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The scientific journal News of the National Academy of Sciences of the Republic of Kazakhstan, Series of Geology and Technical Sciences has been indexed in the international abstract and citation database Scopus since 2016 and demonstrates stable bibliometric performance.

The journal is also included in the Emerging Sources Citation Index (ESCI) of the Web of Science platform (Clarivate Analytics, since 2018).

Indexing in ESCI confirms the journal's compliance with international standards of scientific peer review and editorial ethics and is considered by Clarivate Analytics as part of the evaluation process for potential inclusion in the Science Citation Index Expanded (SCIE), Social Sciences Citation Index (SSCI), and Arts & Humanities Citation Index (AHCI).

Indexing in Scopus and Web of Science ensures high international visibility of publications, promotes citation growth, and reflects the editorial board's commitment to publishing relevant, original, and scientifically significant research in the fields of geology and technical sciences.

«Қазақстан Республикасы Ұлттық ғылым академиясының Хабарлары. Геология және техникалық ғылымдар сериясы» ғылыми журналы 2016 жылдан бастап халықаралық реферативтік және ғылымиметриялық Scopus дерекқорында индекстеледі және тұрақты библиометриялық көрсеткіштерді көрсетіп келеді.

Сонымен қатар журнал Web of Science платформасының (Clarivate Analytics, 2018) халықаралық реферативтік және наукометриялық дерекқоры Emerging Sources Citation Index (ESCI) тізіміне енгізілген.

ESCI дерекқорында индекстелуі журналдың халықаралық ғылыми рецензиялау талаптары мен редакциялық этика стандарттарына сәйкестігін растайды, сондай-ақ Clarivate Analytics компаниясы тарапынан басылмды Science Citation Index Expanded (SCIE), Social Sciences Citation Index (SSCI) және Arts & Humanities Citation Index (AHCI) дерекқорларына енгізу қарастырылуда.

Scopus және Web of Science дерекқорларында индекстелуі жарияланымдардың халықаралық деңгейде жоғары сұранысқа ие болуын қамтамасыз етеді, олардың дәйексөз алу көрсеткіштерінің артуына ықпал етеді және редакциялық алқаның геология мен техникалық ғылымдар саласындағы өзекті, бірегей және ғылыми тұрғыдан маңызды зерттеулерді жариялауға ұмтылысын айқындайды.

Научный журнал «News of the National Academy of Sciences of the Republic of Kazakhstan, Series of Geology and Technical Sciences» с 2016 года индексируется в международной реферативной и наукометрической базе данных Scopus и демонстрирует стабильные библиометрические показатели.

Журнал также включён в международную реферативную и наукометрическую базу данных Emerging Sources Citation Index (ESCI) платформы Web of Science (Clarivate Analytics, 2018).

Индексирование в ESCI подтверждает соответствие журнала международным стандартам научного рецензирования и редакционной этики, а также рассматривается компанией Clarivate Analytics в рамках дальнейшего включения издания в Science Citation Index Expanded (SCIE), Social Sciences Citation Index (SSCI) и Arts & Humanities Citation Index (AHCI).

Индексирование в Scopus и Web of Science обеспечивает высокую международную востребованность публикаций, способствует росту цитируемости и подтверждает стремление редакционной коллегии публиковать актуальные, оригинальные и научно значимые исследования в области геологии и технических наук.

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MEASURES FOR REMOVAL OF CARBONATE SCALE DEPOSITS FORMED IN THE WELLBORE AND DOWNHOLE EQUIPMENT

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Abstract. The article addresses the removal of carbonate scale deposits contaminated with heavy hydrocarbon compounds from the near-wellbore zone and downhole equipment. *Problem statement and relevance.* The deposition of inorganic salts in the bottomhole zone and on downhole equipment reduces formation permeability, impairs the operation of electric submersible pumps and shortens the workover cycle. When the scale is coated with asphaltenes, resins and paraffins, the hydrophobic film prevents contact of aqueous treatment fluids with the mineral phase and considerably reduces the efficiency of chemical treatments. *Methods.* Plates with carbonate deposits coated with an oil film were treated with aqueous sulfanol solutions (0.01–0.10%) to hydrophilize the surface and

with ammonium chloride solutions (1–6%) to remove the deposits; the removal efficiency was determined gravimetrically. The effect of treatment time was studied, and the effect of the injected fluid volume on permeability was evaluated on linear formation models. The technology was tested in well No. 1614 of the Surakhani field equipped with an electric submersible pump. *Key findings/results.* A 0.05% sulfanol solution removed 98.0% of the oil film, and a 4% ammonium chloride solution removed 96.7% of the deposit mass. Since the weakly acidic ammonium chloride solution does not dissolve the bulk of calcium carbonate under static conditions, deposit removal is presumably due to partial localized dissolution at intercrystalline contacts followed by detachment of the weakened deposit. Injection of one pore volume of the treatment fluid increased the permeability of the models fivefold. After the field treatment, oil production increased from 3.1 to 4.2 t/day, and the workover cycle was extended from 42 to 78 days. *Practical application of the results.* The method can be applied without pulling the pump in wells with carbonate scale complicated by hydrocarbon deposits; it is not intended for sulfate or halite deposits.

Keywords: carbonate scale, asphaltene–resin–paraffin deposits, sulfanol, ammonium chloride, hydrophilization, bottomhole zone, electric submersible pump

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ҰҢҒЫМА ОҚПАНЫНДА ЖӘНЕ ҰҢҒЫМА ІШИНДЕГІ ЖАБДЫҚТА ТҮЗІЛГЕН КАРБОНАТТЫ ТҮЗ ШӨГІНДІЛЕРІН ЖОЮ ШАРАЛАРЫ

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Аннотация. *Өзектілігі.* Мақалада ауыр көмірсутекті қосылыстармен ластанған карбонатты тұз шөгінділерін ұңғыма түбі аймағынан және ұңғыма ішіндегі жабдыктан жою мәселесі қарастырылады. Ұңғыма түбі аймағында және ұңғыма ішіндегі жабдықта бейорганикалық тұздардың шөгуі қабаттың өткізгіштігін төмендетеді, электрлі ортадан тепкіш сораптардың жұмысын бұзады және ұңғымалардың жөндеуаралық кезеңін қысқартады. Шөгінділер асфальтендермен, шайырлармен және парафиндермен жабылған жағдайда гидрофобты қабықша сулы технологиялық ерітінділердің минералды фазамен байланысуына кедергі келтіріп, химиялық өңдеулердің тиімділігін айтарлықтай төмендетеді. *Әдістер.* Мұнай қабықшасымен жабылған карбонатты шөгінділері бар пластиналар бетті гидрофильдеу үшін сульфано́лдың сулы ерітінділерімен (0,01–0,10%), ал шөгінділерді жою үшін аммоний хлоридінің ерітінділерімен (1–6%) өңделді; жою тиімділігі гравиметриялық әдіспен анықталды. Өңдеу ұзақтығының әсері зерттелді, ал қабаттың сызықтық модельдерінде айдалған ерітінді көлемінің өткізгіштікке әсері бағаланды. Технология электрлі ортадан тепкіш сораппен жабдықталған Сураханы кен орнының № 1614 ұңғымасында сыналды. *Негізгі қорытындылар/нәтижелер.* Сульфано́лдың 0,05%-дық ерітіндісі мұнай қабықшасының 98,0%-ын, ал аммоний хлоридінің 4%-дық ерітіндісі шөгінді массасының 96,7%-ын жойды. Статикалық жағдайларда әлсіз қышқылды аммоний хлориді ерітіндісі кальций карбонатының негізгі массасын ерітпейтіндіктен, шөгінділердің жойылуы, болжам бойынша, кристаллитаралық түйіспелердегі ішінара жергілікті еруге және әлсіреген шөгіндінің кейіннен беттен ажырап түсуіне байланысты. Кеуек көлеміне тең көлемде ерітінді айдау модельдердің өткізгіштігін бес есе арттырды. Кәсіпшілік өңдеуден кейін мұнай дебиті тәулігіне 3,1 тоннадан 4,2 тоннаға дейін өсті, ал жөндеуаралық кезең 42 тәуліктен 78 тәулікке дейін ұзарды. *Нәтижелердің практикалық қолданылуы.* Әдісті карбонатты шөгінділері ауыр көмірсутектермен ластанған ұңғымаларда сорапты көтермей қолдануға болады; ол сульфатты және галитті шөгінділерге арналмаған.

Түйін сөздер: карбонатты тұз шөгінділері, асфальт-шайыр-парафин шөгінділері, сульфано́л, аммоний хлориді, гидрофильдеу, ұңғыма түбі аймағы, электрлі ортадан тепкіш сорап

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МЕРЫ ПО УДАЛЕНИЮ КАРБОНАТНЫХ СОЛЕВЫХ ОТЛОЖЕНИЙ, ОБРАЗУЮЩИХСЯ В СТВОЛЕ СКВАЖИНЫ И НА ВНУТРИСКВАЖИННОМ ОБОРУДОВАНИИ

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Аннотация. В статье рассматриваются методы удаления карбонатных солевых отложений, загрязненных тяжелыми углеводородными соединениями, из призабойной зоны пласта и с поверхности внутрискважинного оборудования. *Постановка проблемы и актуальность.* Образование неорганических солевых отложений в призабойной зоне пласта и на внутрискважинном оборудовании приводит к снижению проницаемости пласта, нарушению работы электроцентробежных насосов и сокращению межремонтного периода эксплуатации скважин. При наличии на поверхности отложений асфальтенов, смол и парафинов формируется гидрофобная пленка, препятствующая непосредственному контакту водных технологических растворов с минеральной фазой, что существенно снижает эффективность химической обработки. *Методы.* В ходе лабораторных исследований пластины с карбонатными отложениями, покрытыми нефтяной пленкой, обрабатывали водными растворами сульфанола концентрацией 0,01–0,10 % для гидрофилизации поверхности и растворами хлорида аммония концентрацией 1–6 % для удаления солевых отложений. Эффективность

удаления определяли гравиметрическим методом. Исследовано влияние продолжительности обработки на эффективность удаления отложений. На линейных моделях пласта оценено влияние объема закачиваемого раствора на изменение проницаемости. Промысловые испытания технологии проведены на скважине № 1614 месторождения Сураханы, оборудованной электроцентробежным насосом. *Основные результаты.* Установлено, что применение 0,05%-ного раствора сульфанола обеспечивает удаление 98,0 % нефтяной пленки, тогда как обработка 4%-ным раствором хлорида аммония позволяет удалить 96,7 % массы карбонатных отложений. Поскольку в статических условиях слабокислый раствор хлорида аммония не обеспечивает растворения основной массы карбоната кальция, предполагается, что удаление отложений обусловлено частичным локальным растворением минеральной фазы в местах межкристаллитных контактов с последующим отслаиванием ослабленного осадка. Закачка раствора в объеме, соответствующем одному поровому объему модели пласта, способствовала пятикратному увеличению ее проницаемости. По результатам промысловой обработки скважины дебит нефти увеличился с 3,1 до 4,2 т/сут, а межремонтный период эксплуатации - с 42 до 78 суток. *Практическое применение результатов.* Предложенный метод может применяться для удаления карбонатных солевых отложений, загрязненных тяжелыми углеводородными соединениями, без необходимости подъема электроцентробежного насоса. При этом область применения технологии ограничивается карбонатными отложениями и не распространяется на сульфатные и галитовые отложения.

Ключевые слова: карбонатные солевые отложения, асфальтосмоло-парафиновые отложения, сульфанол, хлорид аммония, гидрофилизация, призабойная зона пласта, электроцентробежный насос.

Introduction. At all stages of oilfield development, including drilling, field development and the various periods of well operation, the main objective of oilfield management is to maintain and enhance well productivity. However, the periodic occurrence of well complications creates considerable difficulties for any operating strategy and directly affects production rates. Complications arising during operation lead to the formation of various deposits in the bottomhole zone, in the tubing and in surface equipment, which restrict the inflow of fluids from the formation and their lifting to the surface.

The deposition of inorganic salt compounds in the near-wellbore area, in well equipment, and in-field junctions creates serious difficulties in oil production, transportation and treatment (Mirzajanzade et al., 2010; Shangaraeva and Petukhov, 2013; Valekzhanin et al., 2017b).

Carbonate scale is one of the most widespread types of inorganic deposits in oil production. Its formation is governed by the carbonate equilibrium in the produced water (Olajire, 2015; Kamal et al., 2018):



Under reservoir conditions, the dissolved carbon dioxide keeps this equilibrium shifted to the left. As the pressure decreases in the bottomhole zone, at the pump intake and in the tubing, CO_2 is released into the gas phase, the pH of the water increases and the equilibrium shifts towards the precipitation of calcium carbonate. An increase in temperature, which reduces the solubility of CaCO_3 , and the mixing of incompatible waters act in the same direction (Olajire, 2015; Kumar et al., 2018). Since the pressure drop is greatest in the near-wellbore zone and in the pump, carbonate deposits accumulate primarily in the perforation zone, in the pore space of the bottomhole zone and on the stages of electric submersible pumps, reducing the formation permeability and shortening the workover cycle of the wells.

Solid salt deposits found in oil production systems can consist of organic and inorganic components depending on their composition. For example, salt deposits in oil fields may contain calcium, calcium–magnesium and iron carbonates, iron oxides and hydroxides (corrosion products), sodium chloride (halite), gypsum, quartz and other components (Frenier and Ziauddin, 2008; Kelland, 2014; Kamal et al., 2018). The present study, however, addresses only carbonate (calcium and calcium–magnesium carbonate) deposits whose removal is complicated by co-deposited heavy hydrocarbon compounds. Sulfate (gypsum, barite), siliceous and halite deposits are beyond its scope, since they require different treatment approaches, such as chelating scale dissolvers for sulfate scale and fresh-water washing for halite (Frenier and Ziauddin, 2008; Kamal et al., 2018).

In Azerbaijan, carbonate scaling of oilfield equipment was first observed in reservoirs at the late stages of development, which are characterized by a high water cut of the produced fluid. Studies indicate that salt precipitation is most intensive in the wells of the Absheron Peninsula fields: Balakhani–Sabunchu–Ramana, Surakhani–Garachukhur, Gala, Bibiheybat, the Siyazan monocline, etc. (Ibrahimov and Latifov, 2018).

Literary review. Scale deposits that have already formed are removed by mechanical or chemical methods. Mechanical methods (milling, scraping, jetting) require pulling the downhole equipment or the use of coiled tubing and are not applicable to deposits in the pore space of the formation. Among chemical methods, carbonate deposits are most often treated with hydrochloric acid, which dissolves calcium carbonate rapidly and completely. However, hydrochloric acid is highly corrosive to tubing and pump equipment and requires the use of corrosion inhibitors; because of its rapid reaction, it is spent mainly in the immediate vicinity of the wellbore, and in contact with asphaltenic crude oils it may cause sludge formation (Olajire, 2015; Kamal et al., 2018). Organic acids and chelating agents (EDTA, DTPA, GLDA) are less corrosive and allow a more uniform treatment, but they are considerably more expensive and react more slowly (Gamal et al., 2021; Barri et al., 2022).

Solid deposits within oilfield equipment, especially in wells, frequently contain heavy hydrocarbon compounds such as paraffin, asphaltenes and resins. These compounds reduce the efficiency of the interaction between the chemical reagents and inorganic salts, thereby hindering the removal of the solid deposits (Yang et al., 2025).

Therefore, treatment technologies are required that combine the removal of the hydrocarbon film from the scale surface with the subsequent action on the mineral phase and that are sufficiently mild for downhole equipment to allow the treatment to be performed without pulling the pump. The aim of this study is to substantiate, on the basis of laboratory and field investigations, a technology for removing carbonate deposits contaminated with heavy hydrocarbon compounds from the bottomhole zone and downhole equipment by sequential treatment with an aqueous solution of an anionic surfactant (sulfanol) and an aqueous solution of ammonium chloride, and to clarify the mechanism of deposit removal.

Materials and Methods. Despite the availability of numerous methods of combating salt deposits, the use of chemical reagents (inhibitors), due to their operational simplicity and efficiency, remains the main method today (Kirboga and Öner, 2012; Glushchenko et al., 2013; Valekzhanin et al., 2017a; Kazybayeva et al., 2014; Ragulin et al., 2019; Spanov et al., 2019; Jabbarova, 2021; Shahbazov et al., 2022). Nevertheless, there is a critical need to improve existing methods and develop new technological processes (Garayev et al., 2016; Abdullayev, 2018). Current research highlights that, to achieve effective removal of precipitated salt crystals, it is first necessary to prepare the crystal surface for chemical action. High-molecular-weight hydrocarbons precipitating onto these crystals convert their naturally hydrophilic surface into a hydrophobic one. As a result, chemical reagents injected to remove precipitated salts in the pores and equipment around the wellbore cannot penetrate this hydrophobic barrier, rendering the treatment ineffective. Therefore, before injection of the scale-removal reagent, the hydrophobic surface must be hydrophilized (converted to a water-wet state).

The possibility of using ammonium chloride and surfactant solutions to remove carbonate deposits contaminated with heavy hydrocarbon compounds from the near-wellbore zone and downhole equipment was investigated in laboratory conditions.

Sulfanol, a technical mixture of sodium alkylbenzenesulfonates, was used as the surfactant. Anionic surfactants of this type adsorb at oil–water and solid–water interfaces and are widely used as detergents and wetting agents (Rosen and Kunjappu, 2012). Ammonium chloride (NH_4Cl) was used as the main active reagent. Aqueous solutions of sulfanol with concentrations of 0.01–0.10% and of ammonium chloride with concentrations of 1–6% were tested.

The laboratory study comprised four series of experiments. In the first series, the effect of sulfanol concentration on the removal of the oil film from the surface of salt deposits was determined. In the second series, the optimal concentration of ammonium chloride was established. In the third series, the effect of the treatment

time in the 4% ammonium chloride solution on the residual mass of the carbonate deposit was studied. In the fourth series, the effect of the injected volume of the treatment fluid on the permeability of linear formation models was evaluated. The procedures of the individual series are described below together with the results.

The masses of the plates were determined by weighing before and after each treatment stage. The removal efficiency of the oil film (Table 1) and of the salt deposit (Table 2) was calculated as

$$E = (m_0 - m_1)/m_0 \cdot 100\%, \quad (2)$$

where m_0 and m_1 are the masses of the oil film (or of the salt deposit) on the plate before and after treatment, respectively, 10^{-3} kg. In the time-dependence experiments (Table 3), the residual deposit was expressed as a percentage of the initial deposit mass:

$$R = (m_t - m_p)/(m_s - m_p) \cdot 100\%, \quad (3)$$

where m_s is the mass of the plate with the deposit before treatment, m_t is the mass of the plate with the residual deposit after treatment for time t , and m_p is the mass of the clean plate, 10^{-3} kg. The permeability of the linear models was determined from Darcy's law:

$$K = Q\mu L/(A\Delta p), \quad (4)$$

where Q is the volumetric flow rate, m^3/s ; μ is the dynamic viscosity of the fluid, $\text{Pa}\cdot\text{s}$; L is the length of the model, m ; A is its cross-sectional area, m^2 ; Δp is the pressure drop across the model, Pa . The treatment effect was characterized by the ratio K/K_0 , where K_0 and K are the permeabilities of the model before and after treatment, respectively. The volume of the injected treatment fluid V_i was expressed as a percentage of the pore volume of the model.

Results and Discussions. In the first stage of the study, the plates were immersed in a beaker containing carbonate-bearing formation water and kept for several hours to allow salt deposits to accumulate. Then, to simulate field conditions under which the salt deposits are coated with a hydrocarbon layer, the plates with the deposits were immersed in oil to form a film. After a hydrophobic surface had been obtained, the masses of the deposits were determined. To evaluate the effect of the surfactant on the oil film, the plates were then immersed in aqueous sulfanol solutions of various concentrations. The test results are presented in Table 1 and Figure 1.

Table 1. Effect of sulfanol concentration on the removal of the oil film from salt deposits.

Sulfanol aqueous solution concentration, %	Mass of the oil film on salt deposits, 10^{-3} kg		Efficiency, %
	before treatment	after treatment	
0.01	2	1.2	40.0
0.02	2	1.03	48.5
0.05	2	0.04	98.0
0.07	2	0.04	98.0
0.09	2	0.039	98.1
0.10	2	0.04	98.0

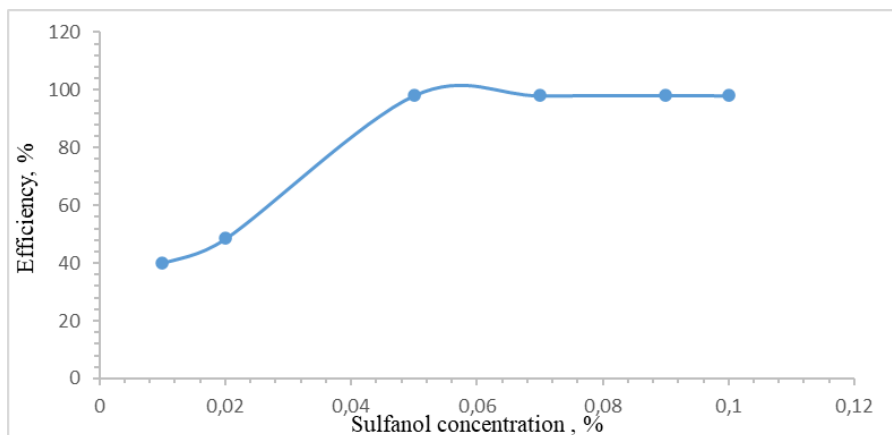


Figure 1. Dependence of the oil film removal efficiency on the sulfanol concentration.

Table 1 shows that the oil film is almost completely (98.0%) removed from the salt deposits when a 0.05% aqueous sulfanol solution is used. A further increase in the surfactant concentration does not noticeably improve the cleaning efficiency. The dependence has a threshold character: at sulfanol concentrations of 0.01–0.02%, only 40.0–48.5% of the oil film is removed, whereas at 0.05% the removal efficiency reaches 98.0%. Such behaviour is typical of anionic surfactants: their detergent action increases sharply as the concentration approaches the level at which the interfaces become saturated with adsorbed surfactant molecules, which for alkylbenzenesulfonates corresponds to the region of the critical micelle concentration, and changes little at higher concentrations (Rosen and Kunjappu, 2012). Therefore, the 0.05% sulfanol solution was considered optimal, since higher concentrations increase reagent consumption without improving the result.

In the second stage of the experiments, the optimal concentration of ammonium chloride was determined. The results are given in Table 2 and Figure 2.

Table 2. Effect of ammonium chloride concentration on the removal of carbonate deposits.

Ammonium chloride solution concentration, %	Mass of salt deposits, 10^{-3} kg		Efficiency, %
	before treatment	after treatment	
1	3	2.2	26.7
2	3	1.0	66.7
3	3	0.5	83.3
4	3	0.1	96.7
5	3	0.1	96.7
6	3	0.096	96.8

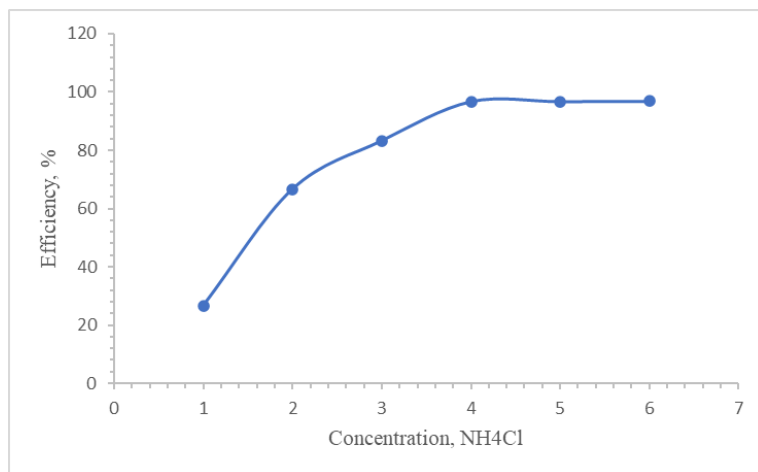


Figure 2. Dependence of the salt deposit removal efficiency on the ammonium chloride concentration.

Table 2 shows that a 4% ammonium chloride solution can be considered optimal: at this concentration, 96.7% of the deposit mass is removed from the plate surface. A further increase in concentration does not significantly affect the result. The efficiency increases most strongly in the concentration range of 1–3% (from 26.7 to 83.3%), whereas above 4% the dependence reaches a plateau. Thus, the 4% concentration provides the maximum effect at the minimum reagent consumption.

Based on the findings of the previous two studies, aqueous solutions of 0.05% sulfanol and 4% ammonium chloride were used in subsequent experiments. During the third stage of the experiments, the time dependence of the carbonate deposit removal was examined. For this purpose, glass plates with carbonate deposits were immersed in beakers containing 4% ammonium chloride solution and weighed after being kept for various time intervals. The results are presented in Table 3 and Figure 3.

Table 3. Effect of treatment time in 4% ammonium chloride solution on the residual mass of the carbonate deposit.

Number of experiments	Mass of the plate with the deposit, 10 ⁻³ kg			Treatment time, min.
	Before treatment	After treatment (residue)		
		mass	%	
1	5	4.2	60	60
2	5	3.92	46	120
3	5	3.68	34	180
4	5	3.48	24	240
5	5	3.32	16	300
6	5	3.2	10	360
7	5	3.06	3	420
8	5	3.04	2	480

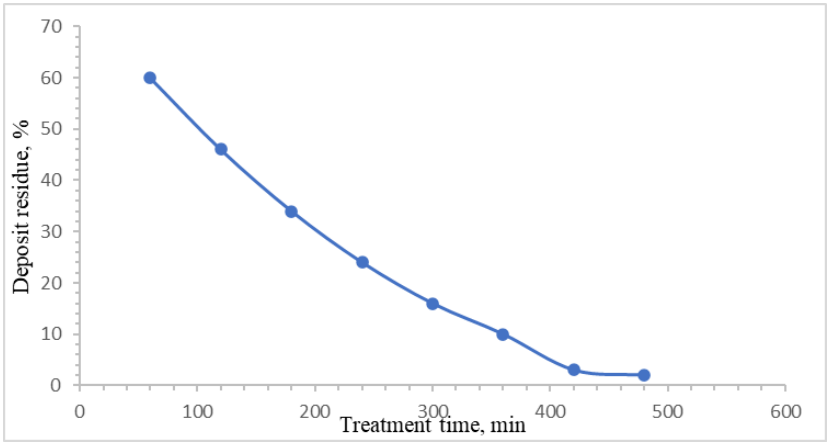


Figure 3. Dependence of the residual carbonate deposit on the treatment time in 4% ammonium chloride solution.

In these experiments, the initial mass of each plate with the deposit was $m_s = 5 \cdot 10^{-3}$ kg and the mass of the clean plate was $m_p = 3 \cdot 10^{-3}$ kg; thus, the initial deposit mass was $2 \cdot 10^{-3}$ kg, and the residue in Table 3 was calculated by Eq. (3).

As Table 3 shows, within 8 hours the carbonate deposit is almost completely removed from the glass plates (only 2% of the initial deposit mass remains). The removal rate decreases with time. During the first hour, 40% of the deposit is removed; over the following five hours, the hourly removal gradually decreases from 14 to 6% of the initial deposit mass; during the seventh hour, a further 7% is removed, and during the eighth hour, only 1%. Interpolation of the data in Table 3 shows that half of the deposit is removed in about 1.7 hours, about three quarters (76%) in 4 hours and 90% in 6 hours. The high initial rate can be attributed to the detachment of the least strongly bonded outer part of the deposit, whereas the subsequent stage is presumably controlled by the gradual weakening of the intercrystalline contacts and of the adhesion of the deposit to the substrate (see the

discussion of the mechanism below). These kinetic data are important for selecting the soaking time in field treatments.

Further studies were conducted on two linear models simulating the formation, into which the treatment fluid was injected in volumes of 50–200% of the pore volume. As a result, it was determined that the filtration properties of the models can be improved by injecting the treatment fluid of the proposed composition in an amount equal to the pore volume (Figure 4).

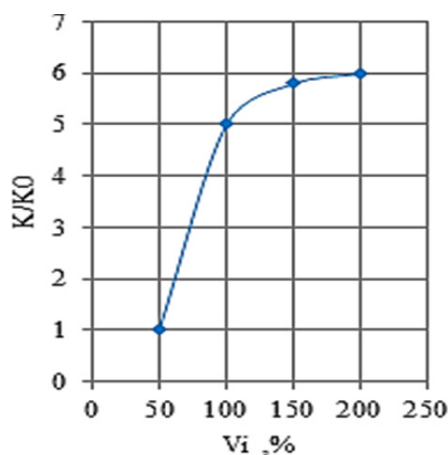


Figure 4. Dependence of the permeability ratio K/K_0 on the injected volume of the treatment fluid V_i (% of the pore volume).

As Figure 4 shows, injection of the treatment fluid in a volume equal to 50% of the pore volume does not change the permeability of the model ($K/K_0 \approx 1$). When the injected volume is increased to one pore volume, the permeability increases fivefold ($K/K_0 \approx 5$), whereas a further increase to 150 and 200% of the pore volume raises K/K_0 only to about 5.8 and 6.0, respectively. Thus, the main effect is achieved when the treatment fluid fills the entire pore volume of the treated zone, and a further increase in the injected volume yields only a small additional gain.

As noted above, the treatment is based on the complementary action of the two solutions. Sulfanol adsorbs on the hydrocarbon-coated deposits and alters their surface molecular properties: the oil accumulated on the deposits is dispersed and washed off, and the surface becomes hydrophilic (Kelland, 2014). This stage is a prerequisite for the subsequent treatment, since the hydrocarbon film prevents contact of the aqueous ammonium chloride solution with the mineral phase (Yang et al., 2025).

Ammonium chloride is a salt of a weak base (ammonia) and a strong acid (hydrochloric acid). Owing to the hydrolysis of the ammonium ion,

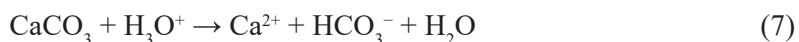


the ammonium chloride solution is weakly acidic. Since NH_4^+ is a weak acid ($\text{p}K_a = 9.25$ at 25°C), the pH of the solution can be estimated as

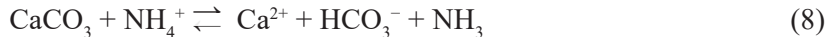
$$\text{pH} = \frac{1}{2}(\text{p}K_a - \lg C), \quad (6)$$

where C is the molar concentration of NH_4Cl , mol/L. For the 4% solution ($C \approx 0.75$ mol/L), Eq. (6) gives $\text{pH} \approx 4.7$, and over the entire concentration range studied (1–6%), the calculated pH varies only from about 5.0 to 4.6.

Although the solution is weakly acidic, the concentration of free hydronium ions in it is very low (about $2 \cdot 10^{-5}$ mol/L at pH 4.7), i.e., several orders of magnitude lower than in the hydrochloric acid solutions used for the treatment of carbonate deposits. The capacity of the ammonium chloride solution to react with calcium carbonate is therefore determined not by the current pH value but by the total content of NH_4^+ ions, which serve as a reservoir of acidity. As hydronium ions are consumed in the reaction with the carbonate,



equilibrium (5) shifts to the right, and the consumed H_3O^+ ions are regenerated at the expense of NH_4^+ ions. The overall process can be represented as



In a closed system, this process is self-limiting: the ammonia formed raises the pH of the solution and converts hydrogen carbonate ions into carbonate ions, which favours the reprecipitation of CaCO_3 . Consequently, under static conditions and in the absence of removal of the reaction products, equilibrium (8) is established at a low degree of conversion, and the solution is not capable of dissolving the bulk of a calcium carbonate deposit; complete dissolution of carbonate scale requires strong mineral or organic acids or chelating agents (Kamal et al., 2018; Gamal et al., 2021; Barri et al., 2022).

The removal of the deposit observed in the present study is therefore attributed mainly to a different mechanism. The limited dissolution presumably proceeds preferentially at the sites where the deposit structure is least stable, primarily at intercrystalline contacts and at the deposit–substrate interface, which are characterized by an increased density of structural defects and, consequently, by higher reactivity. Even limited dissolution at these sites weakens both the cohesion between the crystals and the adhesion of the deposit to the surface; as a result, the deposit loses its integrity, breaks into fragments and detaches from the surface. Under downhole conditions, the detached fragments are carried away by the fluid flow, whereas in the static laboratory test they separate from the plate.

This interpretation is consistent with the effect of the reagent concentration.

When the NH_4Cl concentration increases from 1 to 4%, the content of NH_4^+ ions available for interaction with the deposit increases fourfold, whereas the calculated pH decreases only from 5.0 to 4.7. The strong increase in the removal efficiency over the same range, from 26.7 to 96.7% (Table 2), therefore indicates that the result is determined primarily not by the bulk acidity of the solution but by the reservoir of NH_4^+ ions, in agreement with the mechanism described above.

In the well, the action of the solution can be expected to be more pronounced than in the static laboratory tests, for two reasons. First, the dissociation of the ammonium ion is endothermic, so that the acidity of the solution increases with temperature. Second, in the porous medium of the bottomhole zone, the contact of the solution with the deposit is not purely static: during the injection and displacement of the solution into the formation, fresh portions of the reagent continuously come into contact with the deposit, while the reaction products are carried away by the flow; this prevents equilibrium (8) from being established locally and favours further dissolution of the carbonate. In addition, after the well is brought back into operation, the weakened deposit is removed by the produced fluid flow. The quantitative assessment of these factors requires dynamic tests under reservoir conditions, as noted below among the limitations of the method.

It should be emphasized that the removal efficiency reported in Tables 2 and 3 was determined gravimetrically, from the decrease in deposit mass on the plates. It therefore reflects the combined effect of partial dissolution and detachment of the deposit and should not be interpreted as complete dissolution of calcium carbonate; quantitative separation of these two contributions was beyond the scope of the present study. In the porous medium, the increase in permeability observed in the linear models (Figure 4) suggests that, at the applied injection volumes, the detached particles were displaced by the flow without causing additional pore plugging.

The results obtained show that well productivity can be increased by treating the carbonate deposits contaminated with heavy hydrocarbon compounds in the bottomhole zone with a 0.05% aqueous sulfanol solution followed by a 4% ammonium chloride solution. Tests of the developed technology were carried out in a well of the Surakhani field, which is more aggressive in terms of salt deposition. For this purpose, well No. 1614, operated with a centrifugal electric submersible pump (ESP), was selected. When choosing well No. 1614, it was taken into account that, since the submersible pump discharges into the filter section, the reagents injected into the bottomhole zone would also act on the salt crystals deposited on the pump equipment.

The hydrogeochemical characteristics of the waters of the Surakhani field vary significantly across a wide interval of the layers. The waters of the Absheron stratum belong to the COD KX type, their mineralization varies between 119.3–159.6 g/l. The concentration of $\text{Na}^+ + \text{K}^+$ and Cl^- ions, which constitute the primary salt composition, is 36.0–49.0 and 74.7–99.1 g/l, respectively. In the waters, Ca^{2+}

and Mg^{2+} ions rank second after $\text{Na}^+ + \text{K}^+$ and Cl^- ions with concentrations 3.8–8.3 and 2.1–4.4 g/l, respectively. SO_4^{2-} and $\text{HCO}_3^- + \text{CO}_3^{2-}$ ions are in the minority, not exceeding 0.5 g/l. The waters have high hardness, their secondary salinity (S_2) is 18.60–25.78 %-eq, while their secondary alkalinity (A_2) does not exceed 0.24 %-eq. The $r\text{Na}/r\text{Cl}$ ratio varies between 0.74–0.11. The waters distributed in the Surakhani, Sabunchu, and Balakhani layers of the upper branch of the productive layer have high hardness. However, the hardness gradually decreases with increasing depth. The waters of the Surakhani layer are of the KX type with mineralization of 97.1–162.3 g/l. The most highly mineralized waters occur in the A, AB, and B horizons of the Surakhani layer. The mineralization of these waters varies between 152.9–160.4; 140.2–162.3 and 133.4–157.7 g/l, respectively. The content of $\text{Na}^+ + \text{K}^+$ and Cl^- ions, which are the main components of the salt composition, ranges from 33.0–51.3 and 59.4–101.4 g/l, respectively. The concentration of Ca^{2+} and Mg^{2+} ions varies between 1.4–7.1 and 0.7–5.3 g/l. The SO_4^{2-} ion is encountered only rarely, in concentrations not exceeding 0.4 g/l. The concentration of $\text{HCO}_3^- + \text{CO}_3^{2-}$ ions is minimal and mainly varies between 0.0–0.9 g/l, in rare cases this limit reaches 0.6–1.0 g/l, primarily in the waters of the D, CD, IV and V horizons. The secondary salinity (S_2) of these waters varied between 8.40 and 28.60 %-eq, and their secondary alkalinity (A_2) varied between 0.08 and 0.84 %-eq. These formation waters, characterized by a very high salinity, precipitate intensively as pressure and temperature change. Since the formation has been in operation for a long time, a “lithological window” has developed. They mix with the waters filtering through this “lithological window” further accelerating the precipitation process. Although $\text{HCO}_3^- + \text{CO}_3^{2-}$ ions are minor components of these waters, their high Ca^{2+} content makes the carbonate equilibrium sensitive to CO_2 release as the pressure decreases, which favours CaCO_3 precipitation in the bottomhole zone and on the pump equipment. This is consistent with the intensive salt precipitation reported for the wells of the Surakhani field (Ibrahimov and Latifov, 2018); well No. 1614 was therefore considered a suitable candidate for the treatment of carbonate deposits. Since the ESP discharges directly into the filter section, it is not removed from the well during the technological process. Initially, 1.5 m³ of 0.05% sulfanol solution was injected into the annular space, followed by 1.5 m³ of 4% ammonium chloride solution. The solutions were then displaced into the formation with a displacement fluid and kept there for a period of 4 hours. The 4-hour soaking period is shorter than the time required for almost complete removal of the deposit under static laboratory conditions (Table 3). However, approximately three quarters of the deposit mass is removed within this period even in the static test, and after the well is brought back into operation, the weakened residual deposit is additionally removed by the produced fluid flow.

After the well was put into operation, oil production increased from 3.1 t/day to 4.2 t/day. The workover cycle was extended from 42 to 78 days. Thus, the oil production rate increased by about 35%, and the workover cycle was extended by

a factor of 1.86. Under otherwise equal conditions, this corresponds to a reduction in the number of workovers from about 8.7 to 4.7 per year, which, in addition to the increase in oil production, reduces the costs of well servicing and the production losses associated with well downtime. The results demonstrate that the proposed method can effectively enhance production in the oil fields of Azerbaijan where carbonate scaling complicated by heavy hydrocarbon deposits is encountered.

The results obtained make it possible to formulate recommendations for the application of the technology. Candidate wells should be selected on the basis of an analysis of the composition of the produced water and, where possible, of the deposits removed from the well or from the pump equipment. The technology is advisable for wells in which carbonate deposits predominate and are contaminated with heavy hydrocarbon compounds and in which the produced water has a high Ca^{2+} content and a tendency towards carbonate precipitation as the pressure decreases. The presence of significant amounts of sulfate (gypsum, barite) or halite deposits is a contraindication, since such deposits are not removed by the proposed composition.

The treatment includes the sequential injection of the sulfanol solution, which hydrophilizes the surface of the deposits, and the ammonium chloride solution, followed by their displacement into the formation and a soaking period. In accordance with the results of the filtration experiments (Figure 4), the volume of the treatment fluid should be not less than the pore volume of the zone to be treated, which can be estimated as

$$V = \pi(R^2 - r_w^2)h\varphi, \quad (9)$$

where R is the radius of the treated zone, m; r_w is the well radius, m; h is the thickness of the treated interval, m; φ is the formation porosity, fraction. When the distribution of the deposits in the treated zone is uncertain, the volume can be increased to about 1.5 pore volumes; a larger increase is not justified, since it yields only a small additional gain in permeability. The soaking time should be selected on the basis of the deposit removal kinetics (Table 3); for the conditions considered, a period of about 4 hours was sufficient. Since the detached fragments of the deposit are carried out with the produced fluid, it is advisable to monitor the content of mechanical impurities in the produced fluid and the operating parameters of the pump after the well is brought back into operation.

Being a weakly acidic medium ($\text{pH} \approx 4.7$), the proposed composition can be expected to be considerably less corrosive to tubing and pump equipment than hydrochloric acid, which makes it possible to perform the treatment without pulling the electric submersible pump, as was done in well No. 1614. At the same time, the method has certain limitations. First, it is intended only for carbonate deposits. Second, thick asphaltene–resin–paraffin deposits may require preliminary treatment with a hydrocarbon solvent, since the sulfanol solution is

effective mainly against relatively thin hydrocarbon films. Third, the laboratory experiments were carried out under static conditions; the effects of temperature, pressure and flow on the removal kinetics, as well as the quantitative contributions of dissolution and detachment, should be determined in further studies, including dynamic core-flood tests and the determination of the Ca^{2+} concentration in the spent solutions.

Conclusion.

1. The factors affecting well productivity and the efficiency of various stimulation methods in the near-wellbore zone were analyzed.

2. The negative impact of salt deposits accumulated in the near-wellbore zone and on downhole equipment was examined, and the mechanism of carbonate scale formation was considered.

3. The need to hydrophilize the hydrophobic surface of the deposits before the main treatment was substantiated: a 0.05% aqueous sulfanol solution removes 98.0% of the oil film from the surface of carbonate deposits.

4. It was determined that sequential treatment with a 0.05% aqueous sulfanol solution and a 4% ammonium chloride solution can enhance well productivity by removing carbonate deposits contaminated with heavy hydrocarbon compounds from the bottomhole zone and downhole equipment. According to the proposed mechanism, the removal is achieved mainly through partial dissolution and detachment of the deposit rather than through its complete dissolution.

5. Under static laboratory conditions, the 4% ammonium chloride solution removes 96.7% of the deposit mass, and about three quarters of the deposit is removed within 4 hours. Injection of the treatment fluid in a volume equal to the pore volume increases the permeability of linear formation models fivefold, whereas a further increase in the injected volume yields only a small additional gain.

6. The field application of the method in well No. 1614 of the Surakhani field, performed without pulling the electric submersible pump, increased the oil production rate from 3.1 to 4.2 t/day and extended the workover cycle from 42 to 78 days.

7. The proposed method is intended for carbonate deposits; it is not applicable to sulfate (gypsum, barite), siliceous and halite deposits, which require other treatment approaches.

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