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DEVELOPMENT OF A MULTIFUNCTIONAL CORROSION INHIBITOR, POSSESSING THE PROPERTIES OF A MICROEMULSION

Abstract: To protect the oilfield equipment from corrosion, a multifunctional bactericide inhibitor with microemulsion properties was developed that promotes oil displacement. Laboratory researches have shown that the reagent has high inhibiting and bactericidal properties at concentration of 500 mg/l. At the same time the protective effect of the general corrosion constitutes 94-96% and suppression extent of SRB - 99%. While conducting experimental studies on linear models of layer it has been established that at the reagent concentration of 10% the coefficient of oil replacement relatively to the layer water increases by 16%.

Field tests showed that, during the application of this reagent, the protective effect of corrosion was 90%, and the degree of SRB suppression constituted 97%.

As a result of reagent influence on productive layer in oil production of the wells has increased in average by 11%.

Key words: corrosion, bactericide inhibitor, degree of protection, suppression extent, increase of oil production, maintenance of layer pressure.

Introduction. Various technological methods such as: heat treatment of layer, pumping of the chemical reagents and injection of gas or sea water were applied on oil layers to strengthen the oil production. The application scales of influence methods on oil deposits are enormous.

One of the dominating influence methods on layer that applied on the Azerbaijan fields is the maintenance of layer pressure (MLP) by downloading water into the layer through the system of injection wells.

The MLP in its turn is very metal - and power-intensive system that is related to the arrangement of the parting and bringing conduits (pipelines), construction of sectional pump stations, power supply objects and their protection for the purpose to increase in service life.

The acquired practice of long-term exploitation in Azerbaijani oil fields has shown that, the main reason of MLP system damages is the corrosion destruction of pipelines in consequence of sea water injection without the preliminary sterilization. At the same time the corrosion aggression of layer water amplifies because of the existence of corrosion aggressive bacteria in the environment as well as the increase in concentration of such ions as Cl⁻, SO₄²⁻, H₂S and CO₂ gases [1].

A sharp increase in the corrosion rate of steel with an increase in sulfide ion concentration in alkaline and neutral media was noted. The second after hydrogen sulfide on aggressiveness component of oilfield environments is oxygen [2,3].

Microbiologically influenced corrosion is a big concern in oil and gas industry [4-6]. Pits and other damage arising from microbiological corrosion damage downhole equipment, manifolds, and pipelines. The most aggressive among bacteria stimulating bio-corrosion are sulfate reducing bacteria (SRB) [7-10].

During operation of oil deposits, asphalt-tar-paraffin (ATP) compounds in heavy and high viscosity oils precipitate in well bottom zone (WBZ) and thus, weaken the filtration ability of layer fluids and cause a sharp decrease in production. In order to eliminate such difficulties, the physical and chemical methods were developed to affect WBZ depending on physical, chemical and filtration properties of fluids.

However, due to the use of expensive techniques and chemical reagents, the economic benefits of these operations are not considered as satisfactory.

Methods developed for intensifying oil production need to be improved. For this reason, it is expedient to develop effective methods to prevent complications that occur during well operation.

Chemical method, especially microemulsion flooding, plays an important role in enhanced oil recovery technique due to its ability to reduce interfacial tension between oil and water to a large extent as well as alter wettability of reservoir rocks [11].

Microemulsion is used to increase permeability of well bottom zone and to rise oil recovery factor of injection wells. The efficiency of microemulsion depends on the dissolution of ATP compounds contained in oil, intensification of oil flow to the well bottom, recovery and increase of well bottom zone conductivity. Compared to the ordinary emulsions, microemulsions mix well with layer water and hydrocarbons and have small dimensions and suspended particles. Dilution of microemulsion with water (over 40%) leads to its transformation. This transformed microemulsion is used for wider application areas by mixing with oil and water [12-17].

Researches show clearly that mixing cationic and non-ionic surfactants is useful in testing and supporting microemulsion conductivity models [18].

However, in chemical enhanced oil recovery (EOR), the microscopic sweep efficiency depends primarily on achievement of a low interfacial tension [19].

Aims and Objectives. Considering the urgency of the existing problem, a new combined bactericide-inhibitor was developed based on naphthenic acid salts, isopropyl alcohol, light gas oil fraction and technical hydrated phosphatide, which has emulsifier properties that influence various processes in the formations.

Laboratory research. The study of inhibitory and bactericidal properties of the reagent under the laboratory conditions is carried in accordance with standards. For testing, steel samples 1020 (USA standard) were prepared and installed into the U-shaped cell with a stirring device. Fluid velocity relatively to the samples is 0.3 m/sec. Duration of the experiments is 6 hours at the 25°C degree. Testing of reagent at various concentrations (100-600 mg/l) was carried out in acidic and alkaline environments. The results of laboratory researches are presented in the figure 1.

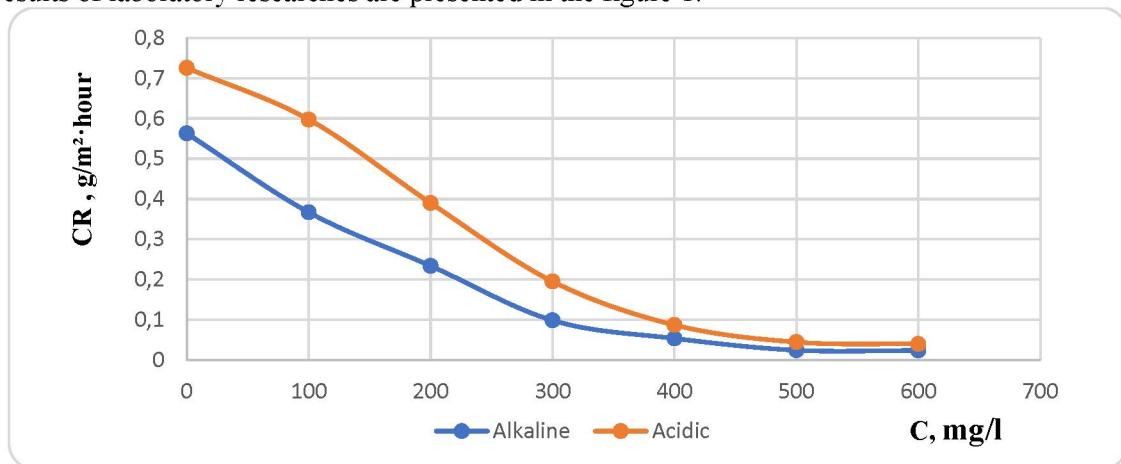


Figure 1 – The dependence of the corrosion rate (CR) in various environments on the concentration of the reagent (C)

Determination of the inhibitor efficiency was conducted by gravimetric method. The essence of the method constitutes determining the rate of corrosion by mass loss of witness specimens in the control and test environment.

The corrosion rate is computed by the expression given below:

$$CR = \frac{m - m_1}{St} \quad (1)$$

where CR - corrosion rate, g/m²·hour; m - mass of the test specimen before the test, g; m₁ - mass of the test specimen after the test, g; S - the surface area of the witness specimen, m²; t - test time, hour.

The effectiveness of the protective action of the inhibitor was characterized by the degree of protection IE, %.

$$IE = \frac{CR - CR_1}{CR} 100\% \quad (2)$$

where CR и CR_1 - corrosion rates of the sample without inhibitor and with inhibitor

As shown in figure 1, the speed of corrosion without inhibitor in various environments was 0.5631 - 0.7257 g/m²·hour. Depending on the reagent concentration, corrosion speed in the corresponding environment has reached 0.0236-0.5974 g/m²·hour and at the same time the protective effect constituted 18-96%.

Laboratory researches have shown that the reagent has high inhibiting properties at optimum concentration of 500 mg/l. At the same time the protective effect of general corrosion was 94-96% (0.0240-0.0447 g/m²·hour).

To study the mechanism of the protective action of the reagent, a potentiostatic method of obtaining polarization curves of 1020 steel was also used. The research results are shown in figure 2.

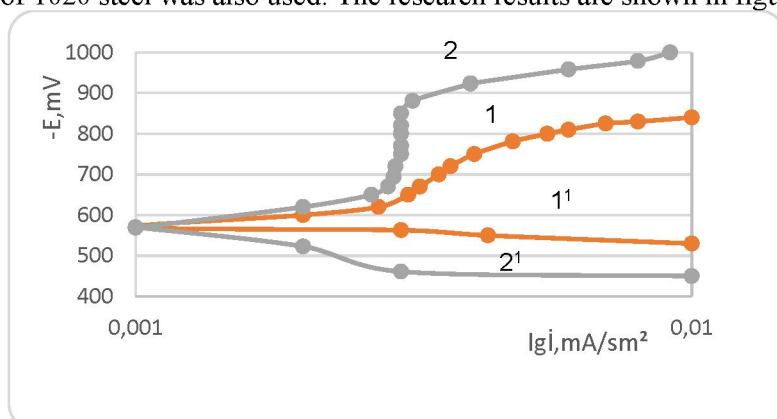


Figure 2 – Cathode (1-2) and anodic (1'-2') potentiostatic polarization curves:
1, 1' - cathode and anode curves without reagent; 2, 2' - cathode and anode curves with a reagent (500 mg/l)

As can be seen from figure 2, a mixed-type reagent is capable of equally effectively inhibiting both electrochemical reactions on an electrode at a concentration of 500 mg/l, which is consistent with gravimetric tests.

Determination of bactericidal properties of reagent with concentrations of 100-600 mg/l was carried out on the culture of SRB with the load equal to 10³ bacteria/ml, at the temperature of 30-32^oC within 15 days. The culture of SRB for these researches has been marked out from layer waters of the “Bibieybat” field.

The effectiveness of the bactericide is characterized by the degree of suppression of sulfate reducing bacteria, which is determined by the formula:

$$IE_{bak.} = \frac{C - C_1}{C} 100\%$$

where $IE_{bak.}$ - degree of suppression; C and C_1 - the presence of H₂S in test of the studied water without reagent and with reagent respectively.

Researches have shown that at concentration of 500 mg/l suppression extent of SRB becomes 99% (figure 3).

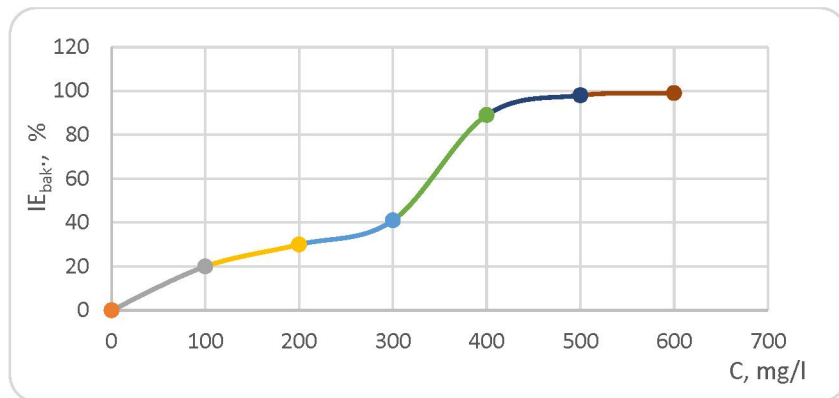


Figure 3 – Bactericidal properties of reagent in various concentrations

Under laboratory conditions effect of reagent in different concentrations on the viscosity of the oil also have been studied. Dynamic viscosity (mPa·s) was carried out at the viscometer "Reotest-2" at the temperature of 25° C and a strain rate equal to 0.33sec⁻¹. For this purpose, was used oil from well № 43 of "Muradkhanli" filed (table 1).

Table 1 – Physico-chemical properties of the studied oil

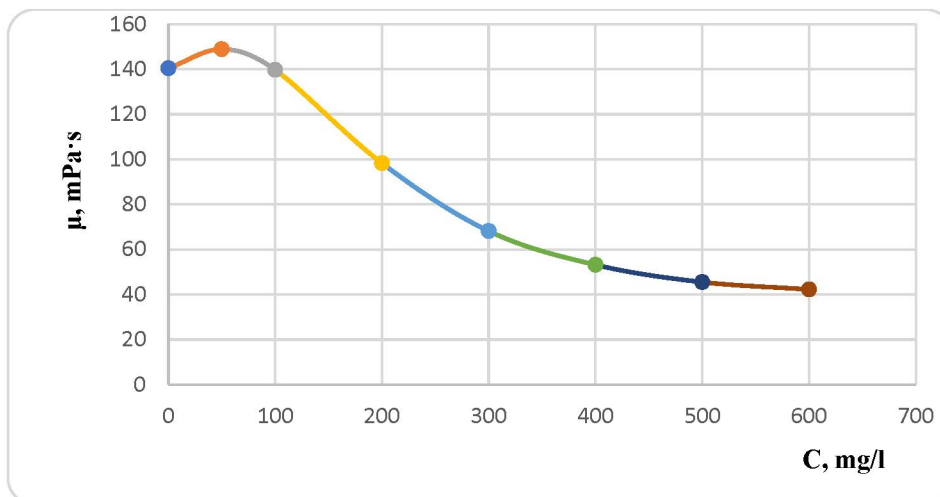
Options	Meanings
Dynamic viscosity of oil, mPa · s	140,4
Density of oil, kg /m ³ at 20°C	915
The content of asphaltenes, %	0,72
Sulfur content in oil,%	0,3
The paraffin content in oil, %	7,2
The content of silica gel resin, %	16
Water content, %	28
Freezing point, °C	16
Mechanical impurities, %	0,62

To assess effectiveness of the reagent regulating oil viscosity, the efficiency index (E_{eff}) is estimated by the formula:

$$E_{\text{eff}} = \frac{\mu_o - \mu_k}{\mu_o} \quad (4)$$

where E_{eff} - the efficiency index of the reagent; μ_o - the dynamic viscosity of the initial oil, Pa·s; μ_k - the dynamic viscosity of the oil with the reagent, Pa·s.

The reagent efficiency index (E) shows how many percent the dynamic viscosity of the oil with the reagent has decreased relative to the dynamic viscosity of the original oil. The results are depicted in figure 4.

Figure 4 – Dependence of dynamic viscosity (μ) of high viscosity oil on reagent concentration (C)

The data in figure 4 indicates that, as the concentration of the reagent increases, shear stress and the dynamic viscosity decreases. For optimum concentration of the reagent 500 mg/l dynamic viscosity are equal to 45.72 Poise correspondingly, herewith the dynamic viscosity is decreased in 3 times, what is 67%.

The improvement in the fluidity of high-viscosity oils can be explained by the fact that the test reagent possesses surface-active properties and is capable of changing the phase and energy interactions at the interfaces between the polar and nonpolar phases.

Technical phosphatide in turn consists of residues of glycerol, fatty acids, phosphoric acid and nitrogen-containing compounds - serine, ethanolamine and choline, and in some cases other substances. Hydration of technical phosphatide leads to the formation of a phosphatide emulsion containing 45-70% water [20]. Taking into account the fact that phosphatides, which are emulsifiers, as well as alcohol and hydrocarbons, which form a microemulsion, are present in the developed reagent. 10% mixture of reagent with water can be used as a rim injected into the formation. Therefore, in laboratory conditions, the effect of the reagent on oil displacement was also studied.

Moreover, to study the reagent effects on oil extrusion process some researches were conducted under the laboratory conditions. Results of the laboratory researches are presented in figure 5.

Experimental studies (at 25° C) on linear model of layer with the initial oil saturation of 76% loaded by quartz sand with permeability 1.2 mkm². At the first stage of experiment at the room temperature and constant pressure difference of 0.025 MPas oil was forced out by layer water. At the same time the displacement coefficient after passing through the layer model of 1.9 steam volumes of water, and in the final period is 0.49 (figure 5 (a)). Thus, layer water has forced out only 49% available oil and this indicates the low oil washout ability of layer water.

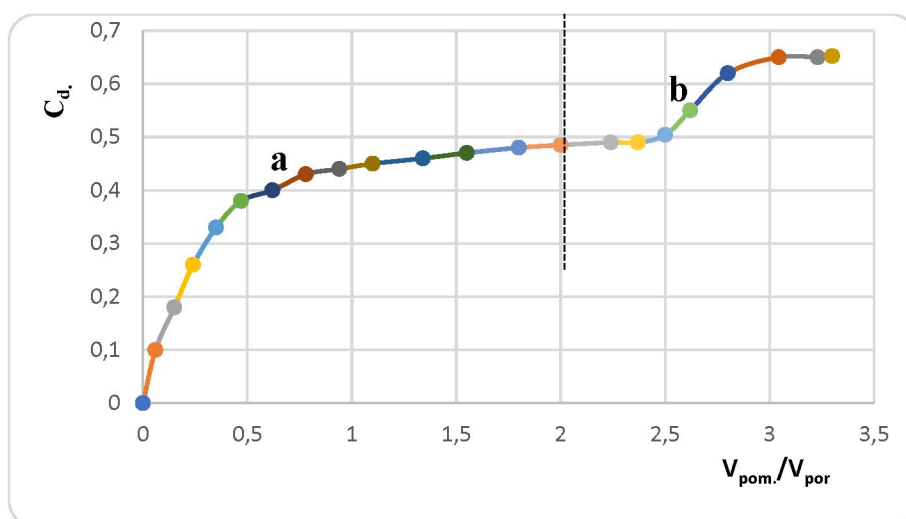


Figure 5 – Dependence of oil displacement coefficient from the porous environment with layer water (a) and 10% solution of reagent (b).
 $V_{pom.}/V_{por.}$ - Volume of pumped agents from pore volume, C_d - Displacement coefficient

At the second stage of experiment reagent solution in concentration of 10% was applied to the layer water before full replacement of residual oil. At this stage 1.4 volumes of solution were injected into the model of layer that has forced out another 16% of residual oil (figure 5 (b)).

It should be noted that the developed microemulsion, which displaces oil from heterogeneous layers, has some features:

- improves the rheological properties of highly viscous oil;
- helps to improve the movement of oil in the reservoir and reduce the breakthrough of the injected water to the production wells, thereby improving its oil-bearing capacity;
- due to the wetting of the surface of the rock with a 10% solution of the reagent, the relationship of the oil with the rock is reduced.

Thus, laboratory studies have shown that the reagent, due to the diphylic properties owing to the presence of polar (hydrophilic) and non-polar (hydrophobic) groups, can be used in small concentrations as a corrosion inhibitor, and at high concentrations, being a microemulsion, stimulates oil displacement by increasing the permeability of rocks.

Field tests. Due to injection of raw layer water to maintain layer pressure, field tests of the reagent on the results of laboratory tests were carried out at injection wells of OGEU (Oil Gas Extraction Unit) “Bibiebatneft”.

Batcher pump delivery rate can be determined by calculation using the amount of injected liquid to the well and concentration of inhibitor working solution.

Firstly, 25 pore volume of reagent solution with concentration of 10% was pumped by impact dose to increase the rate of oil extrusion and carrying out bactericidal treatment. Further, the reagent was pumped with the working concentration of 500 mg/l.

For corrosion speed determination samples of steel 1020 were installed in cartridges from inert materials located in water conduits supplying pumped water into the well. Tests were carried out within 2 months: the first month without the inhibitor, the second month - with reagent supply. Endurance duration of samples was 30 days and then they were selected for further assessment of protective effect. Determination of protective action of bactericide inhibitor was carried out in the laboratory by a gravimetric method on mass loss of steel samples. In parallel, for the chemical and microbiological analyses, the layer water was taken to study the bactericidal properties of reagent.

Field tests have shown that while using reagent the speed of corrosion has on average decreased from 0.1129 to 0.0112 g/m²·hour, the protective effect at the same time constituted 90%. The amount of hydrogen sulfide decreased from 36.3 to 1.2 mg/l. Moreover, the amount of sulfate-reducing bacteria has decreased from 10⁶ to 10¹ bacteria/ml, at the same time suppression extent of SRB constituted 97%.

It is also necessary to note that as a result of the reagent influence on productive layer, oil production in the corresponding oil-extracting wells has increased on average by 11%.

Protection of equipment against corrosion allow to reduce the number of damages and, respectively, to cut down expenses on their elimination, to increase reliability and to prolong service life of pipelines, and finally to increase ecological safety of objects.

Multifunctional reagent was developed for the protection of underground and above ground oil-field equipment of the MLP system from the general and microbiological corrosion. In this case, the reagent can be used in drilling, operating of steel tanks, receiving and pumping oil, as well as to improve oil displacement in reservoirs.

Conclusion.

1. Based on salts of naphthenic acids, isopropyl alcohol, light gas oil fraction and technical hydrated phosphatide, a new combined bactericide-inhibitor has been developed that has microemulsion properties and influences various processes occurring in reservoirs. At the same time the protective effect in laboratory conditions of the general corrosion constitutes 94-96%, and SRB suppression extent is 99%.

2. The results of filtration studies performed on bulk reservoir models showed that the developed reagent has a complex effect. At the reagent concentration of 10% displacement coefficient relatively to layer water increases by 16%.

3. In trade conditions the protective effect constitutes 90%, SRB suppression extent - 97%. At the same time as a result of reagent influence on productive layer oil production has increased in average by 11%.

4. The alternation of various concentrations during the periodic injection of this reagent solves the corrosion protection problems of oilfield equipment of the MLP system and the displacement of residual oil from the oil-bearing layers without additional costs.

5. Application of this reagent possessing oil extrusion ability, bactericidal and inhibiting properties, is represented economically expedient as the technology of its obtaining is quite simple. Moreover, the prime cost is low because of the usage of available local raw materials.

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МИКРОЭМУЛЬСИЯНЫҢ ҚАСИЕТТЕРІНЕ ИЕ КӨПФУНКЦИОНАЛДЫ КОРРОЗИЯ ИНГИБИТОРЫН ӘЗІРЛЕУ

Аннотация. Әзірбайжан кен орындарында қабатқа әсер етудің басым түрде қолданылып келе жатқан әдістерінің бірі – қабаттық қысымды сүйемелдеуді (ҚҚС) қысымдарға айдау ұңғымаларының жүйесі арқылы су айдаумен ұстап тұру. ҚҚ жүйесіндегі микробиологиялық коррозияны тудыратын зақымданудың негізгі

себебі – алдын ала стерилизациялаусыз теңіз суын айдау, және соның салдарынан құбырлардың коррозиялық бұзылуы көрініс табады. Биокоррозды қоздыратын бактериялардың ішіндегі ең агрессивтісі – сульфатты қалпына келтіруші бактериялар (СҚҚБ).

Пайдалану ұңғымаларының кенжар маңы аймағының өткізгіштігін арттыру және айдау ұңғымаларының қабылдағыштығын жақсарту үшін қабатқа әсер ету әдістерінің бірі – микроэмульсияны пайдалану, ал ол, әдетте қабатқа қайту түрінде айдалады.

Қазіргі проблеманың өзектілігін ескере отырып, нафтен қышқылы тұздары, изопропил спирті, жеңіл газойл фракциясы және техникалық гидратталған фосфатид негізінде микроэмульсия қасиеттеріне ие және қабаттарда өтетін түрлі процестерге әсер ететін жаңа біріктірілген бактерицид-ингибитор әзірленді.

Зертханалық жағдайларда реагенттің ингибициялаушы және бактерицидтік қасиеттерін зерттеу стандарттарға сәйкес жүзеге асырылды.

Зертханалық жағдайларда ингибитордың тиімділігін анықтау гравиметриялық әдіспен жүзеге асырылды. Реагентті әртүрлі концентрацияларда (100-600 мг/л) сынау қышқыл және сілтілі ортада жүргізілді. 100-600 мг/л концентрациясындағы реагенттің бактерицидтік қасиеттерін анықтау СҚҚБ дақылында жүргізілді. Зерттеулер 500 мг/л оңтайлы концентрациясы кезінде реагенттің қорғаныш әсері – 94-96 %-ды, ал СҚҚБ басу дәрежесі 99 %-ды құрағанын көрсетті.

Зертханалық жағдайларда реагенттің түрлі концентрациялардағы мұнайдың тұтқырлығына және мұнайға әсері зерттелді. Реагенттің оңтайлы концентрациясы 500 мг/л болғанда, мұнайдың динамикалық тұтқырлығы 3 есе төмендейді, бұл 67 %-ды құрайды. Қабаттың желілік моделінде жүргізілген зерттеулер әзірленген микроэмульсияның 10 %-дық концентрация кезінде қабаттық суды салыстырмалы ығыстыру коэффициентін 16 %-ға арттырағынын көрсетті. Бұл жағдайда өте тұтқыр мұнайдың реологиялық қасиеттері жақсарып, жыныстың бетін суландыруға байланысты, мұнайдың жыныспен байланысы азаяды, сондай-ақ қабатта мұнайдың жылжуы жақсарып және пайдалану ұңғымаларына айдалатын судың ағуы азаяды.

Сонымен, зертханалық зерттеулер реагенттің аз концентрациялардағы коррозия ингибиторы ретінде қолданылуы мүмкін екендігін көрсетті, ал жоғары концентрациялар кезінде жыныстардың өткізгіштігін арттыру есебінен мұнайдың қысылуын ынталандырады.

Әзірленген реагенттің кәсіптік сынағы «Бибиэйбат-нефть» МГӨБ-да ҚҚС жүйесінде жүргізілді. Алдымен, мұнайдың қысылуын арттыру және қабатқа соққы дозасымен бактерицидті өңдеу жүргізу үшін реагенттің 10 %-дық ерітіндісінің (микроэмульсияның) 25 кеуектік көлемі айдалды, содан кейін реагентті 500 мг/л жұмыс концентрациясында айдау жалғастырылды.

Коррозия жылдамдығын анықтау үшін 1020 болаттан жасалған болат үлгілер ұңғымаға айдалатын суды беретін су өткізгіштерде орналасқан инертті материалдардан жасалған кассеталарға орнатылды.

Бактерицид-ингибитордың қорғаныш әсерін анықтау зертханада болат үлгілердің массасының жоғалуы бойынша гравиметриялық әдіспен жүргізілді.

Реагенттің бактерицидтік қасиеттерін зерттеуде химиялық және микробиологиялық талдау үшін қабаттық су қатар алынды.

Кәсіпшілік сынақтар 500 мг/л концентрациясы кезінде, реагенттің қорғаныш әсері 90 %-ды, ал СҚҚБ басу дәрежесі – 97 %-ды құрағанын көрсетті.

Сондай-ақ реагенттің өнімді қабатқа әсері нәтижесінде тиісті мұнай өндіру ұңғымаларында мұнай өндіру орташа есеппен 11 % - ға артқанын атап өту қажет.

Осылайша, әзірленген көпфункционалды реагент жалпы және микробиологиялық коррозиядан ҚҚС жүйесінің жер асты және жер үсті мұнай кәсіпшілігі жабдығын қорғау үшін ұсынылған. Бұл ретте реагент бұрғылау, мұнайды жинау, қабылдау және айдау үшін болат резервуарларды пайдалану кезінде, сондай-ақ қабаттардағы мұнайдың қысылуын жақсарту үшін қолданылуы мүмкін.

Түйін сөздер: коррозия, бактерицидті ингибитор, қорғаныс деңгейі, басу дәрежесі, мұнай өндіруді арттыру, қабатты қысымын сүйемелдеу.

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РАЗРАБОТКА МНОГОФУНКЦИОНАЛЬНОГО ИНГИБИТОРА КОРРОЗИИ, ОБЛАДАЮЩЕГО СВОЙСТВАМИ МИКРОЭМУЛЬСИИ

Аннотация. Одним из доминирующих методов воздействия на пласт, применяемых на месторождениях Азербайджана, остается поддержание пластового давления (ППД) закачкой в пласт воды через систему нагнетательных скважин. Основной причиной повреждений в системе ППД является коррозионное разрушение трубопроводов вследствие нагнетания морской воды без предварительной стерилизации, которое вызывает

микробиологическую коррозию. Наиболее агрессивными среди бактерий, стимулирующих биокоррозию, являются сульфатвосстанавливающие бактерии (СВБ).

Одним из методов воздействия на пласт для повышения проницаемости призабойной зоны эксплуатационных скважин и улучшения приемистости нагнетательных скважин является использование микроэмульсии, которая обычно закачивается в пласт в виде оторочки.

Учитывая актуальность существующей проблемы, на основе солей нафтеновых кислот, изопропилового спирта, легкой газойлевой фракции и технического гидратированного фосфатида разработан новый комбинированный бактерицид-ингибитор, обладающий свойствами микроэмульсии и оказывающий влияние на различные процессы, протекающие в пластах.

Изучение ингибирующих и бактерицидных свойств реагента в лабораторных условиях осуществлялось согласно стандартам.

Определение эффективности ингибитора в лабораторных условиях осуществлялось гравиметрическим методом. Испытания реагента в различных концентрациях (100-600 мг/л) проводили в кислых и щелочных средах. Определение бактерицидных свойств реагента в концентрации 100-600 мг/л проводилось на культуре СВБ. Исследования показали, что при оптимальной концентрации 500 мг/л защитный эффект реагента составил 94-96%, а степень подавления СВБ -99%.

В лабораторных условиях изучалось также влияние реагента в различных концентрациях на вязкость нефти и нефтевытеснение. При оптимальной концентрации реагента 500 мг/л динамическая вязкость нефти снижается в 3 раза, что составляет 67%. Исследования, проведенные на линейной модели пласта показали, что разработанная микроэмульсия при 10% концентрации увеличивает коэффициент вытеснения относительно пластовой воды на 16%. Это происходит за счет того, что улучшаются реологические свойства высоковязкой нефти, уменьшается связь нефти с породой в связи со смачиванием поверхности породы, а также улучшается продвижение нефти в пласте и уменьшение прорыва закачиваемой воды к эксплуатационным скважинам.

Итак, лабораторные исследования показали, что реагент в малых концентрациях может использоваться как ингибитор коррозии, а при высоких концентрациях стимулирует нефтевытеснение за счет увеличения проницаемости пород.

Промысловые испытания разработанного реагента проводились в системе ППД в НГДУ "Бибиэйбат-нефть". Сначала для повышения нефтевытеснения и проведения бактерицидной обработки пласта ударной дозой было закачено 25 поровых объемов 10% раствора реагента (микроэмульсии), а затем продолжена закачка реагента уже в рабочей концентрации 500 мг/л

Для определения скорости коррозии стальные образцы-свидетели из стали 1020 устанавливались в кассетах из инертных материалов, расположенных в водоводах, подающих нагнетаемую воду в скважину.

Определение защитного действия бактерицид-ингибитора проводилось в лаборатории гравиметрическим методом по потере массы стальных образцов.

Для изучения бактерицидных свойств реагента параллельно была взята пластовая вода для химического и микробиологического анализов.

Промысловые испытания показали, что защитный эффект реагента при концентрации 500 мг/л составил 90%, а степень подавления СВБ - 97%.

Необходимо также отметить, что в результате воздействия реагента на продуктивный пласт добыча нефти в соответствующих нефтедобывающих скважинах увеличилась в среднем на 11%.

Таким образом, разработанный многофункциональный реагент рекомендован для защиты подземного и наземного нефтепромыслового оборудования системы ППД от общей и микробиологической коррозии. При этом реагент может найти применение при бурении, эксплуатации стальных резервуаров для сбора, приема и откочки нефти, а также для улучшения нефтевытеснения в пластах.

Ключевые слова: коррозии, бактерицидный ингибитор, степень защиты, степень подавления, увеличение добычи нефти, поддержание пластового давления.

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