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ИЗВЕСТИЯ

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АО «Институт топлива, катализа и
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Қазақстан Республикасы Ұлттық ғылым академиясы «ҚР ҰҒА Хабарлары. Химия және технология сериясы» ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Socia1 Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество в глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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APPLICATION OF NEW CORROSION INHIBITOR FOROILFIELD EQUIPMENT AND PIPELINES FOR IMPROVING THE ECOLOGICAL SECURITY

Abstract: extending the life ofoilfield equipment andpipelines along with ensuring reliable environmental protection is one of the urgent problems. Considering this, the factors influencing the corrosion and erosion processes of field equipment and gathering pipelines were investigated. Thus, in order to inhibit corrosion and erosion process within the field equipment and pipeline system, it is recommended to use the new multifunctional reagent made on the basis of technical phosphatide and monoethanolamine, which provides protection against corrosion and erosion damage, microbiological corrosion and reduces the viscosity of oil. The optimal consumption of an inhibitor is recommended to take 500 mg/l. In this case, the corrosion protection effect is 94%, and the destruction efficiency of sulfate-reducing bacteria is 98%.

In addition, to increase the viscosity reduction efficiency of the obtained reagent, the mechanism of complex application of the cavitation process and the reagent was described based on the positive results of the experiments.

Also, the results of tests via "cold finger" method showed that new reagent has 53% efficiency in paraffin deposition inhibiting at its optimal anti-corrosion concentration (500 mg /l).

As a result of the conducted field tests, it was revealed that theuse of the new multifunctional reagent ensures the continuous operation of pipeline network and reliable environmental protection.

Key words: environment, complex reagent, pipeline, aggressive environment, corrosion, cavitation, viscosity, paraffin deposition.

Introduction. It is known that the study of the causes of corrosion and the improvement of corrosion protection methods, in order to ensure the continuous operation offield equipment and gathering pipelines, reduce transportation costs and protect the environment by regularly studying the corrosiveness of transported products, is an urgent task.

It should be noted that it is precisely because of corrosion-erosion damage to pipelines that unplanned accidents occur, due to which harmful substances pollute the soil and groundwater. Moreover, it leads to a violation of the ecological balance of the environment. Currently, various methods are used to protect oil field equipment and pipelines from corrosion-erosion and microbiological corrosion [1-3]. The selection of optimal methods of reliable protection is carried out taking into account various factors that cause corrosion-erosion destruction of internal surfaces of oilfieldequipment and pipelines.

The processes of corrosion and erosion on the inner wall of the pipeline and equipment occur due to corrosive elements and mechanical combinations contained in oil, gas and produced water [4]. In addition, internal corrosion also depends on the metal grade, the flow regime of the transported medium, the ability to wet the metal surface, flow rate, pressure, temperature and so on [5]. These processes are intensified as a result of an increase in the velocity, pressure and temperature regime of the fluid flow.Erosionand cavitation processes in equipment and pipes are also considered as a stimulating factor in corrosion. Therefore, they should be studied in parallel with the study of the intensity of corrosion processes [6-11].

Protection of the field equipment and pipeline system against erosion-corrosion and mechanical wear for reliable operation, and ultimately for environmental protection, is carried out by the following actions:use of galvanic anodes and cathodic protection, research of anticorrosive coatings for corrosion protection, the use of nonmetallic compositions, use of corrosion resistant pipes, the use of bactericidal reagents and complex inhibitors, regulation of the operating modes of pipelines, depending on environmental conditions and purification of the transported product from mechanical impurities and aggressive gases[12-16].

It can be noted that the use of inhibitors is one of the most effective ways to protect equipment and pipelines from internal corrosion. As a result, the development of new multifunctional inhibitors remains relevant [17-18].

Given the above, on the basis of laboratory studies, a new multifunctional reagent was produced that has surfactant properties based on technical phosphatide and monoethanolamine which protects oilfield equipment and pipeline system from corrosion.

Laboratory research. The inhibitory properties of the developed reagent at a concentration of 100-600 mg/l were studied in laboratory conditions according to the ASTM G170 – 06 on steel grades 20 (St.20) in alkaline (pH = 7.2) formation waters. The effectiveness of the inhibitor was determined by the gravimetric method. The essence of the method is to determine the corrosion rate by the weight loss of witness samples in the control and studied environments.For testing, witness samples were prepared and installed in a U-shaped cell with a mixing device. The velocity of the fluid relative to the samples is about 0.5 m/s. The duration of the experiments is 6 hours at a temperature of 25°C.

The effectiveness of the inhibitor was characterized by the degree of protection Z,%.

$$Z = \frac{K_0 - K_{inh}}{K_0} 100\% \qquad (1)$$

whereK_0 and K_{inh} are corrosion rates of the sample without inhibitor and with inhibitor.

In further studies, tests were conducted to identify the bactericidal-inhibitory properties of the obtained reagent, namely, the effect on sulfate-reducing bacteria (SRB). The studies were carried out according to NACE Standards TMO 194-94 and TMO 194-2014 using the nutrient enrichment method in Postgate's medium, which is necessary for the development of SRB. The sulfate-reducing bacteria used in the studies were taken from the formation waters of the Bibi Heybatoilfield. The experiments were carried out for 15 days at 28-30°C in an inhibitor solution of 100-600 mg/l. the results are shown in Figure 1.

Suppression extent of SRB was determined by formula:

$$Z_{SRB} = \frac{C - C_P}{C} 100\% \qquad (2)$$

where C and Cp - the presence of H_2S in test of the studied water without reagent and with reagent, respectively.

The results of experiments showing the protection degree of reagent against corrosion and destruction of SRB are presented in Figure 1.

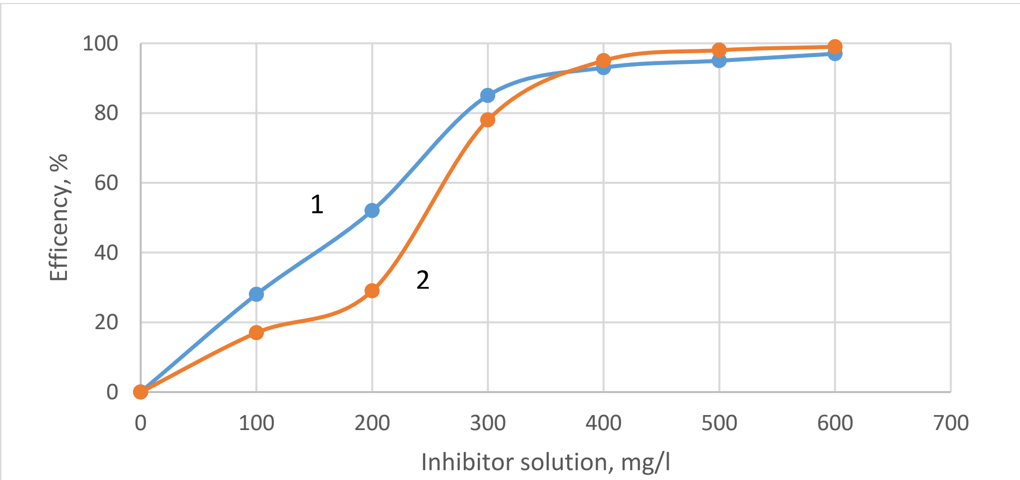

Figure 1. Corrosion protection and the efficiency of the destruction of SRB depending on the amount of inhibitor in the medium:
1-efficiency of protection against corrosion;
2 - the effectiveness of the destruction of SRB.

As can be seen from the figure, in an alkaline medium, at an optimal concentration of reagent – 500 mg/l the protection efficiency equal to 94%. It is necessary to note that the corrosion rate of samples at this optimal concentration is 0.0449 $g/m^2 \cdot hour$ while without using the inhibitor it was 0.7019 $g/m^2 \cdot hour$ which means the corrosion reduction rate coefficient in these media is 16.

Analysis of the research results shows that the used reagent has strong inhibitory and bactericidal properties. The optimal consumption of an inhibitor is advisable to take 500 mg/l. In this case, the corrosion protection effect is 94%, and the destruction efficiency of SRB is 98%.

It is worth noting that one of the factors causing emergency shutdowns of the field pipeline system in combination with corrosion is the transportation of highly viscous oils. This is due to the fact that with an increase in the viscosity of oil, the necessary working pressure can significantly exceed the capabilities of the field pipeline system taking into account leaking corrosion process. To eliminate this complication, additives are used that change the rheological properties of oil, namely viscosity. Since most of the products of the field pipeline system are oil-water emulsions, which are non-Newtonian fluids, the concept ofeffective or dynamic viscosity is used to describe the properties of non-Newtonian oil. The value of the dynamic viscosity of oil at various shear rates and shear stresses is determined by calculation using the following well-known formula:

$$\mu = \frac{\tau}{\gamma}, \qquad (3)$$

Where: τ- instantaneous value of shear stress, Pa;γ- instantaneous value of shear rate, 1/s.

For this purpose, the effect of the obtained reagent in various concentrations on the viscosity of oil was also studied in laboratory conditions. The determination of dynamic shear stress (Pa) and dynamic viscosity (Pa·s) was carried out on a Reotest-2 viscometer at a temperature of 40 °C and a shear rate of 0.33 s^{-1}. Oil from well No. 34 of the "Muradkhanli" field with 20% water cut and with density of 965 $kg/m^3$was used for testing.The efficiency index (E_{eff}) for assessing the effectiveness of the reagent that regulates the viscosity of the oil was calculated by the formula:

$$E_{eff} = \frac{\mu_d - \mu_r}{\mu_d} \qquad (4)$$

Where: E_{eff} - reagent efficiency index;

μ_d - dynamic viscosity of the initial oil, Pa·s;

μ_r - dynamic viscosity of oil with a reagent, Pa·s.

The reagent efficiency index (E_{eff}) shows how many times the dynamic viscosity of oil with a reagent differs from the dynamic viscosity of the original oil.

It should also be noted thatrecent studies revealed the possibility of using cavitation to increase the efficiency of various kinds of physicochemical reactions in oil. During cavitation in oil, chemical bonds are broken between the atoms of large molecules of hydrocarbon compounds due to high-amplitude oscillations in its volume, caused by the collapse of bubbles with a high velocity. The formation and collapse of cavitation bubbles in oil resembles a kind of multitude of microreactors where microcracking occurs, under the influence of extreme physicochemical conditions [19].

As a result of this process, along with other structural changes, an improvement in the rheological characteristics of oil is also observed. Namely, the viscosity of heavy oil decreases under the influence of cavitation. It should be noted that the use of only one cavitation to improve fluidity of oil is not always effective, since after reaching a certain value, the viscosity begins to increase despite the continuation of the cavitation effect. This is due to the fact that the free radicals of hydrocarbons formed as a result of cracking can combine under the influence of cavitation microflows, creating larger compounds [20].

But in the case of heterogeneous liquid-liquid (oil-reagent) reactions, cavitation collapse leads to the destruction of spatial structures formed by large supramolecular oil components, transforming them into small structures and increasing the surface area available for interaction with the added reagent, thereby accelerating the ongoing reactions.

Taking into account the fact that the decomposition of largesupramolecular oil compoundsinto free radicals as a result of cavitation, creates good conditions for the various kinds of reactions, further studies of the complex effect of the obtained multifunctional reagent for reducing the viscosity of oil with the simultaneous use of cavitation were carried out.

The experiments were carried out on a device of hydrodynamic cavitation, installed on the pipeline, which is a hollow cylindrical body of variable cross-sectionswith areas of local resistance, which ensures the occurrence of cavitation. During the study the obtained reagent was added to the flow beforeentering the cavitatorin the concentration range (50-600 mg/l) with further sampling and measurements of the dynamic viscosity of oil, after passing through cavitation zone,in the Reotest-2 viscometer. The results of the performed laboratory experiments to identify the effect of the reagent on the viscosity of oil without cavitation and with the simultaneous use of cavitationare presented in Figure 2.

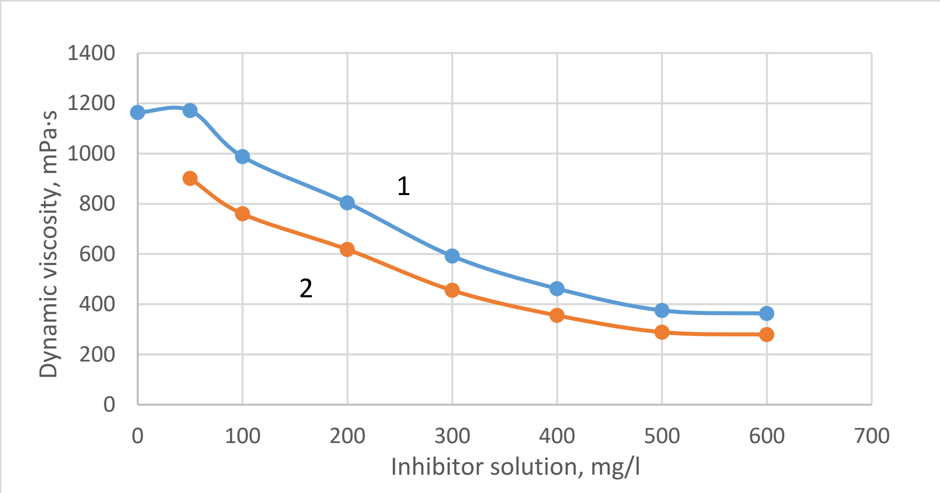

Figure 2. Change in dynamic viscosity of high-viscosity oil depending on reagent concentration with simultaneous use of cavitation and without cavitation: 1- effect of complexreagent on viscosity of oil; 2- effect of simultaneous use of a complex reagent and cavitation on viscosity of oil.

As can be seen from the graph, with an increase in the concentration of the reagent, the dynamic viscosity decreases. At an optimal reagent concentration of 500 mg/l the dynamic viscosity of oil is 375.3mPa·s, hence the dynamic viscosity of oil is reduced by 3.1 times which gives the reagent efficiency index (E_{eff}) equal to 68%.

The improvement in the flowability of highly viscous oils can be explained by the fact that the test reagent has surface-active properties and is capable of changing phase and energy interactions at the interfaces between polar and nonpolar phases.The action of the surfactant introduced into the pipeline is oriented not only at the interphase boundaries that are formed between the well product as a whole and the pipeline wall or in the product itself between the oil-water phases,but it also penetrates the oil composition and affects its components, changing the properties and structure of spatial supramolecular structures. And this, in turn, leads to an improvement in fluidity associated with a decrease in rheological parameters such as shear strength.

Figure 2 also shows that the complex application of the obtained multifunctional reagent and cavitation contributes to an increase in the efficiency of the reagent application for the improvement of transportation characteristics of oil. As a result, a decrease in viscosity ≈1.3 times greater than when using only the reagent. The role of cavitation is that it allows the reagent to affect the group of oil components more effectively by reducing their size and increasing the contact area. In other words, this phenomenon promotes the process of surfactant adsorption on the surface of high-molecular oil components, which prevents their association into strong structural frameworks that determine its rheology, thereby increasing the effectiveness of such a reagent outcome as a decrease in oil viscosity.

As it is known, from the integrity point of view of technological equipment, cavitation is not a desirable process, since it leads to its accelerated destruction caused by such phenomena as cavitation corrosion and erosion. This happens as a result of the destruction of protective films formed by corrosion inhibitors on the metal surface under the action of shock waves during the collapse of cavitation caverns. And inhibitors with surfactants, in turn, can also reduce this negative effect of cavitation.The essence of the positive effect of a surfactant in this case is that when it is added to the flow, it causes some kind of foaming of the liquid, that is, the formation of more or less bubbles filled with gas/air. These bubbles, getting into the cavitation zone, namely, diffusing into the cavitation cavity when it occurs, reduce the impact force of the collapse of the cavity. This is due to the fact that accumulated gas inside the cavitation bubble plays the role of a kind of shock absorber when the sphere collapses and thereby affects the force of the shock wave, reducing its effect on the protective film on the metal surface [21].

Another factor that hinders the pumping of oil through pipelines is the deposition of paraffins on the inner surface of the pipe wall, which reduces its cross-section, decreasing the throughput. And as known, surfactants have the ability to reduce the amount of deposited paraffin by changing the structure of oil dispersed systems.This occurs as a result of the destruction of the volumetric associative network and enveloping of its constituent nodes, which are supramolecular components (resins, paraffins, asphaltenes), thereby keeping them in suspension and preventing their further agglomeration. And this, in turn, leads to a decrease in the volume of paraffin deposits. Taking this into account, the "cold finger" method was used to test the effectiveness of the obtained reagent as the inhibitor for paraffin deposition process. Oil from well No. 34 of the "Muradkhanli" field was used for testing. The results of the experiment are shown in Figure 3.

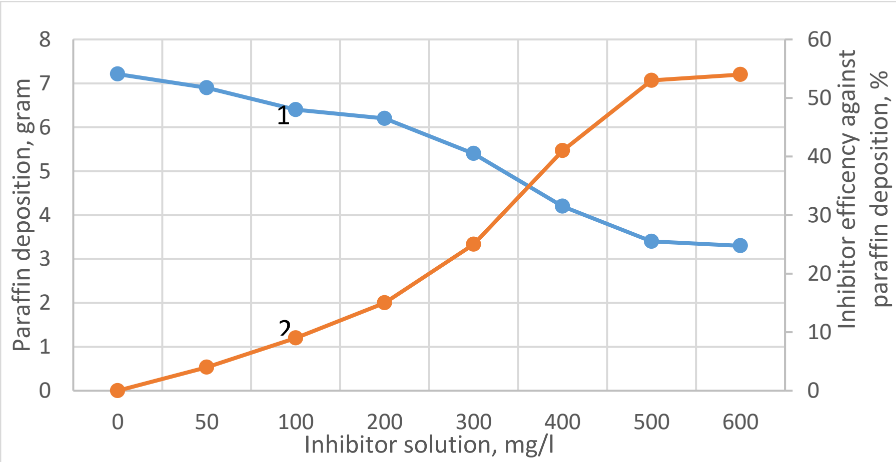

Figure 3. Effect of inhibitor on Paraffin deposition rate.
1 - Paraffin deposition rate depending on reagent concentration;
2 - The effectiveness of the reagent against paraffin deposition.

As can be seen from the figure, without the use of the inhibitor, the amount of paraffin deposits was 7.21 grams, while when using the inhibitor in concentrations from 50-600 mg/l, the amount of paraffin deposits was 6.9-3.3 grams, respectively. And this, in turn, means that the use of the reagent reduces paraffin deposition by 1.04 - 2.19 times with an efficiency of 4-54%, respectively. The optimal concentration of inhibitor to reduce paraffin deposition is 500 mg /l, at which its efficiency is 53%.

The optimal concentration of reagent against corrosion and paraffin deposition is approximately 400-500 mg/l, which is approximately in line with the optimal concentration of reagent for oil viscosity reduction. Consequently, the use of the obtained reagent at optimal concentrations for inhibiting corrosion also has a positive effect on reducing hydraulic losses and paraffin deposits, which indicates its multifunctional properties.

Positive results of laboratory tests allowed to recommend the developed reagent for field test, since this reagent has inhibitory properties, and reduces the dynamic viscosity of oil.

Field tests: Field tests were carried out on the pipelines of the Bibi Heybat oilfield. Control samples were installed in order to determine the rate of corrosion by the gravimetric method and to evaluate the inhibitory effect of the inhibitor 30 days before and after injection of the reagent.

Field tests showed that when using the reagent, the corrosion rate decreased on average from 0.6726 $g/m^2 \cdot$ hour to 0.0631 $g/m^2 \cdot$ hour, while the protective effect was 91%.

Experiments in the pipelinesystem of the field showed that after injection of the developed reagent, due to a decrease in oil viscosity and a decrease in hydraulic losses, the flow pressure decreased from 0.14 to 0.1 MPa, which contributes to an increase in the efficiency of operation and integrity of the pipeline network.

Also, on the basis of the experiments and the study of the effect of cavitation on oil, it can be concluded that with the combined use of a chemical reagent and cavitation, a greater effect on improvement of rheological properties of oil can be achieved than they used separately.

The results of tests conducted in the pipeline system of Azneft Production Association oil fields confirmed the above properties of the reagent. The use of the reagent reduces the number of accidents caused byoil field equipment and pipeline corrosion, thereby minimizing the cost of repair work and reducing the risks of environmental pollution due to emergency shutdowns of pipelines, which is the primary task of the oil industry.

Conclusions. 1. A new multifunctional reagent, made on the basis of technical phosphatide and monoethonolamine, leads to a decrease in the viscosity of oil, and also protects oilfield equipment from corrosion;

2. Laboratory studies have shown that the optimal concentration of the reagent to reduce the dynamic viscosity of oil and provide proper corrosion protection is 500 mg/l, while the dynamic viscosity of oil is reduced by 3.1 times, and the protective effect against corrosion is 94%;

3. Cavitation technology can be used simultaneously with injection of inhibitor in order to increase the effectiveness of the reagent on the reduction of the viscosity of oil. And the surfactants included in the reagent, in turn, can reduce the negative effect of cavitation, such as destruction of the protective layer of inhibitor;

4. The obtained composition also shows good effectiveness 53% in inhibiting the paraffin deposition process;

5. Field tests showed that when using the reagent, the corrosion rate decreased from0.6726 $g/m^2\cdot$ hour to 0.0631 $g/m^2\cdot$hour, the protective effect was 91%. Alsodue to a decrease in oil viscosity and a drop on hydraulic losses, the flow pressure decreased by 28% - from 0.14 to 0.1MPa.

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МҰНАЙ КӘСІПШІЛІГІ ЖАБДЫҚТАРЫ МЕН ҚҰБЫРЖОЛДАРЫ ҮШІН КОРРОЗИЯНЫҢ ЖАҢА ТЕЖЕГІШІН ҚОЛДАНУ АРҚЫЛЫ ЭКОЛОГИЯЛЫҚ ҚАУІПСІЗДІКТІ АРТТЫРУ

Аннотация: кәсіптік жабдықтар мен құбырлардың пайдалану мерзімін ұзарту қоршаған ортаны сенімді қорғауды қамтамасыз етумен қатар, өзекті міндеттердің бірі болып табылады. Осыны ескере отырып, өндірістік жабдықтар мен құбырлардың коррозиялық-эрозиялық процестеріне әсер ететін факторлар зерттелді. Осылайша, өнеркәсіптік құбырлар жүйесіндегі коррозия мен эрозия процесін тежеу үшін коррозиялық және эрозиялық зақымданудан, микробиологиялық коррозиядан қорғауды қамтамасыз ететін және мұнайдың тұтқырлығын төмендететін техникалық фосфатид пен моноэтаноламин негізінде жасалған жаңа көп функциялы реагентті қолдану ұсынылады. Ингибитордың оңтайлы шығыны 500 мг/л қабылдау ұсынылады, бұл жағдайда коррозиядан қорғаудың әсері 94%, ал сульфатты төмендететін бактериялардың жойылу тиімділігі 98% құрайды.

Сонымен қатар, эксперименттердің оң нәтижелеріне сүйене отырып, мұнайдың тұтқырлығын төмендетуде дамыған реагенттің тиімділігін арттыру үшін кавитация процесі мен ингибиторды кешенді қолдану механизмі сипатталған.

Сондай-ақ, "суық өзек" әдісімен сынау нәтижелері реагенттің оңтайлы коррозияға қарсы концентрациясы (500 мг/л) кезінде парафин шөгінділерінің процесін тежеуде тиімді (53%) екенін көрсетті. Кәсіпшілік сынақтар нәтижесінде әзірленген көпфункционалды реагентті пайдалану кәсіпшілік құбыр жүйесі ішінде үздіксіз жұмыс істеуді және қоршаған ортаны сенімді қорғауды қамтамасыз ететіні анықталды.

Түйін сөздер: қоршаған орта, күрделі реагент, құбыр, агрессивті орта, коррозия, кавитация, тұтқырлық, парафинді тұндыру.

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ПОВЫШЕНИЕ ЭКОЛОГИЧЕСКОЙ БЕЗОПАСНОСТИ С ПРИМЕНЕНИЕМ НОВОГО ИНГИБИТОРА КОРРОЗИИ ДЛЯ НЕФТЕПРОМЫСЛОВОГО ОБОРУДОВАНИЯ И ТРУБОПРОВОДОВ

Аннотация: продление срока эксплуатации промыслового оборудования и трубопроводов наряду с обеспечением надежной защиты окружающей среды – одна из актуальных задач. Учитывая это, были исследованы факторы, влияющие на коррозионно-эрозионные процессы промыслового оборудования и трубопроводов. Таким образом, чтобы ингибировать процесс коррозии и эрозии в системе промысловых трубопроводов, рекомендуется использовать новый многофункциональный реагент, изготовленный на основе технического фосфатида и моноэтаноламина, который обеспечивает защиту от коррозионных и эрозионных повреждений, микробиологической коррозии и снижает вязкость нефти. Оптимальный расход ингибитора рекомендуется принимать 500 мг/л. В этом случае эффект защиты от коррозии составляет 94%, а эффективность разрушения сульфатредуцирующих бактерий составляет 98%.

Кроме того, на основе положительных результатов экспериментов был описан механизм комплексного применения процесса кавитации и ингибитора с целью повышения эффективности разработанного реагента в снижении вязкости нефти.

Также результаты испытаний методом "холодного стержня" показали, что реагент эффективен (53%) в ингибировании процесса парафина отложения при его оптимальной антикоррозионной концентрации (500 мг/л).

В результате проведенных промысловых испытаний было выявлено, что использование разработанного многофункционального реагента обеспечивает бесперебойную работу внутри промысловой трубопроводной системы и надежную защиту окружающей среды.

Ключевые слова: окружающая среда, комплексный реагент, трубопровод, агрессивная среда, коррозия, кавитация, вязкость, отложение парафина.

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