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ИССЛЕДОВАНИЕ ЭФФЕКТИВНОСТИ ПРОТИВ КОРРОЗИИ И СОЛЕОТЛОЖЕНИЯ КОМПОЗИТОВ, СОДЕРЖАЩИХ ГОССИПОЛОВУЮ СМОЛУ

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Одним из важных вопросов, который необходимо решать в странах с развитой нефтегазовой промышленностью, является эффективная борьба с солеотложениями и коррозией. В то же время разработка ингибиторов, композиций с многофункциональным комплексным действием против солеотложений и коррозии, проведение испытаний в лабораторных и полевых условиях остается актуальной задачей, вытекающей из требований времени. Представленная статья посвящена лабораторным испытаниям многофункциональных составов, препятствующих процессам коррозии и солеотложения в системе сбора и транспорта нефтяных скважин. При приготовлении составов использовали смолу госсипол, ингибитор МАРЗА-2, керосин и дизельное топливо. Год назад было приготовлено двенадцать составов (шесть на керосине и шесть на дизельном топливе) с различным процентным содержанием компонентов и изучены их физико-химические и технологические свойства. Установлено, что исследуемые композиции обладают необходимой вязкостью и ингибиторами коррозии, стабильны при пластовой температуре, стабильны до -40 °С и являются гомогенными флюидами, совместимыми с пластовыми водами и тампонажными растворами. Затем была изучена эффективность приготовленных составов против отложений карбоната кальция и коррозии в лабораторных условиях. В качестве объекта исследования использовалась модель пластовой воды скважины 326 месторождения Гюнешли. Эксперименты проводились как в реагентной, так и в безреагентной среде. Результаты многочисленных экспериментов показали, что в целом исследуемые соединения обладают комплексным действием против образования накипи и коррозии. Замечено, что эффективность повышается при постоянном соотношении количества керосина и дизельного топлива в композициях, увеличении количества ингибитора МАРЗА-2 и уменьшении количества госсиполовой смолы. Наибольшая эффективность против отложений карбоната кальция и коррозии отмечена у ингибитора комплексных действии отложения солей и коррозии К5, содержащего 99% ингибитор коррозии (ИК) и 98% ингибитор солей (ИС) на 100 мг/л, а также у С5, содержащего 100% ИК и 99% ИС на 100 мг/л. Начальная оптимальная концентрация К5 составила 40 мг/л (эффективность ИК 92%, ИС 91%) и С5 - 30 мг/л (эффективность ИК 91%, ИС 91%).

Ключевые слова: пластовая вода, госсиполовая смола, МАРЗА-2, состав, коррозия, солеотложение, керосин, дизельное топливо, эффективность, комплексное воздействие, оптимальная вязкость, карбонат кальция, ингибитор

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INVESTIGATION OF THE EFFICIENCY OF THE COMPOSITION CONTAINING GOSSYPOL RESIN AGAINST CORROSION AND SALT DEPOSITIONS

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One of the important issues that need to be addressed in countries with a developed oil and gas industry is the effective fight against scaling and corrosion. At the same time, the development of inhibitors, compositions with multifunctional complex action against scaling and corrosion, testing in laboratory and field conditions remains an urgent problem arising from the requirements of the time. The presented article is devoted to laboratory tests of multifunctional compositions that prevent corrosion and scaling processes in the oil well collection and transportation system. The gossypol resin, a MARZA-2 inhibitor, kerosene, and diesel fuel were used in the preparation of the compositions. A year ago, twelve compositions (six in kerosene and six in diesel fuel) were prepared with different percentages of components and their physicochemical and technological properties were studied. It has been established that the studied compositions have the required viscosity scale and corrosion inhibitors, are stable at reservoir temperature, stable up to -40 °C and are homogeneous fluids compatible with formation waters and plugging solutions. Then the effectiveness of the prepared compositions against calcium carbonate salts and corrosion in laboratory conditions was studied. The model of formation water of well 326 of the Guneshli field was used as a research environment. The experiments were carried out in both reagent and reagentless media. The results of numerous experiments have shown that, in general, the compounds understudy have a complex action against scaling and corrosion. It is noted that the efficiency increases with a constant ratio of the amount of kerosene and diesel fuel in the compositions, an increase in the amount of the MARZA-2 inhibitor, and a decrease in the amount of gossypol resin. The highest efficiency against calcium carbonate deposits and corrosion was noted for the inhibitor of the complex action of salt deposition and corrosion K5, containing 99% corrosion inhibitor (CI) and 98% salt inhibitor (SI) per 100 mg/l, as well as C5, containing 100% CI and 99% IC at 100 mg/L. The initial optimal concentration of K5 was 40 mg/l (efficiency IC 92%, SI 91%) and C5 - 30 mg/l (efficiency IC 91%, SI 91%).

Key words: formation water, gossypol resin, MARZA-2, composition, corrosion, scaling, kerosene, diesel fuel, efficiency, complex effect, optimal viscosity, calcium carbonate, inhibitor

INTRODUCTION

Currently, the main energy source for humanity, which is at a technologically advanced stage, remains oil due to its physical and chemical properties. Countries of the world with developed oil industries produce millions of tons of oil every day. Electrochemical corrosion processes caused by asphaltene-resin-paraffin deposits, salt deposits, corrosive media, and microorganisms in the production, storage, treatment, and transportation of oil through pipelines create complex problems petroleum engineers. This is because that the above factors cause premature failure of the lifting pipes of the elevator, oil-well tubing, rod pumps, injection lines and other linear pipelines, tanks, oily pipelines and main pipelines at all stages of the collection, and transportation system. Problems caused by scale, and corrosion aggression leads to failure not only of equipment, devices, pipes, etc., made of precious metals and their alloy, but also violate the ecological balance of nature. It should be noted that the growth of oil production and refining since the end of the twentieth century has exacerbated the problem of salt deposition and corrosion in general.

In the countries of the world oil industry, up to five times more formation, water is extracted than produced oil. This amount is even higher if we consider the injection of water into the reservoir in the reservoir pressure maintenance system. As you know, formation waters, being electrolytes, contain hydrogen sulfide, carbon dioxide, oxygen, microorganisms, mineral salts of various compositions, including sodium chloride, calcium chloride, magnesium chloride, sodium carbonate, sodium bicarbonate, calcium bicarbonate, sulfates, sulfides, boron compounds, organic substances (compounds of naphthenic acid, etc.). Iron, aluminum, and silicon oxides are also found in some formation waters. It is known from the composition of associated water that it plays the role of both an agent of scaling and electrochemical corrosion of oil field equipment [1-2].

Protecting metal equipment used in the oil industry from corrosion and scale is an urgent issue. The combined damage caused by these problems to the global economy amounts to billions of dollars a year. As mentioned above, corrosive elements in the composition of oil and formation water lead to equipment corrosion during operation. On the other hand, the presence of sulfate-reducing bacteria in such an environment intensifies the process, and increases the rate of electrochemical corrosion of equipment. As a result, the oil industry suffers both economic and environmental damage.

The presence of hydrogen sulfide in associated water is considered very dangerous for plants and equipment. This is because that hydrogen sulfide, in addition to its high reactivity also acts as a catalyst for the formation of hydrogen embrittlement of metals.

Although the process of corrosion of metals in hydrogen sulfide environments is currently widely studied by researchers, namely, in the oil industry, research and solutions to this problem has both practical and economic significance. On the other hand, it is known that seawater, reservoir water, and freshwater are injected into the reservoir to maintain reservoir pressure. Microorganisms or bacteria in these waters penetrate the formation. The most dangerous of these microorganisms in terms of corrosion are sulfate-reducing bacteria (SRB). One of their main features is the ability to adapt to any extreme conditions. SRBs grow and multiply very quickly when conditions are favorable. SRBs can also develop in an oxygen-free environment. They increase the environment's corrosiveness by reducing sulfate ions (SO_4^{2-}) to sulfite ions (S^{2-}). In addition to drastically reducing the conductivity of the bed, SRB also increases the corrosion rate of oil field equipment. This, in turn, leads to a reduction in turnaround time and decreased productivity [3-8].

It should be noted that since Azerbaijan has developed oil and gas production, oil and gas processing, petrochemical and chemical industries, corrosion of metal structures and equipment used in these industries is one of the most serious problems for our country. Depending on the environment, along with the corrosion process, other processes occur, which in turn makes it difficult to solve the problem. This is especially acute in the oil industry. Thus, corrosion in oil production, storage and transportation systems occurs rapidly in the presence of microorganisms and salt deposition processes.

As mentioned above, during the development and operation of oil fields, the formation of the reservoir and injected water in the well product is inevitable, which occurs at a relatively high rate during field irrigation at the final stage of development. Namely, the water cut of the produced product leads to the formation of salt deposits. The problem of salt scale formation is considered a constant companion of the oil production process both at the initial and final stages of field development. Scale formation during the development and operation of oil fields is a rather complex and multifaceted process associated with natural and technogenic phenomena. Associated water is the main source of salt deposition in oil production. This is due to its re-saturation with poorly soluble salts, which occurs under the influence of changing production conditions - temperature, pressure, the concentration of salt-forming ions and other factors.

Injection of sulfuric acid into oil wells to increase the oil recovery factor, in turn, leads to a significant increase in the number of sulfate ions in the formation water, which leads to the formation of hardly soluble salts of barium sulfate (barite) and calcium sulfate (gypsum, anhydrite). If we compare the distribution zones of wells complicated by barite and gypsum deposits and the zones of sulfuric acid injection, it seems that these zones in the field overlap. Thus, the introduction of sulfuric acid into the productive stratum affects the processes of salt deposition. In addition, the injection of sulfuric acid changes the properties of the oil. When this acid reacts with oil, sulfate resin is formed. Rather, the content of resins and asphaltenes in oil increases, which are also considered natural oil surfactants and can also affect the scaling processes in wells. Scale formation begins when the state of any natural solution is disturbed by an increase in the solubility of one or more components. The solubility of the minerals has a complex relationship with temperature and pressure. Typically, an increase in temperature leads to an increase in the solubility of various minerals in the water. Most ions dissolve at high temperatures. A decrease in pressure also leads to a decrease in solubility. However, not all minerals are subject to typical temperature dependence.

Oil production processes are accompanied by the formation of solid deposits of mineral salts in the drilling zone of production wells, walls of tubing and production strings, pumping equipment, ground communications of oil treatment and storage systems. Formation water is the main source of scale formation along with oil. In operating conditions, when the product is watered, wells and surface equipment are subject to scale deposition. Precipitation of mineral salts in solution occurs when the concentration of these substances and ions in the solution exceeds equilibrium.

Operational processes are disrupted due to the fact that salt deposits partially or completely cover the cross-sectional areas of the pipes. For oil field practice, this means the loss of oil and a significant rise in its cost due to extensive repairs. In the oil industry, the main challenge is to improve oil production efficiency, storage, and transportation. One of the main directions in solving this problem is the fight against the deposition of mineral salts.

There are numerous information in the practice of local and foreign oil fields on the study of the causes, mechanisms, and kinetics of the formation of solid salt deposits on the surface of the ground and underground equipment, in the area of drilling of production wells, field oil gathering pipelines, measuring instruments, and oil treatment plants, as well as in maintenance systems of reservoir pressure.

Prevention of scale formation in wells, oil storages, and plants is the main direction of control against this process. Different approaches can be used to solve this problem depending on the nature and conditions of field development and technical means. Despite the variety of means of controlling salt deposits, the main method for preventing scale formation is special chemical reagents and scale formation inhibitors.

In the literature, it is recommended to use hydrochloric acid to prevent scale formation on the pipes' inner surface. However, this method does not prevent scale build-up during operation and can only be used after the scale has formed. There is also a method for separating mineral salts in the composition of formation waters inside the well to prevent the scale, and then removing these salts to the surface together with the well product. However, some shortcomings of this method do not allow to effectively use it in production.

Modern scale inhibitors, used in industry, are mainly composed of phosphorus compounds, some of which are very toxic. For example, oxyethylene diphosphonic acid, a widely used as scale inhibitor, is highly irritating to mucous membranes and human skin. It also has teratogenic and embryotropic effects. In addition to the direct effects on personnel's health phosphorus compounds are also considered very harmful to the environment. Corrosion inhibitors in the oil industry usually include organic compounds and compositions based on them [9-19].

At present, for the simultaneous prevention of scale deposits and corrosion of oil field equipment, a chemical method using inhibiting compositions is considered an effective method. The development of non-toxic, high-perfomance compositions also plays a key role in solving environmental problems.

Thus, the creation of complex effective compositions with a high anti-scale and anti-corrosion the effect remains an urgent problem not only in our country but also in developed oil countries. Of course, despite some difficulties in creating such reagents, it is desirable to continue research in this direction. This is because the most effective and technologically advanced method of combating corrosion and deposits of mineral salts is the use of chemical reagents. Currently, the global oil industry has a rather large range of corrosion and scale inhibitors. The main condition for preventing corrosion and scale of inorganic salts in the equipment of wells and pipelines is the correct observance of the requirements and rules for choosing inhibitors and technologies for their use.

By the nature of the scale inhibitors and the mechanism of action on saturated solutions, they are divided into three types: blocking, complexing and mixed reagents.

Reagents of the first type form a protective coating on the surface of the centers of the salt crystals, weakening the speed of their growth, blocking the merging of crystals with each other, the deposition of salts on the surface of the equipment. The second type of reagents prevents the accumulation of crystals of solid salts on the surface of the metal due to the formation of water-soluble anionic complexes or chelatetype complexes with cations of alkaline earth metals in the formation of water. The third class of scale inhibitors combines the properties of both types of reagents.

As a rule, to ensure effective protection of field equipment, chosen for this condition, corrosion and scale inhibitors should constantly be present in the system in the required quantity. Also, to achieve the maximum protective effect, the basic condition is the addition of corrosion reagents and mineral salts to the moment of crystallization [21-24].

The aim of the study is the development of the composition with a complex action against scaling and corrosion with the participation of the plant-based gossypol resin and the study of the effectiveness of protection in laboratory conditions.

METHODOLOGY EXPERIMENT

The main requirement for corrosion and scale inhibitors in the oil industry is their high protective effect. It should also be noted that technological characteristics of the reagents do not play a final role in assessing their overall effectiveness and significantly affect the choice of inhibitor. Depending on the conditions of application, different requirements may be imposed on the physicochemical and technological characteristics of chemical reagents. For this reason, the study of their physicochemical and technological properties is one of the most important requirements for the development and selection of reagents in the laboratory.

At the initial stage of research in the laboratory was prepared twelve compositions of the different compound, including MARZA-2, gossypol resin, kerosene, and diesel fuel as scale and corrosion inhibitors with a complex effect (Table 1 a, b). MARZA-2 inhibitor is a triple-bonded organic compound that contains carbon, hydrogen, oxygen, halogen, etc. element retains atoms [7]. Gossypol resin is an herbal inhibitor and an intermediate in the production of cottonseed oil [25].

Table 1

Composition and brand of composites

***Таблица 1.* Состав и марка композитов**

№	Components included in the composition	The amount of interest in the composite,%	The brand of the composite
a			
1	MARZA-2 + gossypol resin + kerosene	5:45:50	CESCİ – C1
2	MARZA-2 + gossypol resin + kerosene	7:43:50	CESCİ – C2
3	MARZA-2 + gossypol resin + kerosene	9:41:50	CESCİ – C3
4	MARZA-2 + gossypol resin + kerosene	11:39:50	CESCİ – C4
5	MARZA-2 + gossypol resin + kerosene	13:37:50	CESCİ – C5
6	MARZA-2 + gossypol resin + kerosene	15:35:50	CESCİ – C6
b			
1	MARZA-2 + gossypol resin + diesel fuel	5:45:50	CESCİ - S1
2	MARZA-2 + gossypol resin + diesel fuel	7:43:50	CESCİ - S2
3	MARZA-2 + gossypol resin + diesel fuel	9:41:50	CESCİ – S3
4	MARZA-2 + gossypol resin + diesel fuel	11:39:50	CESCİ – S4
5	MARZA-2 + gossypol resin + diesel fuel	13:37:50	CESCİ – S5
6	MARZA-2 + gossypol resin + diesel fuel	15:35:50	CESCİ – S6

The following physical, chemical, and technological properties of the prepared compositions are defined.

Determining the appearance of composition. The inhibitor’s appearance is determined visually on a white background in a test tube of colorless transparent material. To do this, 30 ml of the tested regent was added to the appropriate test tube, and the color was determined in the conductive light. The inhibitor responds to the requirements of color homogeneity, absence of suspended and precipitated particles in the composition.

Determination of composition density. Areometers were used for determination the density of the composition at a temperature of 200 according to the method given in [26]. In this case, a 300 ml volumetric flask was filled with 250 ml of reagent and placed in a thermostat. When the inhibitor’s temperature was 20 °C, an aerometer was inserted into the cylinder, and the readings were recorded in 60 s.

Determination of the kinematic viscosity of the composition. Kinematic viscosity was determined by the rule given in [27]. Viscosity was determined on the viscometer Reotes-2 in the temperature range +20 °C – (-30 °C).

Determination of thermostability (thermal resistance) of the composition. The determination of the heat resistance of the reagent is based on its storage in the heating chamber at room temperature for 24 h. The thermal stability of the composition was determined visually. During the process, the color of the reagent, its stratification, and the number of foreign substances and particles suspended in the medium and deposited at the bottom of the test tube, were determined.

Determination of the freezing point of the composition. The determination of the the composition's freezing point was carried out according to the method described in [28]. In this case, the test reagent was placed in a cryostat, and its fluidity was visually recorded at every 3 °C. It has been found that the freezing point of the compositions varies from -30 °C to 40 °C.

Determination of the hydrogen index (pH) in the composition. The hydrogen content in the reagents was determined using a pH meter. The measurement of the potential difference between a glass electrode and a silver chloride reference electrode is the basis of the pH determination method. The electrodes are immersed in the reagent, mixed with a magnetic stirrer until a stable pH value is determined. The test liquid temperature 20(±1) °C. As a result of the analysis, the arithmetic average of the results of two parallel definitions was taken, and it was found that the difference between them did not exceed 0.1 pH.

Compatibility evaluation of composition with the model of formation water.

The inhibitor solution was added to a test tube with 10 ml of saline water using a pipette through the dosimeter; the inhibitor's concentration in the resulting mixture was 50 g/l. Then, after thorough mixing of the mixture, the tube was closed with a stopper. The tube was first stored in the heat chamber at 20 °C and then at 90 °C for 3 h.

The absence of sediment at the bottom of the tube and colloidal particles suspended in the solution after thermostating, and the absence of stratification in the sample, suggest that it is compatible with the formation water model.

Determination of the compatibility of the composition with the plugging solution. Evaluation of compatibility of prepared compositions with a plugging solution was carried out with a mixture of solutions KCl (= 1.16 g/cm^3), NaCl (= 1.18 g/cm^3), $CaCl_2$ (= 1.32 g/cm^3). The inhibitor concentration in the resulting mixtures was 20, 30, 40, 50, 70, 100, 120 mg/l, respectively. To assess reagent's compatibility with the plugging solution, the required volume of plugging solution was poured into the test tube using a pipette, the reagent tested with the dosimeter was added. After thorough mixing, the tube was closed with a cork. The tube was first stored in the heating chamber at 20 °C for 3 h and then at 90 °C at the same time.

The absence of sediment and colloidal particles suspended in the solution at the bottom of the test tube after thermostating, as well as the absence of stratification in the sample, suggest that it is compatible with plugging solution.

To assess the complex effective protective action of the compositions against salt deposition and corrosion, a model of the formation water of well, 1802 of the NGDU "Bibiheybatneft" field was prepared in the laboratory (Table 2).

Table 2

Ionic composition of formation water of well 1802 of the NGDU "Bibiheybatneft" field

Таблица 2. **Ионный состав пластовой воды скважины 1802 месторождения НГДУ «Бибихейбатнефть»**

№	Ions	Ions concentration, mg/l	Equivalent concentration of ions, mg·eq/l	Equivalent amount, %
1	$Na^+ + K^+$	31298.987	1304.12	46.57
2	Ca^{2+}	1122.24	56	1.9998
3	Mg^{2+}	486.4	40	1.4284
4	Fe^{3+}	2561.58	853.86	-
5	Cl^-	49010.49	1382.52	49.37
6	SO_4^{2-}	28.81	0.60	0.0214
7	CO_3^{2-}	0.00	0.00	0.0000
8	HCO_3^-	1037.00	17.00	0.6071

As can be seen from the table, the formation water of well 1802 of the NGDU "Bibiheybatneft" field is sodium-hydrocarbonate water of the first category of salinity. The procedure for determining the protective properties of complex effective scale and electrochemical corrosion inhibitors was carried out in the following sequence.

Methodology for determining the effectiveness of protecting compositions against calcium carbonate salts. This technique is based on evaluating the properties of the compositions to "hold" calcium cations in solution. The effectiveness of reagent protection was determined for their concentrations of 20, 30, 40, 50, 70, 100, 120 mg/l. Initially, two solutions were prepared to contain 1% inhibitor, 20% potassium hydroxide, trilon B solution, and murexide indicator, as well as calcium carbonate A and bicarbonate anions B to prevent calcium carbonate deposition in the reservoir water model.

Solutions of the 1% inhibitor were prepared by dissolving one gram of the reagent sample in distilled water in a 100 ml volumetric flask, 20% potassium hydroxide by dissolving 20 g of a potassium hydroxide sample in distilled water in a 100 ml volumetric flask and 0.05 N trilion B by dissolving 1 mol of the standard titrimetric substance in distilled water in a 2 l volumetric flask. Fine grinding one also prepared the murexid indicator part murexid and 50 parts sodium chloride crystals in a porcelain mortar.

In the next step, anti-scale tests in the following sequence:

- 50 ml of solution A was poured into a test tube and placed in the test chamber and added 1% solution of the composite of the given concentration (in one of the test tubes for comparison the reagent was not added). Then in test tubes in turn added 50 ml of solution B, the lids were closed, stirred and kept in the thermobath at the formation temperature for six hours.
- At the end of the period, after cooling the tubes to 25 °C, the liquid inside the flask was filtered through a filter paper and determined the remaining amount of calcium ions in the filtrate. To do this, 10 ml of the test solution was pipetted and poured into a conical distillation flask, then 25 ml of distilled water, 1.5 ml of potassium hydroxide solution and 10-15 mg of murexide indicator were added. Titration process with 0.05 N the solution of Trilon B was continued until the color of the original solution completely disappeared, or, more precisely, until the raspberry color changed to purple. The number of calcium ions (mg/l) in the filtered the solution was calculated by the following expression.

$$[Ca^{+2}] = \frac{V_{trB}\cdot C_{trB}\ \cdot 20{,}04}{V_{\ k}}\cdot 1000$$

where: V_{trB} – volume of trilon B, used for titration, ml; C_{trB} – density of trilon B solution, mg/l; $V_{\ k}$ – sample volume taken for analysis, ml; 20.04 – equivalent amount of calcium, g/mol.

The protective effect for the specified concentration of the composition was calculated according to the following formula.

$$Z_s = \frac{(C_1 - C_2)}{(\frac{C_0}{2} - C_2)}\cdot 100$$

where: Z_s – protective effect at scaling inhibitor,%; C_1 – the amount of calcium ions in the sample with the inhibitor after cooling, mg/l; C_2 – the amount of calcium ions in the "hot" control sample, mg/l; C_0 – the amount of calcium ions in an empty "cold" sample before deposition, mg/l.

By dividing the calcium ion concentration in the prepared solution A into two, the calcium ion concentration in the initial sample ("empty" sample) before deposition was determined.

Thus, the study’s final result was the average algebraic value of two parallel tests (the difference between the values of parallel tests was less than 4%).

Methodology for determining the effectiveness of corrosion protection of compositions. To study the corrosion intensity in the formation of water, samples of steel Ct 3 were used.

To determine the corrosion rate of steel plates Ct3 size 30×20×1 mm by weight loss, studies were conducted in the laboratory for 24 h at a temperature of 25 °C.

Steel plates Ct3 were polish on a polishing machine, cleaned with acetone and alcohol, and weighed on analytical scales. The experiments were conducted in parallel in the same conditions for comparison, both without the composite and with the composite’s addition.

Upon completion of laboratory tests, the steel plates were removed from the medium, and the surface was cleaned of corrosion products. For this plates were cleaned with a cotton swab in a solution of 10% hydrochloric acid and 40% formalin, washed with running water, and dried in acetone. The plates were kept in the desiccator for 10-12 h to stabilize the weight as before and after the experiment. Then the plates were weighed again.

The corrosion rate was calculated based on the following mathematical expression.

$$K = \frac{m_1 - m_2}{S\cdot\tau}$$

where m_1 – pre-test mass of the sample, g; m_2 – sample mass after removal of corrosion products, g; S – sample area, m^2; τ – duration of the test, hour, $K_{inh.}$ – corrosion rate in the presence of composite ($g/m^2\cdot h$).

The protection (Z) effect of the composites was calculated according to the following formula

$$Z_c = \frac{K_0 - K}{K_0}100\%$$

were, Z_c – protective effect at corrosion, K_0 – corrosion rate in the medium without composite, K – corrosion rate in the composite environment ($g/m^2\cdot h$).

The composites’anticorrosive action was determined in the medium of the formation water model +143 mg/l hydrogen sulfide.

RESULTS AND THEIR DISCUSSION

In the laboratory, comprehensive tests were carried out to evaluate the effectiveness of 12 composites against calcium salts and corrosion to select the composition for use in the oil industry and determining the optimal density. The results are presented in Tables 3 and 4.

Based on the results of the experiments presented in the tables, it was determined that:

1. The components CESCİ - C1, CESCİ - C2, CESCİ - C3, CESCİ - C4 and CESCİ - S1, CESCİ - S2, CESCİ - S3, CESCİ - S4 have a complex protective

effect against corrosion and calcium deposits less than 90%, that does not meet the requirements for complex action reagents.

2. Compositions CESCİ - C6 and CESCİ - S6 have a protective effect more than 90% from corrosion and scaling simultaneously only at concentrations of 100 mg/l.

3. Compositions CESCİ-C5 and CESCİ-S5 in all studied concentrations (In addition to 120 mg/l) act comprehensively against corrosion and scaling. The maximum effectiveness of CESCİ-C5 and CESCİ-S5 is observed at concentrations of 100 mg/l.

According to the results of laboratory tests, studies were conducted for concentrations of 20, 30, 40, 50, 70, 100, 120 mg/l, to determine, at what concentrations, the initial protective effect is not less than 90% in the composition CESCİ - C5 and CESCİ – S5.

Table 3

The results of experiments on the effectiveness of the composition of CESCİ against calcium salts and corrosion (solvent - kerosene)

Таблица 3. **Результаты экспериментов по эффективности состава ИКДСК против солей кальция и коррозии (растворитель - керосин)**

Concentration, mg/l	The effectiveness of the composition											
	CESCİ C 1		CESCİ C 2		CESCİ C 3		CESCİ C4		CESCİ C 5		CESCİ C 6	
	Cİ, %	Sİ, %	Cİ, %	Sİ, %	Cİ, %	Sİ, %	Cİ, %	Sİ, %	Cİ, %	Sİ, %	Cİ, %	Sİ, %
50	58	56	71	60	80	65	86	71	92	93	85	83
70	64	61	78	66	83	70	89	75	95	96	88	87
100	67	65	82	73	84	75	90	79	99	98	92	91
120	65	63	79	70	80	71	88	75	89	90	89	88

Notes: Cİ - corrosion inhibitor

SI-salt inhibitor

Примечание: CI – ингибитор коррозии, SI – солевой ингибитор

Table 4

Results of experiments on the effectiveness of the composition of CESCİ against calcium salts and corrosion (solvent - diesel fuel)

Таблица 4. **Результаты экспериментов по эффективности состава ИКДСК против солей кальция и коррозии (растворитель - дизельное топливо)**

Concentration, mg/l	The effectiveness of the composition											
	CESCİ S1		CESCİ S2		CESCİ S3		CESCİ S4		CESCİ S5		CESCİ S6	
	Cİ, %	Sİ, %	Cİ, %	Sİ, %	Cİ, %	Sİ, %	Cİ, %	Sİ, %	Cİ, %	Sİ, %	Cİ, %	Sİ, %
50	60	59	74	63	83	69	87	74	94	96	86	85
70	65	63	81	69	85	72	88	79	97	98	89	88
100	69	70	84	76	88	79	90	83	100	99	93	92
120	67	69	81	89	86	88	87	81	89	90	88	90

Table 5 and table 6 presents the results of the study of the effectiveness of the protection of compositions CESCİ - C5 and CESCİ – S5 against the deposition of calcium carbonate.

Table 5

Protective action of the composition CESCİ-C5 against calcium salts

Таблица 5. **Защитное действие композиции - ИКДСК К5 от солей кальция**

№	Concentration, mg/l	Protection effect,%
1	20	85
2	30	89
3	40	91
4	50	93
5	70	96
6	100	98
7	120	90

Table 6

Protective action of the composition CESCİ - S5 against calcium salts

Таблица 6. **Защитное действие композиции ИКДСК-С5 от солей кальция**

№	Concentration, mg/l	Protection effect,%
1	20	88
2	30	91
3	40	93
4	50	96
5	70	98
6	100	99
7	120	90

As can be seen from the table, there is a gradual increase in their protective action (In addition to 120 mg/l) as the concentration of both composites increases from 20 mg/l to 100 mg/l. The protective effect of CESCİ - C5 in the range from 40 mg/l to 100 mg/l and CESCİ - S5 range from 30 mg/l to 100 mg/l is more than 90%.

At the next stage, the anticorrosive effect of the composition CESCİ - C5 and CESCİ - S5 was determined at the above concentrations (Tables 7 and 8).

Table 7

Anticorrosive effect of the composition CESCİ -C5

Таблица 7. **Антикоррозионное действие состава ИКДСК-К5**

№	Concentration, mg/l	Protection effect,%
1	20	86
2	30	90
3	40	92
4	50	92
5	70	95
6	100	99
7	120	89

Table 8

Anticorrosive effect of the composition CESCİ -S5

Таблица 8. **Антикоррозионное действие состава ИКДСК-С5**

№	Concentration, mg/l	Protection effect,%
1	20	89
2	30	91
3	40	93
4	50	94
5	70	97
6	100	100
7	120	89

As can be seen from table 8, the composition of CESCİ -C5 demonstrates a corrosive efficiency of less than 90% at concentrations below 40 mg/l. However, a further increase in concentration allows increasing the inhibitory effect to 92-9 mg (excluding concentrations of 120 mg/l). The composition CESCİ - S5 (table 9) has an effect of less than 90% at concentrations of 20 mg/l and 120 mg/l. In the range of concentrations from 30 mg/l to 100 mg/l, the reagent's protective effect against corrosion varies from 91 to 100%.

Thus, numerous laboratory studies have shown that the initial optimal effective concentration of not less than 90%, which has a simultaneously complex effect on calcium carbonate deposits and electrochemical corrosion is 40 mg/l for CESCİ -C5 and 30 mg/l for CESCİ -S5 (Fig. 1 and 2).

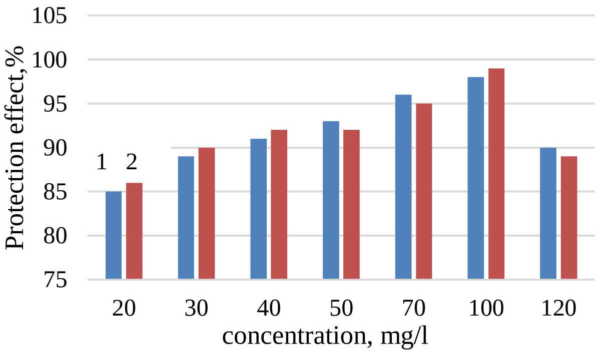

Fig. 1. Generalized results of protection efficiency of CESCİ -C5
Рис. 1. Обобщенные результаты эффективности защиты ИКДСК-К5

The technical result of the development of compositions CESCİ -C5, CESCİ -S5 is a simultaneous double action in the studied compositions, and more precisely their high complex protective effect against the formation of calcium carbonate deposits and corrosion in oilfield equipment. During the development of the compositions, special attention was paid to the verification of their physical, chemical and technological properties. Thus, the composition has the necessary viscosity for scale and corrosion inhibitors, and is a homogeneous fluid which is stable at formation temperature, resistant to negative temperatures, compatible with the formation and plugging solutions. Thus, it was established that the compositions CESCİ - C5 and CESCİ - S5 meet the general requirements of oil companies for the physical, chemical, and technological properties of liquid inhibitors.

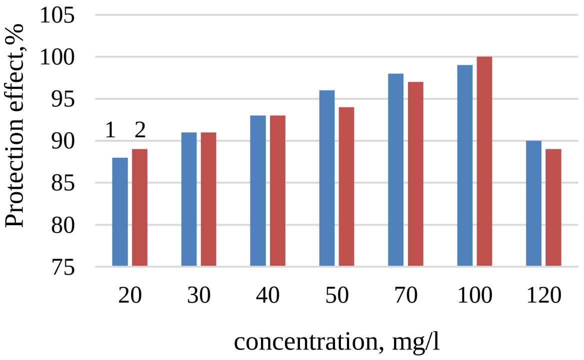

Fig. 2. Generalized results of protection efficiency of CESCİ - S5
Рис. 2. Обобщенные результаты эффективности защиты ИКДСК-С5

CONCLUSION

For the first time, using MARZA-2, gossypol resin, kerosene and diesel fuel components, twelve composites with a complex action against calcium carbonate salts and corrosion were prepared, their physicochemical and technological properties were determined. It is established that the physicochemical and technological properties of the developed compositions fully correspond to the requirements of oil companies for such reagents.

To study composites' effectiveness against the deposition of calcium carbonate in the laboratory was developed a model of formation water wells 1802 of the NGDU "Bibiheybatneft" field. The experiments were performed at concentrations of composites 50,70,100,120 mg/l. At the same time, maximum effect against the deposition of calcium carbonate and corrosion was observed at a concentration of 100 mg/l of composites CESCİ - C5, CESCİ - S5. Cİ for CESCİ - C5 was 99%, Sİ was 98%, Cİ for CESCİ - S 5 was 100%, and Sİ was 99%.

To determine the initial optimal concentration in CESCİ - C 5, CESCİ - S 5 composites, studies were conducted for their concentrations of 20, 30, 40, 50, 70, 100, 120 mg/l. Analysis of the results of experiments showed that this concentration is 40 mg/l for CESCİ - C 5 and 30 mg/l for CESCİ - S 5.

The authors declare the absence a conflict of interest warranting disclosure in this article.

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ЛИТЕРАТУРА

1. **Шахбазов Э.К., Ибрагимов Х.М., Асадов М.Ф., Джаббарова К.Ш.** Наносистема против отложения солей при добыче нефти. *Нефтяная пром-сть Азербайджана.* 2015. № 1. С. 31-34 (на азерб.).
2. **Гасанова У.Е.** Защита нефтепромыслового оборудования от коррозии и отложений солей комплексными эффективными ингибиторами. *Нефтяная пром-сть Азербайджана.* 2015. № 4. С. 26-28 (на азерб.).
3. **Асадов М.М.** Защита от коррозии резьбовых соединений оборудования композицией на основе местного сырья. *Нефтяная пром-сть Азербайджана.* 2018. № 7-8. С. 43-45 (на азерб.).
4. **Искендаров Э.Х, Гурбанов М.М., Садыгов Р.Е.** Теоретические и практические основы защиты от коррозии нефтепромыслового оборудования. *Нефтяное хоз-во Азербайджана.* 2017. № 10. С. 41-45 (на азерб.).
5. **Исмаилов Г.К., Садыгов Р.Э.** Разработка и применение инновационных методов защиты от коррозии металлического оборудования и труб в нефтяных и газовых скважинах и транспортных системах. *Изв. высш. технич. школ Азербайджана*. 2006. № 4 (120). С. 43-48 (на азерб.).
6. **Гулиев М.М., Мамедов К.А., Гамидова Н.С.** Влияние многофункциональных ингибиторов на коррозию и механический износ нефтепромыслового оборудования. *Нефтяная пром-сть Азербайджана.* 2015. № 5. С. 56 (на азерб.).
7. **Гурбанов Х.Р., Адыгозалова М.Б., Мамедли С.М.** Изучение влияния бактерицида-ингибитора на защиту от коррозии нефтепромыслового оборудования. *Нефтяная пром-сть Азербайджана.* 2019. № 1. С. 38-41 (на азерб.).
8. **Гурбанов М.М., Мамедов К.А.** Исследование эффективности комбинированного ингибитора в нефтедобыче. *Нефтяное хоз-во Азербайджана.* 2010. № 7. С. 50-52 (на азерб.).
9. **Мурсалова М.А., Мирзаджанов З.Б.** Состояние и перспективы предупреждения солеотложений в системе сбора нефти НГДУ “Балаханынефть”. *Азербайджан. нефт. хоз-ва.* 2010. № 8. С. 47-49.
10. **Кязимов В.М., Мамедов М.А., Мирзоева М.А., Джафарова Т.Д.** Ингибирующая композиция для защиты водооборотных систем от коррозии и солеотложений. *Азербайджа. нефт. хоз-ва.* 2010. № 11. С. 47-50.
11. **Сибиряков К.А., Коробейникова Д.С., Тархов Л.Г.** Исследование разработанного ингибитора комплексного действия для защиты от коррозии и солеотложениея в процесе нефтедобычи. *Вестн. ПНИПУ.* 2016. № 4. С. 95-50-104.
12. **Шангараева Л.А., Петухов А.В.** Условия и особенности образования от отложений солей на поздних стадиях разроботки нефтяных месторождений. *Записки горн. ин-та.* 2013. Т. 206. С. 112-115.
13. **Шангараева Л.А., Сулианова Д.А.** Изучение механизма отложений солей на глубинно-насосном оборудовании при эксплутации многопластовых скважин. *Мир Науки.* 2015. Вып. 2. С. 1-8.
14. **Шангараева Л.А., Петухов А.В.** Исследования адсорбционно-десорбционных свойств состава для предотвращения солеотложений в скважинном оборудовании. *Совр. пробл. науки и образов*. 2012. № 6. С. 1-8.
15. **Сисенбаева М.Р.** Исследование ингибиторов солеотложений и АСПО в условиях месторождения “Узень”. *Разраб. и экспл. нефт. и газ. месторожд.* 2013. № 3. С. 5-8.

REFERENCES

1. **Shahbazov E.Q, Ibrahimov X.M, Asadov M.F, Jabbarova K.Sh.** Nanosystem against salt deposition in oil production. Azerbaijan Oil Industry. 2015. N 1. P. 31-34 (in Azerbaijan).
2. **Hasanova U.E.** Protection of oilfield equipment from corrosion and salt deposition with complex effective inhibitors. *Azerbaijan Oil Industry.* 2015. N 4. P. 26-28 (in Azerbaijan).
3. **Asadov M.M.** Corrosion protection of threaded joints of equipment using local raw material-based composition. *Azerbaijan Oil Industry.* 2018. N 7-8. P. 43-45 (in Azerbaijan).
4. **Isgandarov E.X., Gurbanov M.M., Sadigov R.E.** Theoretical and practical bases of corrosion protection of oil mining equipment. *Azerbaijan Oil Economy.* 2017. N 10. P. 41-45 (in Azerbaijan).
5. **Ismayilov Q.Q., Sadigov R.E.** Development and application of innovative methods for corrosion protection of metal equipment and pipes in oil and gas wells and transportation systems. *Izv. Vyssh. Tekhnich. Shkol Azerbaydzhana.* 2006. N 4 (120). P. 43-48.
6. **Guliyev M.M., Mammadov K.A., Hamidova N.S.** Influence of multifunctional inhibitors on corrosion and mechanical wear of oil mining equipment. *Azerbaijan Oil Economy.* 2015. N 5. P. 56 (in Azerbaijan).
7. **Gurbanov H.R., Adigozalova M.B., Mammadli S.M.** Research of bactericidal-inhibitor effect in corrosion protection of oil mining equipment. *Azerbaijan Oil Industry.* 2019. N 1. P. 38-41 (in Azerbaijan).
8. **Gurbanov M.M., Mammadov M.M.** Research of efficiency of the combined inhibitor in oil extraction. *Azerbaijan Oil Economy.* 2010. N 7. P. 50-52 (in Azerbaijan).
9. **Mursalova M.A., Mirzadjanov Z.B.** Status and prospects of salt prevention in the system of oil collection NGDU "Balakhanyneft". *Azerbaijan Petroleum Economy.* 2010. N 8. P. 47-49 (in Azerbaijan).
10. **Kyazimov V.M., Mamedov M.A., Mirzoeva M.A., Jafarova T.D.** Inhibiting composition for protection of water circulation systems from corrosion and salinization. *Azerbaijan Oil Industry.* 2010. N 11. P. 47-50 (in Russian).
11. **Sibiryakov K.A., Korobeynikova D.S., Tarkhov L.G.** Investigation of the developed complex inhibitor of action for corrosion protection and salinization in the process of oil extraction. *Vestn. PNIPU.* 2016. N 4. P. 95-50-104 (in Russian).
12. **Shangaraeva L.A., Petukhov A.V.** Conditions and peculiarities of education from deposits of salt at later stages of development of oil fields. *Zapiski Gorn. In-ta.* 2013. V. 206. P. 112-115 (in Russian).
13. **Shangaraeva L.A., Sulianova D.A.** Study of the mechanism of salt deposition on deep-pump equipment during operation of multilayer wells. *Mir Nauki.* 2015. V. 2. P. 1-8 (in Russian).
14. **Shangaraeva L.A., Petukhov A.V.** Study of adsorption-desorption properties of the composition for the prevention of salinization in the well equipment. *Sovr. Probl. Nauki Obrazovaniya.* 2012. N 6. P. 1-8 (in Russian).
15. **Sisenbaeva M.R.** Research of salt inhibitors and ASPO in the conditions of Uzen mines. *Razrab. Ekspl. Neft. Gaz. Mestorozhd.* 2013. N 3. P. 5-8 (in Russian).
16. **Salov S.A., Ochered’ko T.B.** Explain the technology of the struggle with salt deposits in the wells of the mammoth uninhabited area. *Otrasl. Nauch. Prikl. Issl.: Nauka Zemle.* 2017. 4. P. 51-73 (in Russian).

16. **Салов С.А., Очередько Т.Б.** Обоснование технологий борьбы с солеотложениями в скважинах мамонтовского неятяного месторождения. *Отрасл. науч. и прикл. иссл.: Наука о земле.* 2017. 4. С. 51-73.
17. **Плотникова М.Д., Шеин А.Б.** Ингибирование коррозии низкоуглеродистой стали в кислых и нейтральных средах. *Изв. вузов. Химия и хим. технология.* 2013. Т. 56. Вып. 3. С. 35-40.
18. **Меньшиков И.А., Шеин А.Б.** Низкая коррозионная защита углеродистой стали в кислых средах ингибиторами серии СОЛИНГ. *Изв. вузов. Химия и хим. технология.* 2016. Т. 59. Вып. 2. С. 70-73.
19. **Меньшиков И.А., Шеин А.Б.** Защитные свойства солингоров ряда в кислых сероводородсодержащих средах. *Изв. вузов. Химия и хим. технология.* 2018. Т. 61. Вып. 7. С. 91 -98. DOI: 10.6060/ivkkt.20186107.5703.
20. **Султанова (Хусаинова) Д.А., Майорова Т.А., Максютин А.В.** Экспериментальные исследования попутной добываемой воды фонда скважин, осложненных солеотложением в глубиннонасосном оборудовании. XIII Междунар. молодеж. науч. конф. Севергеоэкотех − 2012. Ухта. 2012. С. 230-234.
21. **Маркин, А.Н., Низамов Р.Э., Суховерхов С.В.** Нефтепромысловая химия: практическое руководство. Владивосток: Дальнаука. 2011. 288 с.
22. **Люшин С.Ф., Глазков Г.В., Галеева А.А.** Отложения неорганических солей в скважинах, в призабойной зоне пласта и методы их предотвращения. Обзорн. информ. Сер. Нефтепромысл. дело. М.: ВНИИОЭНГ. 1983. 100 с.
23. **Кащавцев В.Е., Мищенко И.Т.** Солеобразование при добыче нефти. М.: Орбита-М. 2004. 432 с.
24. **Ибрагимов Н.Г., Хафизов А.Р., Шайдаков В.В.** Осложнения в нефтедобыче. Уфа: Монография. 2003. 302 с.
25. **Гурбанов Г.Р., Адыгезалова М.Б., Пашаева С.М**. Исследование универсального комбинированного ингибитора для нефтегазовой промышленности. *Изв. вузов. Химия и хим. технология.* 2020. Т. 63. Вып. 10. С. 78-89. DOI: 10.6060/ivkkt.20206310.6063.
26. ГОСТ 18995.1 − 73 «Продукты химические жидкие. Методы определения плотности». М.: Изд-во станд. 1974. 4 с.
27. ГОСТ 3300 − 2000 «Нефтепродукты. Прозрачные и непрозрачные жидкости. Определение кинематической вязкости и расчет динамической вязкости». М.: Изд-во станд. 2008. 21 с.
28. ГОСТ 20287 − 91 «Нефтепродукты. Методы определения температур текучести и застывания». М.: Изд-во станд. 2006. 7 с.

17. **Plotnikova M.D., Shein A.B.** Inhibition of corrosion of мild steel in acidic and neutral environments. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.].* 2013. V. 56. N 3. P. 35-40 (in Russian).
18. **Menshikov I.A., Shein A.B.** Low corrosion protection carbon steel in acidic environments inhibitors of series SOLING. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.].* 2016. V. 59. N 2. P. 70-73 (in Russian).
19. **Menshikov I.A., Shein A.B.** Protective properties of series solingors in acid hydrogen sulfide-containing environments. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.].* 2018. V. 61. N 7. P. 91-98 (in Russian). DOI: 10.6060/ivkkt.20186107.5703.
20. **Sultanova (Khusainova) D.A., Mayorova T.A., Maksyutin A.B.** Experimental studies of the associated water in the background of the well, complicated by deep salinization in the deep-pumping equipment. XIII International Youth Scientific Conference Severgeoekotekh 2012. Ukhta. 2012. P. 230-234 (in Russian).
21. **Markin, A.N., Nizamov A.N., Sukhoverkhov S.B.** Petrochemical chemistry: practical guidance. Vladivostok: Dalnauka. 2011. 288 p. (in Russian).
22. **Lyushin S.F., Glazkov A.A., Galeeva G.B. et al.** Sedimentation of inorganic salts in wells, in the subsurface zone of the formation and methods of their prevention. Review information. Neftepromyslovoe delo. M.: VNIIOENG. 1983. 100 p. (in Russian).
23. **Kashchavtsev V.E., Mishchenko I.T.** Sole formation during extraction of oil. M.: Orbita-M. 2004. 432 p. (in Russian).
24. **Ibragimov N.G., Khafizov A.R., Shaidakov V.V.** Complications in oil extraction. Ufa: Monografiya. 2003. 302 p. (in Russian).
25. **Gurbanov G.R., Adygezalova M.B., Pashaeva S.M.** Research of a combined combined inhibitor for the oil and gas industry. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.].* 2020. V. 63. N 10. P. 78-89 (in Russian). DOI: 10.6060/ivkkt.20206310.6063.
26. GOST 18995.1 - 73 «Chemical liquid products. Methods for determining the density ». M.: Izd-vo stand. 1974. 4 p. (in Russian).
27. GOST 3300 - 2000 “Petroleum products. Transparent and non-transparent liquids. Determination of kinematic viscosity and calculation of dynamic viscosity ». M.: Izd-vo stand. 2008. 21 p. (in Russian).
28. GOST 20287 - 91 «Petroleum products. Methods for determining the temperature and cooling. M.: Izd-vo stand. 2006. 7 p. (in Russian).

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