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INVESTIGATION OF INHIBITOR-BIOCIDE PROPERTIES OF SULFONATE- AND BENZALKONIUM CHLORIDE-BASED COMPOSITIONS AGAINST CORROSION INVOLVING H_2S, CO_2, AND MICROORGANISMS

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A new multifunctional corrosion inhibitor, SS-41ABAC, has been developed. The inhibitor consists primarily of the sodium salt of a sulfonic acid derived from the sulfation of aminoethylethanolamine, benzalkonium chloride, and an organic solvent. The main objective in developing this inhibitor was to provide a comprehensive approach to mitigating multiple types of corrosion. The effect of the prepared composition-type inhibitor on CO_2 corrosion was studied at different concentrations. It was found that at a concentration of 150 mg/L the inhibitor's protective efficiency was 98.3%. At the same concentration, the protective efficiency against H_2S corrosion was 96%. The biocidal effect of the SS-41ABAC inhibitor against various corrosion-inducing bacteria was studied at different concentrations. It was determined that at 150 mg/L the inhibitor exhibited a 100% protective effect against all three types of bacteria tested: sulfate-reducing bacteria, iron bacteria, and acid-producing bacteria.

Keywords: iron bacteria, heterotrophic bacteria, acid-producing bacteria, sodium sulfonate, aminoethylethanolamine, corrosion rate.

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Introduction

Carbon steel, owing to its favorable mechanical properties and low cost, is widely used in industry. However, this material exhibits low corrosion resistance, which reduces the performance and service life of engineering products. Therefore, it is necessary to employ strategies that mitigate corrosion, such as surface pre-treatments and the use of corrosion inhibitors. Among the various inhibitors, organic compounds, also referred to as adsorption inhibitors, are the most important. Organic corrosion inhibitors are a class of molecules that slow down or suppress the corrosion process. Their effectiveness is mainly attributed to adsorption on the metal surface [1], where they form a barrier layer that limits the access of aggressive species [2]. According to the literature, these molecules are typically adsorbed onto the metal surface by displacing water molecules [3], and their bonding efficiency is enhanced by the presence of polar functional groups containing S, O, or N atoms, as well as by heterocyclic structures and p electrons [4].

The serious consequences of corrosion have become a problem of global significance. In addition to everyday encounters with this type of degradation, corrosion can lead to plant shutdowns, loss of valuable resources, product loss or contamination, reduced efficiency, costly maintenance, and expensive overdesign. It also poses safety risks and hinders technological progress [5].

One type of corrosion is microbiologically influenced corrosion (MIC). MIC is recognized as a major problem in various sectors of the oil and gas industry, as biological growth can lead to both pollution and corrosion. Many microorganisms can accelerate the corrosion of metals. It has been found that the presence of microorganisms in an environment results in more localized corrosion rather than uniform general corrosion [6–8]. MIC is responsible for most internal corrosion observed in oil, gas, and water transmission pipelines.

When bacteria grow on pipe walls, they form colonies composed of multiple bacterial species that interact and support each other. Well-known corrosive types include acid-producing bacteria (APB), sulfate-reducing bacteria (SRB), iron bacteria (FeB), and manganese-oxidizing bacteria (MoB). Among these, SRB and APB are the two types most commonly found in oil and gas pipelines. SRB produce hydrogen sulfide, while APB generate acetic acid or sulfuric acid, both of which are highly corrosive to pipelines. Other bacteria, such as manganese-oxidizing and heterotrophic bacteria, may also be present. Iron bacteria precipitate iron from the solution generated during corrosion and form tubercles on top of corrosion pits.

Microorganisms in aqueous environments form biofilms on solid surfaces. A biofilm consists of populations of microorganisms along with their hydrated polymeric secretions. Numerous types of organisms can coexist within a single biofilm, ranging from strictly aerobic bacteria at the water interface to anaerobic bacteria, such as SRB, at the oxygen-depleted metal surface [9–14]. Biofilms can contribute to corrosion through three mechanisms: physical deposition, production of corrosive by-products, and depolarization of the corrosion cell caused by chemical reactions.

Various chemical reagents, known as bactericidal inhibitors, are used to prevent microbiologically influenced corrosion. The main objective of this study is to investigate the bactericidal inhibitor SS-41ABAC, which is based on sulfonates and a quaternary ammonium compound. The SS-41ABAC inhibitor was evaluated under different aggressive environments.

The primary requirement for corrosion bactericidal inhibitors in the oil industry is their high protective efficiency. It should be noted, however, that the technological characteristics of these reagents do not solely determine their overall effectiveness, but they significantly influence the choice of an inhibitor. Depending on the application conditions, different requirements may be imposed on the physicochemical and technological properties of chemical reagents. Therefore, the study of these properties is one of the most important steps in the development and selection of inhibitors in the laboratory.

Experimental, results and discussion

A new bactericidal inhibitor, SS-41ABAC, with a multifunctional effect was synthesized under laboratory conditions based on SS-41A and benzalkonium chloride (BAC) in a 4:1 ratio. The SS-41A inhibitor was prepared from sodium sulfonate and aminoethylethanolamine at room temperature over 1–2 hours, while benzalkonium chloride (BAC) was used as a commercially available product. During laboratory investigations, the physicochemical properties of the SS-41ABAC reagent were determined (Table 1), and its protective efficiency against CO_2, hydrogen sulfide, and microbiologically influenced corrosion was evaluated.

Determination of the protective effect against CO_2 corrosion

The ACM GIL AC device is a high-specification corrosion monitoring instrument designed for various AC/DC corrosion tests. It combines a potentiostat, galvanostat, and zero-resistance ammeter, making it suitable for comprehensive corrosion studies. In this work, the device was employed together with the Linear Polarization Resistance (LPR) method to evaluate the corrosion protection ability of sulfonates and their compositions. This electrochemical technique enables real-time measurement of corrosion rates, providing valuable data for assessing the effectiveness of corrosion inhibitors.

The experimental procedure involved preparing a 3% sodium chloride solution, which was stirred for 30 minutes using a magnetic stirrer. The solution was

Table 1

Physicochemical properties of the «SS-41ABAC» inhibitor–biocide

Indicator	Value	Test method
external appearance	dark brown liquid	visual
density at 20^0C, g/cm^3	0.935–0.958	state standard GOST 3900-85
freezing temperature (^{0}C)	<–20	state standard GOST 20287-91
kinematic viscosity at 20^0C, mm^2/s (sSt)	45	state standard GOST 33-2000
pH, diluted solution	9–10, 3% H_2O	pH-meter
ignition temperature (^{0}C)	<72	state standard GOST 6356-75

then distributed into four 4000-ml glass beakers, each containing 1000 ml. The beakers were placed on electric heaters and exposed to carbon dioxide at 9 bar and 50^{0}C for one hour under continuous stirring. After this exposure, electrodes made of 080A15 Erade Steel with a surface area of 7.9 cm^2 were introduced into the cells. Prior to use, the electrodes were cleaned with acetone to remove any residual inhibitors.

The ACM GIL device was connected to the electrodes via an AC potentiometer, and the system was saturated with carbon dioxide for one hour. One of the beakers was left untreated to serve as a control, while the other three received different concentrations of the reagent (in ppm) to evaluate inhibitor performance. The test duration was controlled by program settings. The potentiostat recorded measurements every 15 minutes and transmitted the data to a computer running ACM version 5 software. The results were displayed in graphical formats, including potential vs. current density (mA/cm^2), corrosion rate vs. time (mm/min), and metal loss vs. time (mm).

The LPR method, as applied in this study, is highly suitable for plant monitoring, as it provides an almost instantaneous indication of corrosion rates.

The effect of the inhibitor against CO_2 corrosion was studied at concentrations of 50, 100, and 150 mg/L, and the results are presented in detail in Figs. 1, 2 and Tables 2–5. As shown, the maximum protective effect was observed at a concentration of 150 mg/L. Specifically, while the corrosion rate in the uninhibited environment was 4.77 mm/year over 20 hours, it decreased to 0.08 mm/year in the presence of the inhibitor (150 mg/L). This corresponds to a protective efficiency of 98.3% against CO_2 corrosion.

Determination of the protective effect against H_2S corrosion (weight loss method)

The protective effect of the SS-41ABAC inhibitor against H_2S corrosion was studied using the gravimetric method in accordance with the state standard GOST 9.506-87. Tests were carried out for 6 hours in a U-shaped tube equipped with a mechanical stirrer operating at 500 rpm. Corrosion inhibition studies were performed on mild steel specimens. The specimens were first washed with distilled water, degreased with absolute ethanol, dried, and then stored in a desiccator.

Weight loss was determined at different immersion times by weighing the cleaned samples before and after immersion in 1000 cm^3 of the corrosive solution (1% NaCl saturated with H_2S) in a closed beaker under stirring, both in the absence and presence of various concentrations of the inhibitor under investigation. Triplicate specimens were exposed to each condition, and the mean weight loss was reported.

The corrosion rate (CR) [1], inhibition efficiency η (%) [2], and surface coverage (θ) [3] were calculated using the following equations (1)–(3).

$$CR=(W_b-W_a)/S\cdot t, \quad (1)$$

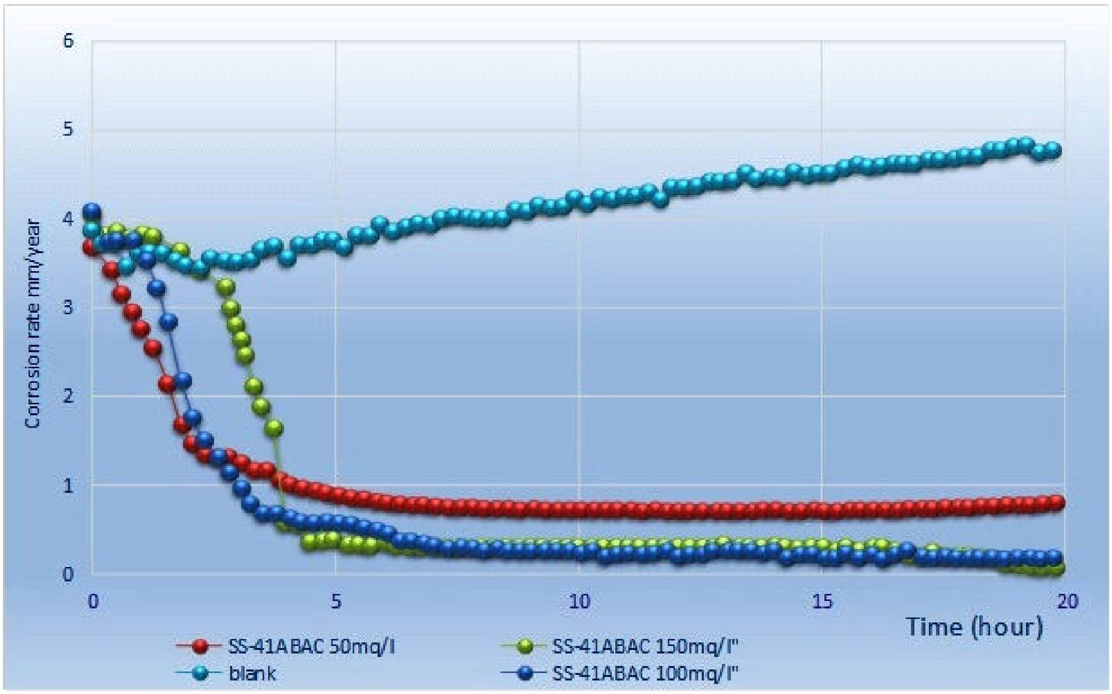

Fig. 1. Corrosion rate over time at different inhibitor concentrations

where CR is the corrosion rate; W_b and W_a are the weights of the sample before and after immersion in the corrosion solution, respectively; S is the exposed surface area; and t is the time in hour.

$$\eta(\%)=((CR(blank)-CR(inh))/CR(blank))\cdot 100\%, \quad (2)$$

where η is the inhibitor efficiency; CR (blank) and CR(inh) represent the corrosion rates in the absence and presence of the inhibitor in the corrosive solution, respectively.

$$\theta=(W_b-W_a)/W_b, \quad (3)$$

where W_b and W_a are the weight losses in the absence and presence of the inhibitors, respectively.

Table 6 presents the results of studies conducted at different concentrations of various inhibitors. The SS-41ABAC inhibitor exhibited the highest performance at a concentration of 150 mg/L. For instance, at 150 mg/L, the maximum inhibition efficiency (% I.E.) reached 96%.

Determination of biocidal activity

It is well known that sessile bacteria accelerate corrosion processes in several ways. Sulfate-reducing bacteria (SRB) produce H_2S, which increases the corrosiveness of brine, causing metals to crack and blister. Acid-producing bacteria generate acids that remove passivating oxide films from metal surfaces.

The quantification of microorganisms was performed according to the following standard: NACE TMO194-2014 Standard Test Method: Field Monitoring of Bacterial Growth in Oil and Gas Systems. Each culture medium supports the growth of only those bacteria capable of utilizing the nutrients provided. For example, sulfate-reducing bacteria are grown in Postgate medium, iron bacteria (FeB) in Wolf medium, and general heterotrophic bacteria (GHB, both aerobic and facultative anaerobic) in heterotrophic bacteria medium and/or phenol red dextrose broth or standard nutrient broth. Phenol red dextrose vials that become turbid between 1 and 14 days are scored as positive for general heterotrophic bacteria, while those exhibiting a color change from red to yellow (or white) are scored as positive for acid-producing bacteria.

In the serial dilution approach to bacterial culturing, progressively smaller portions of the original sample are transferred to successive vials using a stepwise 1:10 dilution scheme until, in theory, no bacteria are transferred. The growth medium in the dilution vials provides nutrients for the proliferation of the transferred bacteria. Bacterial growth produces visible changes in the vials, such as turbidity in general heterotrophic vials, a color change from red to yellow in phenol red vials, or a black precipitate in sulfate-reducer vials. The final vial in the dilution series showing these changes typically contains between 1 and 10 bacteria, representing the dilution factor required to reduce the original inoculum to this concentration. Multiplying by the dilution factor gives an estimate of the number of bacteria per milliliter in the original sample.

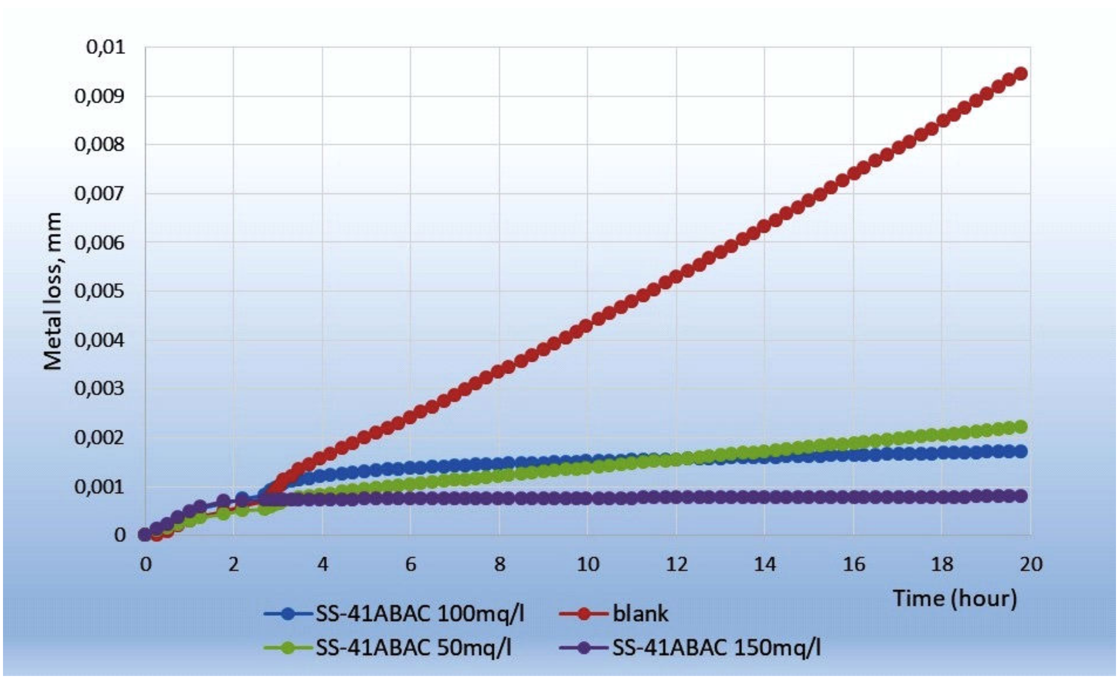

Fig. 2. Metal loss over time at different inhibitor concentrations

The initial bacterial counts in water were: SRB 10^6, FeB 10^6, APB 10^5. After the addition of the biocide, the results obtained are shown in Fig. 3.

The observed high protective efficiency of the SS-41ABAC inhibitor against CO_2 and H_2S corrosion can be attributed to its multifunctional composition. The sodium sulfonate component likely adsorbs on the steel surface, forming a stable barrier layer that reduces direct contact between the metal and aggressive species such as CO_2 and H_2S. Benzalkonium chloride, as a quaternary ammonium compound, enhances the adsorption and contributes to the formation of a compact protective film, while the organic solvent improves the distribution of the inhibitor over the metal surface. The combination of these components results in a synergistic effect, significantly lowering

Table 2

Results of CO_2 corrosion tests in the absence of inhibitor

Time, h	LPR, Ω·cm^2	I_{corr}, mA/cm^2	Corrosion rate, mm/year	Total metal loss, mm
1.0004	83.605	0.3120226	3.6163	0.0004010
3.0500	85.977	0.3034154	3.5165	0.0012176
6.0017	76.831	0.3395344	3.9352	0.0025238
9.0022	74.033	0.3523692	4.0839	0.0039269
11.002	70.865	0.3681191	4.2664	0.0049094
13.003	68.245	0.3822531	4.4303	0.0059263
15.003	66.806	0.3904868	4.5257	0.0069773
17.032	65.296	0.3995168	4.6304	0.0080539
19.033	62.832	0.4151819	4.8119	0.0091757
19.783	63.294	0.4121493	4.7768	0.0095959

Table 3

Results of CO_2 corrosion tests at an inhibitor concentration of 50 mg/l

Time, h	LPR, Ω·cm^2	I_{corr}, mA/cm^2	Corrosion rate, mm/year	Total metal loss, mm
1.0004	120.17	0.2170817	2.7600000	0.0002916
3.0500	242.85	0.1074193	1.2449000	0.0006988
6.0017	375.04	0.0695563	0.8061571	0.0010343
9.0022	413.34	0.0631123	0.7314718	0.0012993
11.002	418.87	0.0622783	0.7218055	0.0014689
13.003	425.43	0.0613184	0.7106806	0.0016366
15.003	425.12	0.0613624	0.7111900	0.0018043
17.032	410.37	0.0635683	0.7367563	0.0019717
19.033	388.23	0.0671930	0.7787664	0.0021500
19.783	375.66	0.0694424	0.8048373	0.0022198

Table 4

Results of CO_2 corrosion tests at an inhibitor concentration of 100 mg/l

Time, h	LPR, Ω·cm^2	I_{corr}, mA/cm^2	Corrosion rate, mm/year	Total metal loss, mm
1.0004	80.588	0.3237068	3.53	0.0004768
3.0500	4324.5	0.0060323	0.97	0.0007275
6.0017	8788.9	0.0029681	0.46	0.0007438
9.0022	10141	0.0025724	0.26	0.0007562
11.002	10531	0.0024770	0.24	0.0007633
13.003	10709	0.0024358	0.27	0.0007700
15.003	11774	0.0022155	0.18	0.0007763
17.032	11753	0.0022196	0.20	0.0007825
19.033	12589	0.0020721	0.19	0.0007883
19.783	12236	0.0021319	0.18	0.0007905

corrosion rates, particularly at the optimal concentration of 150 mg/L. The gravimetric and electrochemical results consistently demonstrate that SS-41ABAC is highly effective under the studied conditions.

The biocidal activity observed against SRB, FeB, and APB further complements the corrosion inhibition. Sulfate-reducing bacteria generate H_2S, which accelerates localized corrosion, while acid-producing bacteria disrupt passive oxide layers, and iron bacteria facilitate tubercle formation on the metal surface. The 100% inhibition at 150 mg/L indicates that SS-41ABAC effectively suppresses bacterial growth, likely by disrupting cell membranes and interfering with microbial metabolism. Consequently, the combined anticorrosion and biocidal effects of SS-41ABAC prevent both chemical and microbiologically influenced corrosion, making it a promising candidate for application in oil and gas systems where CO_2, H_2S, and microbial activity coexist. These results align with previous findings in the literature regarding the importance of adsorption and biocidal properties in multifunctional inhibitors.

Conclusions

1. A new multifunctional corrosion inhibitor, SS-41ABAC, has been developed. The inhibitor mainly consists of the sodium salt of a sulfonic acid obtained from the sulfation of aminoethylethanolamine, benzalkonium chloride, and an organic solvent. The primary objective in developing this inhibitor was to provide a comprehensive approach to mitigating various types of corrosion.

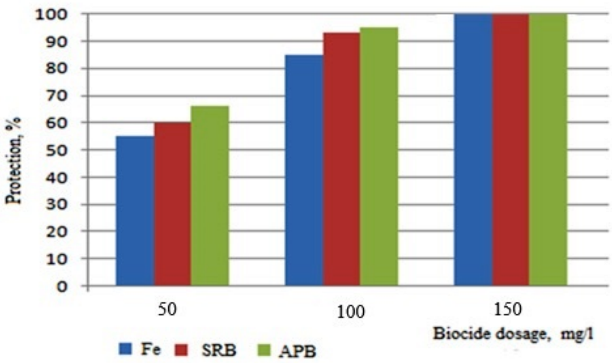

Fig. 3. Biocidal effect of SS-41ABAC against different bacterial types

2. The effect of the developed composition-type inhibitor on CO_2 corrosion was studied at different concentrations over a period of 20 hours. It was found that at a concentration of 150 mg/L, the inhibitor exhibited a protective efficiency of 98.3%. The protection against H_2S corrosion was studied gravimetrically for 6 hours, and at the same concentration, the protective efficiency was 96%.

3. The biocidal effect of the SS-41ABAC inhibitor against various corrosion-inducing bacteria was studied at different concentrations. It was

Table 5

Results of CO_2 corrosion tests at an inhibitor concentration of 150 mg/l

Time, h	LPR, $\Omega\cdot cm^2$	I_{corr}, mA/cm^2	Corrosion rate, mm/year	Total metal loss, mm
1.0004	78.991	0.3302522	3.83	0.0004479
3.0500	167.86	0.1554046	2.64	0.0010118
6.0017	615.36	0.0423926	0.36	0.0013740
9.0022	1314.2	0.0198492	0.31	0.0014840
11.002	1539.1	0.0169493	0.31	0.0015326
13.003	1701.6	0.0153300	0.33	0.0015766
15.003	1714.9	0.0152114	0.31	0.0016186
17.032	1727.4	0.0151016	0.21	0.0016603
19.033	1725.6	0.0151174	0.10	0.0017012
19.783	1790.4	0.0145701	0.08	0.0017163

Table 6

Protective effect of the SS-41ABAC inhibitor–biocide

Inhibitor content, mg/l	Metal loss, g	Corrosion rate, $g/m^2\cdot h$	Delay factor	Protection efficiency,%
without inhibitor	0.01210	1.2870	–	–
50	0.00410	0.4901	2.63	62
100	0.00100	0.1402	9.90	89
150	0.00030	0.0511	25.72	96

determined that at 150 mg/L, the inhibitor provided 100% protection against all three types of bacteria tested: sulfate-reducing bacteria (SRB), iron bacteria (FeB), and acid-producing bacteria (APB).

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ДОСЛІДЖЕННЯ ІНГІБІТОРНО-БІОЦИДНИХ ВЛАСТИВОСТЕЙ КОМПОЗИЦІЙ НА ОСНОВІ СУЛЬФОНАТІВ І БЕНЗАЛКОНІЮ ХЛОРИДУ ПРОТИ КОРОЗІЇ ЗА УЧАСТЮ H_2S, CO_2 ТА МІКРООРГАНІЗМІВ

Е.Ф. Султанов, А.Н. Курбанов, І.З. Сардарова

Розроблено новий багатоцільовий інгібітор корозії SS-41ABAC. Інгредієнт складається переважно з натрієвої солі сульфонової кислоти, одержаної шляхом сульфатації аміноетилетаноламіну, бензалконію хлориду та органічного розчинника. Основною метою розробки цього інгібітору було забезпечення комплексного підходу до протидії різним типам корозії. Вплив підготовленого композиційного інгібітора на корозію, викликану CO_2, вивчали при різних концентраціях. Встановлено, що при концентрації 150 мг/л захисна ефективність інгібітору становила 98,3%. За тієї ж концентрації захисна ефективність щодо корозії, спричиненої H_2S, становила 96%. Біоцидну дію інгібітору SS-41ABAC проти різних бактерій, що спричиняють корозію, вивчали при різних концентраціях. Встановлено, що при 150 мг/л інгібітор проявляв 100% захисну дію щодо всіх трьох типів досліджуваних бактерій: сульфатредукуючих бактерій, залізобактерій та кислотопродукуючих бактерій.

Ключові слова: залізобактерії; гетеротрофні бактерії; кислотопродукуючі бактерії; натрієвий сульфонат; аміноетилетаноламін; швидкість корозії.

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Keywords: iron bacteria; heterotrophic bacteria; acid-producing bacteria; sodium sulfonate; aminoethylethanolamine; corrosion rate.

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