with surfactants, equipment corrosion products, petroleum products, and other contaminants.

Table 1. **Characteristics of associated water of the Struten field, PJSC "UkrNafta"**

Characteristic	Unit of measurement	The actual value of the indicator
Potential of hydrogen	potential of hydrogen, units	6.9
Alkalinity is general	$mg\text{-}eq/dm^3$	10.0
Stiffness is general	$mg\text{-}eq/dm^3$	110.0
Calcium	$mg\text{-}eq/dm^3$	80.0
Magnesium	$mg\text{-}eq/dm^3$	30.0
Chlorides	mg/dm^3	17750.0
Sulfates	mg/dm^3	20.0
Total iron	mg/dm^3	10.0
Dry residue	mg/dm^3	52320.0

Based on the presented indicators, a model solution was developed to evaluate the effectiveness of stabilizers in relation to the scale formation of associated waters (Table 2).

For a preliminary assessment of the effectiveness of water stabilizers in relation to scale formation, a model solution was used (Table 2). First, the inhibitor was added to 100 cm^3 of the model solution in doses of 5–20 mg/dm^3, and then the appropriate amount of soda solution. The process was carried out at temperatures of 95-98°C for 4-6 hours. Reagents were not added to the control samples.

Table 2. **The composition of the model environment for the study of stabilization of associated waters**

Characteristic	Unit of measurement	The actual value of the indicator
Calcium	mg-eq/dm^3	84.6
Magnesium	mg-eq/dm^3	30.0
Chlorides	mg/dm^3	17700.0
$NaHCO_3$	mg-eq/dm^3	5.0

The stabilizing effect was calculated in accordance with the reduction of water hardness as a result of heating. Residual water hardness in the samples was determined by trilonometry with eriochrome black T indicator.

The stabilizing effect (SE) was determined by the formula:

$$SE=\left(1-\frac{\Delta Ti}{\Delta T}\right)\cdot 100\% \qquad (4)$$

where ΔTi – reducing the hardness of the solution that was treated with the inhibitor, mg-eq/dm^3;

ΔT – reducing the hardness of the control solution without adding an inhibitor, mg-eq/dm^3.

Results and Discussion

At the initial stage of the work, the corrosion rates were determined for three types of model solutions, which simulated water-oil mixtures and which differed in the ratio of oil: acetic acid. In addition, studies were conducted for different types of metals. The research results are presented in Table 3.

Table 3. **Corrosion rate of metals in water-oil mixtures of different composition**

Metal	Oil content, cm^3/dm^3	Acetic acid concentration, g/dm^3	The corrosion rate, W, g/(m^2·h)
Copper	10	0	0.009
Brass			0.0006
St3			0.007
Steel 20			0.001
Copper	10	5	0.08
Brass			0.06
St3			0.20
Steel 20			0.16
Copper	10	10	0.05
Brass			0.11
St3			0.20
Steel 20			0.19

The first type of solution, which contained only an emulsion of water with oil, was predicted to have no pronounced corrosive properties for all types of metals, the corrosion rate was observed at 0.0006–0.009 g/(m^2·h). With the addition of acetic acid, which simulated the presence of carboxyl substances in petroleum mixtures, the corrosion aggressiveness of the media increased 10–200 times, depending on the type of metal. For copper, the values of corrosion rate had the lowest values - 0.05 g/(m^2·h), the highest values of corrosion rate were typical for steel - up to 0.2 g/(m^2·h).

Therefore, for further studies to determine the effectiveness of the proposed inhibitors as aggressive media we used water-oil emulsions with the addition of acetic acid, as the creation of the most stringent conditions for research.

The known alkylimidazoline inhibitor and the synthesized AC-1 and AC-2 inhibitors were used as inhibiting reagents. The results of determining the effectiveness of corrosion inhibitors are presented in Table 4.

Table 4. **The effectiveness of protection of metals from corrosion depending on the composition of the medium, type of metal, type of inhibitor and its concentration (I - alkylimidazoline, II - AC-1, III - AC-2)**

Metal	Oil content, cm^3/dm^3	Acetic acid concentration, g/dm^3	Inhibitor dose, mg/dm3	The corrosion rate, W, g/(m^2·h)			Coefficient of the corrosion rate reduction, J			Level of protection, Z, %		
				I	II	III	I	II	III	I	II	III
Copper	10	5	5	0.00	0.13	0.01	---	0.6	7.3	100	0	86.2
			10	0.007	0.11	0.01	11.4	0.7	8.0	91.2	0	87.5
			20	0.001	0.07	0.008	8.0	1.2	10.0	98.8	12.2	90.0
			50	0.007	0.003	0.01	11.4	26.7	8.0	91.2	96.2	87.5
Brass			5	0.02	0.006	0.01	3.0	10.0	6.0	66.6	90.0	83.3
			10	0.04	0.13	0.005	1.5	0.5	12.0	33.3	0	91.7
			20	0.03	0.02	0.002	2.4	3.0	30.0	58.3	66.6	96.7
			50	0.04	0.01	0.04	1.5	6.0	1.5	58.3	83.3	33.3
St3			5	0.05	0.1	0.04	4.0	2.0	5.0	75.0	50.0	80.0
			10	0.05	0.03	0.08	4.0	6.7	2.5	75.0	82.0	60.0
			20	0.02	0.04	0.05	10.0	5.0	4.0	90.0	80.0	75.0
			50	0.03	0.08	0.04	6.7	2.5	5.0	84.9	60.0	80.0
Steel 20			5	0.04	0.09	0.04	4.0	1.8	4.0	75.0	43.8	75.0
			10	0.03	0.27	0.03	5.3	0.6	5.3	81.2	0	81.2
			20	0.01	0.06	0.03	16.0	2.7	5.3	93.7	62.5	81.2
			50	0.02	0.04	0.04	8.0	4.0	4.0	87.5	75.0	75.0
Copper	10	10	5	0.01	0.02	0.008	5.0	2.8	6.8	80.0	64.0	85.2
			10	0.005	0.006	0.006	10.0	0.8	9.4	90.0	0	89.4
			20	0.002	0.005	0.008	25.0	1.0	6.3	96.0	0	84.0
			50	0.003	0.007	0.006	16.7	0.7	8.8	94.0	0	88.6
Brass			5	0.01	0.01	0.01	11.0	11.0	11.0	90.9	90.9	90.1
			10	0.01	0.006	0.01	11.0	18.3	11.0	90.9	94.5	90.1
			20	0.01	0	0.01	11.0	---	11,0	90.9	100	90,1
			50	0.02	0.02	0.01	7.9	5.8	9.2	87.2	82.6	89.1
St3			5	0.05	0.05	0.07	4.0	4.0	2.9	75.0	75.0	64.9
			10	0.09	0.06	0.06	2.2	3.3	3.3	54.9	69.9	69,9
			20	0.06	0.02	0.05	3.3	10.0	4.0	69.9	90.0	75.0
			50	0.04	0.04	0.04	5.0	5.0	5.0	80.0	80.0	80.0
Steel 20			5	0.12	0.10	0.04	1.6	1.9	4.8	36.7	47.4	78.9
			10	0.07	0.04	0.07	2.7	4.8	2.7	63.1	78.9	63.1
			20	0.06	0.04	0.03	3.2	4.8	6.3	68.3	78.9	84,2
			50	0.08	0.006	0.40	2.4	31.6	4.8	57.9	96.8	78.9

As can be seen from Table 4, the use of alkylimidazoline achieved a degree of corrosion protection of 65-95% in the concentration range of 5-50 mg/dm^3 for almost all alloys. Based on the structure of alkylimidazoline and its derivatives, it can be assumed that inhibitor molecules are adsorbed on the metal surface by nitrogen atoms, and hydrocarbon radicals with hydrophobic properties are directed towards the solution and repel water and part of the aggressive medium from the metal surface. In this case, together with the hydro-phobicity of these groups provide shielding of a significant part of the surface. The adsorption sites in this case are nitrogen atoms, which is due to the electronic redistribution in the molecule. Due to this, the nitrogen atom receives a partially positive charge.

When AC-1 and AC-2 inhibitors were used in the same concentration range, the degree of corrosion protection was almost similar.

Study of the processes of stabilization of associated waters of natural gas production

Most of the salt deposits of oil and gas fields consist of salts in which divalent anions are dominant, namely carbonates and sulfates, and divalent metal cations. Usually, several either anionic or cationic interactions are required to hold the stabilizer firmly on the surface. Therefore, it is necessary to use substances that consist of molecules with several similar functional groups and their qualitative distribution, so that they interact with the lattice ions on the crystal surface. Phosphonates, aminophosphonates and nitrile phosphonates are usually good at preventing crystal growth by blocking active nucleation centers, so known reagents HEDP, ATMP, and synthesized sodium nitrilodimethylsulfonate (SDS) were chosen to study the stabilization processes of associated waters.

In [12] it was shown that the stability of water with respect to sedimentation depends little on the level of mineralization, and is determined mainly by the concentration of calcium ions and carbonates or sulfates. Therefore, to create more stringent experimental conditions and determine a reliable stabilizing effect in the model solution (Table 2), simulating the accompanying water, soda was added in the concentration range 0-20 mg-eq/dm^3, the temperature corresponded to 95-98°C, exposure time was 4-6 hours.

The results of the research are presented in Table 5.

Table 5. **Dependence of the stabilizing effect on salt deposition from associated waters on the type of inhibitor and its concentrations**

Reagent concentration, g/dm^3	Stabilization effect, %				
	Na_2CO_3 0 mg-eq/dm^3	Na_2CO_3 5 mg-eq/dm^3	Na_2CO_3 10 mg-eq/dm^3	Na_2CO_3 15 mg-eq/dm^3	Na_2CO_3 20 mg-eq/dm^3
HEDP					
0,5	100	100	67	68	41
1	80	87	80	69	41
1,5	60	60	47	38	41
2	40	60	47	38	41
ATMP					
0,5	60	67	47	44	41
1	50	60	47	44	41
1,5	40	47	47	38	35
2	40	33	33	25	18
SDP					
0,5	50	67	40	38	35
1	50	67	33	38	41
1,5	50	47	33	38	30
2	60	53	53	44	47

Based on the data in Table 5, it is seen that the stabilizing effect reaches 100% only at a dose of HEDP inhibitor 0.5 mg-eq/dm^3 and a soda content of 0-5 mg-eq/dm^3. As the soda content of the initial solution increases further, the stabilizing effect is reduced by more than half to 41%, due to the higher initial carbonate content in the water. In the case of ATMP as a stabilizer of scale formation at doses of 0.5–2 mg-eq/dm^3, the stabilizing effect did not exceed 67%. At the same time, its efficiency decreased both with the increase of the initial content of carbonates in the solution and with the increase of the concentration of the active reagent, as in the case of HEDP.

When using the SDP stabilizer, the effect did not exceed 67% at different ratios of the sediment stabilizer and the components of the model solution. It should be noted that if in the case of HEDP and ATMP with increasing concentrations, the stabilizing effect decreased, while using SDS, on the contrary, increased by about 10%.

Not very high values of the stabilizing effect for all reagents can be explained both by the high concentration of monovalent chloride ions in solution and the concentration of stabilizers, which was below the threshold level, which reduced the probability of preventing crystal nucleation.

Conclusions

As a result of the conducted researches the estimation of efficiency of the offered corrosion inhibitors is made and efficiency of a number of stabilizers of scaling for their application at processing of highly mineralized waters is defined.

It is shown that the effectiveness of protection of metals from corrosion in aqueous-petroleum mixtures using alkylimidazoline inhibitors and inhibitors developed on the basis of sunflower oil and polyalkylenepolyamine (AC-1), ethylenediamine (AC-2) reaches 90% at doses of 5-50 mg/dm^3.

The stabilizing effect with the use of known and proposed stabilizers of scale formation based on phosphonic acids, which corresponds to 40-70% at a reagent consumption of 0.5-2 mg/dm^3, can be considered a good result.

Concomitant waters from gas and oil production are quite stable in terms of sedimentation, but under certain conditions, due to the high content of hardness ions and bicarbonates / carbonates, destabilization of these waters can be observed.

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Надійшла до редакції 28.04.2022 р.

Хімічні засоби захисту обладнання при експлуатації нафтогазових родовищ

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В статті проаналізовано проблеми, пов’язані з протікання корозійних процесів обладнання при нафто- та газовидобутку. Розглянуто основні протикорозійні методи та засоби, що використовуються в сучасних умовах. Враховуючі механізм та умови протікання корозійних процесів при видобутку і транспортуванні нафтовмісних продуктів та газового конденсату, було обрано для досліджень саме хімічних спосіб захисту обладнання. В якості хімічних засобів в дослідженнях використовувались як відомі інгібітори на основі фосфонових кислот, так і синтезовані речовини на основі сульфонатів, імідазолінів та діамінів. В результаті проведених досліджень оцінено ефективність захисту металів від корозії залежно від складу високомінералізованого середовища, типу металу, типу інгібітора та його концентрації та оцінено ефективність розробленого стабілізатора накипоутворення (нітрилдиметилсульфонату натрію) в порівнянні з відомими реагентами. Показано, що ефективність захисту металів від корозії у водно-нафтових сумішах за допомогою інгібіторів алкілімідазоліну та інгібіторів, розроблених на основі соняшникової олії та поліалкіленполіаміну (АС-1), етилендіаміну (АС-2) досягає 90% у дозах 5 - 50 мг/дм^3. Крім того, часто корозійні процеси супроводжуються процесами відкладання солей жорсткості на поверхні обладнання, що призводить до суттєвого ускладнення експлуатації обладнання. Тому були проведенні дослідження протинакипних властивостей даних реагентів в жорстких умовах. В якості середовища використовували реальні супутні води газовидобутку. Встановлено, що нітрилодиметилсульфонат натрію є досить ефективним стабілізатором утворення накипу і не поступається за ефективністю відомим антискалантам. Запропоновані реагенти можуть бути використані для стабілізації водно-нафтових сумішей і супутніх пластових вод, що утворюються при видобутку та транспортуванні нафти і газу.

Ключові слова: корозія, інгібітор, водно-нафтові суміші, захист від корозії, стабілізатор накипу