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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

DEVELOPMENT AND APPLICATION OF NANOSYSTEMS THAT PREVENT COMPLICATIONS TO IMPROVE THE EFFICIENCY OF OIL FIELD EXPLOITATION

Speciality: 2526.01 – "Technology for development of offshore fields"

Field of science: Technical sciences

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The work was performed at "OilGasScientificResearchProject" Institute of State Oil Company of Azerbaijan Republic.

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AZƏRBAYCAN RESPUBLİKASI ELM VƏ TƏHSİL NAZİRLİYİ "AZƏRBAYCAN DÖVLƏT NEFT VƏ SƏNAYE UNİVERSİTETİ" PUBLİK HÜQUQİ ŞƏXS

GENERAL DESCRIPTION OF THE WORK

The actuality of the subject and degree of development. In the process of development and operation of offshore oil and gas fields in the country, a number of technological, economic and environmental problems arise, ultimately resulting in a sharp reduction of the coefficient of oil and gas production, and complications are noticed in the well bottomhole zone. The process of salt deposition (scale formation), which is one of the characteristic complications for under long-term depletion, is one of the problems that seriously prevent the efficient operation of the well. Resting upon the analysis of subsequent salt deposition, due to chemical and mechanical erosion of subsurface and mining equipment significant losses make it urgent to develop new technological and geological approaches.

The flow rate of the well is, in the meantime, reduced, as asphaltene-resin-paraffin (ARP) depositions, formed during the filtration of non-Newtonian oil from the fields in the porous areas and the bottomhole zone drastically derceaeses permeability in wells. It is a fact that the reservoirs, which are part of our fields, are mainly composed of clay rocks inclined to swelling, which in turn, have a negative impact on the filtration process, that complicates the recovery process, finally making the development of advanced solutions and methods urgent. One of the typical complications for our rich hydrocarbons is the violation of the integrity of the bottomhole zone. It is especially important to develop nanoframe technology, which reflects a new scientific-practical approach, as in most cases the productive layer is deformed, or completely destructed.

Despite the fact that sufficient research has been done to combat these complications, the development of new components remains relevant. The dissertation is devoted to the elimination of complications in oil production through the development and application of nanotechnologies from a series of innovative technologies, as well as nanosystems based on fullerene, graphene, taunite and metal nanoparticles.

The object and subject of the research. Development, research and application of nanosystems preventing complications in oil production.

Purpose and tasks of research. It consists of the development and application of anti-complication nanosystems to increase the efficiency of oil field exploıtatıon.

Research methods. The issues were resolved through the implementation of complex experimental and analytical research, the results were applied in the field.

The main provisions submitted to the defense:

- Nanostructured compositions against salt deposition;
- Fullerene, graphene, taunite nanosystems against complications during operation;
- Nano-compositions in order to increase the permeability of the well bottomhole zone;
- Nanosystem for the recovery of swollen clay rocks and ensuring its stability;
- Nanoframe technology that consolidates the well bottomhole zone.

Scientific novelty of the study:

- A nanosystem has been developed to prevent salt deposition in the well-formation system and mining equipment;
- A new generation nanosystems have been proposed that prevent complications arising in the exploitation process based on fullerene, graphene, taunite nanoparticles;
- A high-resolution nanosystem has been developed that allows to increase the permeability of the well bottomhole zone contaminated with ARP sediments and reduce the swelling of the clays in the reservoirs;
- In order to consolidate the well bottomhole zone, nanoframe technology based on expanding portland cement has been proposed.

Theoretical and practical significance of the study. Nanosystems against the complications have been developed to increase the efficiency of oil field development through the implementation of complex experimental and analytical research. The developed nanosystems have been applied in field conditions.

Approbation and application.

The main provisions of the dissertation are reported:

- I International Scientific Conference of Young Scientists, Ganja, Azerbaijan, October 17-18, 2016;
- V International Conference "NANOTECHOİLGAS-2016", Moscow, Russia, November 22-23, 2016;
- IV International Scientific Conference of Young Researchers" dedicated to the 97th anniversary of the National Leader of Azerbaijan H.Aliyev, Baku, Azerbaijan, 2020;
- International scientific-technical conference on "Prospects of innovative development of technical and natural sciences", Baku, Azerbaijan, November 25-26, 2021;
- The XXII International Scientific Symposium "Turkic World between East and West", Andijan, Uzbekistan, 2022.

The results of the dissertation were published in 17 scientific works, including 10 articles, 5 conference materials, 1 monograph and 1 patent.

Developed nanosystems have been applied in field conditions.

The nanosystem which against salt deposition (scale formation) was applied in well No. 2946 located in OGPP No. 2 of “Bibiheybatneft” OGPD. As a result of the application of the nanosystem, there was no complication resulting from scaling for 147 days and the daily oil production of the well increased from 0.7 tons to 1.0 tons.

The nanosystem, which allows to increase the permeability of the well bottomhole zone by clearing it of ARP sediments, was applied in well No. 1331 located on the site No. 1146 of the “Palchig Pilpilasi” field of the “Oil Rocks” OGPD. After the application of the nanosystem, which increases the impact on the well bottomhole zone of the low-permeability clay layer, no complications were recorded and 482 tons of additional oil was produced for one year.

The nanosystem developed to recovery the swollen clay rocks and ensure its stability was applied in well 1282 of the “Palchig Pilpilasi” field of the “Oil Rocks” OGPD. After the application of the nanosystem, no complications were observed and an increase in production of more than 1.25 times was observed.

The name of the organization where the dissertation work was performed. The work was performed at "OilGasScientificResearchProject" Institute of State Oil Company of Azerbaijan Republic.

The total volume of the dissertation with a sign, indicating the volume of the structural units of the dissertation separately. The dissertation work consists of an introduction, three chapters, a conclusion, a list of references and appendices. The total volume of the dissertation work is 202196 characters (introduction – 10289 characters, first chapter – 36295 characters, second chapter – 128010 characters, third chapter – 25331 characters, conclusion – 2271 characters), excluding 18 figures, 16 graphs, 21 tables, 140 bibliographies and appendices.

THE MAIN CONTENT OF THE WORK

In the introduction, the main provisions of the dissertation are given, the relevance of the topic of the dissertation is substantiated, and the scientific innovations of the work are explained.

The first chapter is devoted to the analysis of the current state of complications during the development of oil fields and the justification of research. The first chapter consists of four paragraphs, and the first paragraph examines the problem of salt deposition (scale formation) in oil production and the analysis of its causes. The second paragraph provides an analysis of the current state of research work to eliminate the complications caused by salt deposition in oil production. Various methods, chemical agents used to prevent salt deposition and their impact mechanism are described. The third paragraph analyzes the factors affecting the permeability of the well bottomhole zone and methods of preventing them. Methods for recovering the initial permeability of the well bottomhole zone with the prevention of asphaltene-resin-paraffin deposits and their effectiveness are explained. The principles of methodological approach to research have been developed based on the analysis of the work carried out in the areas mentioned in the fourth paragraph.

Thus, as a result of the conducted analysis, it was determined that, currently despite a sufficient amount of scientific research being conducted for the purpose of salt deposition control and cleaning the well bottomhole zone from asphaltene-resin-paraffin deposits to build up its initial permeability, the effectiveness and technological feasibility of the methods used are not able to fully eliminate the problem in the oil industry, so the development of a new composition and method remains highly relevant. The aim of the research is the development and application of nanosystems for prevention of complication in oil production.

The second chapter is devoted to the development of nanosystems against the complications of oil production. In the first paragraph of the second chapter, the initial components for the development of nanosystems against salt deposition were selected and substantiated [2, 3].

Initially, changes in the interfacial surface tension of solutions of different concentrations of Sulfanol, sodium tripolyphosphate, Alkan DE-202 B, Laprol 3603 and Laprol 4202 surface-active substances (SAS) were studied. Alkane DE-202 B and Laprol 4202 were found to have approximately the same surface activity. Sulfanol and sodium tripolyphosphate have higher activity on the interfacial surface. According to the results of the research, in the following studies mainly used Sulfanol and Alkan DE-202 B, as well as Laprol 4202 chemical agents.

The study of Sulfanol and Alkan DE-202 B reagents, as well as their compositions in different proportions, was carried out by titrimetric method to prevent the process of salt deposition [[1]]. It was found that the protective effect of Alkan DE-202 B chemical agent against salt deposition at consumption of 50 g/t, 150 g/t and 250 g/t is 27.3%, 32.8% and 36.4%, respectively. The protective effect of

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[1] Калюкова, Е.Н. Титриметрические методы анализа / Е.Н.Калюкова. - Ульяновск: УлГТУ, - 2008. - 108 с.

Sulfanol against salt deposition at the specified consumption limits was 50.1%, 52.0% and 55.3%, respectively. The study of the compositions of these agents in different proportions revealed that their protective effect against salt deposition is higher. Thus, at a consumption of 150 g/t, the protective effect of Sulfanol and Alkan DE-202 B reagents from salt deposition in a 1:1 mass ratio is 55.7%, while in the 1:3 and 3:1 mass ratios of these surface-active substances, the scaling respectively 54.0% and 60.1% are prevented. A similar pattern is observed in other consumptions. The analysis of the results shows that the protective effect against salt deposition observed in different proportions and consumption of agents is higher than the additive sum of agents at that concentration, in other words, the combined use of these chemicals provides a synergistic effect. It should be noted that the protective effect against salt deposition of Sulfanol and Alkan DE-202 B surface-active substances in a 3:1 mass ratio is higher.

It was proposed to develop inhibitors on the basis of new innovative technologies - nanotechnology, for the elimination of complications associated with the salt deposition in oil production [2, 3, 4]. For this purpose, the impact of nanoparticles on the change of surface tension of aqueous solutions of surface-active substances was studied for the first time. Initially, Alkan DE-202 B was used to change the surface tension of solutions with low density of non-ionic surface-active substances at different concentrations 50-70 nm aluminium, 60-80 nm copper and 90-110 nm iron nanoparticles and effects were studied. Thus, the reduction of surface tension due to the action of nanoparticles of aluminium, copper and

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2 Мирзаджанзаде, А.Х., Магеррамов, А.М., Нагиев, Ф.Б. О разработке нанотехнологии в нефтедобыче // Азербайджанское Нефтяное Хозяйство, - Баку: - 2005. №10, - с. 51-65.

3 Шахбазов, Э.К. Нанотехнологии в нефтяной промышленности /Э.К.Шахбазов. – Баку: ГНКАР, - 2012.- 231с.

4 Кирчанов, В.С. Наноматериалы и нанотехнологии: учебное пособие / В.С.Кирчанов. – Пермь: Издательство Пермского национального исследовательского политехнического университета, - 2016. – 193 с.

iron in small concentrations (0.0005÷0.01%) in 0.0078% aqueous solutions of the agent Alkan DE-202 B is 38.5-48.0%, 36.0-46.5% and 33.5-44.0%, respectively. Reduction of surface tension due to the action of nanoparticles of aluminium, copper and iron at specified concentrations in 0.0156% of aqueous solutions of this surface-active substances was 28.6-40.3%, 24.7-38.3% and 25.3-35.1%. Finally, the reduction of surface tension in solutions due to the action of nanoparticles in small concentrations on the reagent Alkan DE-202 B with a concentration of 0.0625% was 8.7-33.0%, 6.1-30.4% and 4.3-27.8%, respectively. Thus, the results of the reduction of interfacial surface tension due to the action of copper nanoparticles with a size 60-80 nm in small concentrations are presented in Figure 1. It should be noted that when exposed to the solution of the agent Alkan DE-202 B at a different concentration at a concentration of 0.001% copper nanoparticles of size 60-80 nm, the surface tension is significantly lower than other concentrations. Starting with the concentration of nanoparticles 0.005%, when exposed to surface-active substances, there is a partial increase in surface tension. However, in all cases, the action of nanoparticles in the concentrations indicated in the solution of SAS reduces the surface tension by comparison with the resulting solution. The analog picture is preserved when exposed to this non-ionic surface-active substance nanoparticles of aluminium of size 50-70 nm and iron of size 90-110 nm.

In the next stage of the study, in a similar manner, the effect of aluminium, copper and iron nanoparticles on the surface tension of aqueous solutions of Sulfanol of ionic surface-active substance was considered. For 50-70 nm aluminium nanoparticles, the reduction in surface tension depending on the concentration averaged 38.0-66.7%, while for 60-80 nm copper nanoparticles it was 36.4-62.8%. The reduction of surface tension due to iron nanoparticles of 90-110 nm was 28.7-51.8% on average.

Based on the obtained statistical data, it was determined that the studied metal nanoparticles have the ability to reduce the surface tension of the Sulfanol solution and have an effective impact at concentrations of 0.0005-0.001%. The addition of a metal nanoparticle at a concentration of 0.005% partially increases the surface tension, and the addition of 0.01% significantly increases the surface tension. Even if there is an increase, the value of the surface tension is quite less than the value of the surface tension of SAS solutions without metal nanoparticles. Therefore, it can be concluded that metal nanoparticles affect surface events based on synergistic principles with surface-active substance solutions.

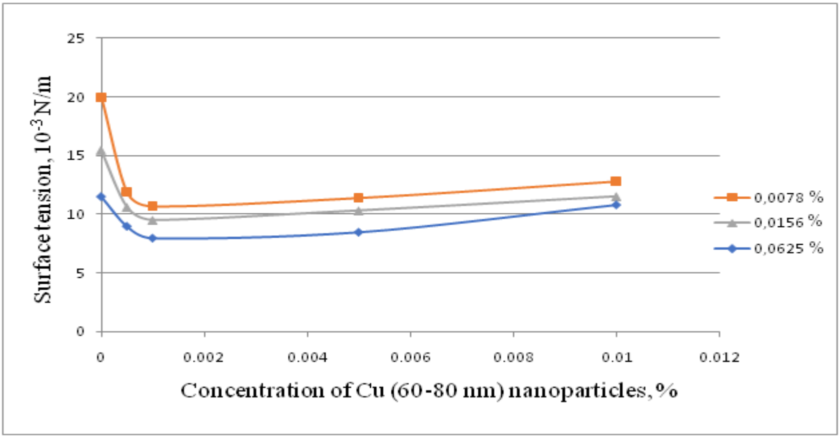

Figure 1. The effect of copper nanoparticles (60-80 nm) of low density on the surface tension of Alkan DE-202 B reagent of different densities

Considering that the metal nanoparticles significantly reduce the surface tension at concentrations of 0.001% and 0.005%, in the next stage of research, the effect of copper nanoparticles of 60-80 nm in the mentioned concentrations on Sulfanol solutions of different concentrations was studied and the obtained results are reflected in Table 1.

As can be seen from Table 1, as the concentration of the aqueous solution of Sulfanol increases, the intensity of the decrease in surface tension due to the effect of metal nanoparticles decreases. Thus, if the surface tension was reduced by 62.8% due to the effect of 0.001% copper nanoparticle on the 0.0078% Sulfanol solution, this indicator was obtained 19.4% for the 1.0% Sulfanol solution.

A similar regularity is observed in the reduction of surface tension as a result of the effect of 0.005% 60-80 nm copper nanoparticle on Sulfanol solution of different concentrations (0.0078-1.0%).

Table 1

Dependence of the reduction degree of surface tension of Sulfanol on the concentration of copper nanoparticles with a size of 60-80 nm

The concentration of Sulfanol in the solution, % weight	The reduction degree of the surface tension of the composition at the concentration of copper nanoparticles with a size of 60-80 nm (% by weight), Δσ, %	
	0.001	0.005
0.0078	62.8	56.7
0.0156	54.8	51.2
0.0625	45.7	40.3
0.125	37.5	32.5
0.25	30.8	23.1
0.5	20.6	14.7
1.0	19.4	12.9

Given the fact that copper nanoparticles increase the activity of surface-active substances and have antibacterial effects, the effect of the studied surface-active substance (SAS) samples on the salt deposition of nanoSAS systems formed by these nanoparticles was studied. Sulfanol, NanoSAS systems with the addition of 60-80 nm copper nanoparticles with 0.0005–0.001% concentration to the composition of Sulfanol and Alkan DE-202 B in a 3:1 mass ratio were developed. The consumption of these nanoSAS systems has been varied to 50–500 g/t to prevent salt deposition. As a result of against salt deposition study of the developed systems, it was determined that in all cases the presence of nanoparticles in the reagent leads to an increase in the activity of the system. Thus, if the protective effect from salt depositions of Sulfanol at the consumption of 250 g/t and 500 g/t is 55.0% and 58.7%, respectively, while the use of the nanoSAS system containing 0.0005% Cu-nanoparticles at the same consumption the effeciency was observed 58.2% and 63.0%, respectively. When the amount of nanoparticles in the nanoSAS system consisting of Sulfanol and copper nanoparticles was doubled to 0.001%, its protective effect against salt deposition at the rate of consumption of 250 g/t was 60.9%. At the consumption of 250 g/t the nanoSAS system formed by Sulfanol and Alkan DE-202B reagents in a 3:1 mass ratio with a 0.001% concentration of 60-80 nm copper nanoparticles had a higher protective effect against salt deposition than the composition without nanoparticles (72.4 %).

Thus, as a result of the research, it was found that the nanoSAS system formed by the copper nanoparticle with SAS prevents salt deposition more effectively than the system without nanoparticles. The essence of the proposed nanoSAS technology is that the used metal nanoparticles have a large surface area, large surface energy and high activity. NanoSAS solutions created due to the addition of nanoparticles can be considered economically advantageous, in addition to having the high potential to impact. Thus, the concentration of metal nanoparticles that was used is small, and the range of effect is large. As a result, the reduction in consumption of used surface-active substances attracts attention. These obtained synergistic effects confirm the necessity of using nanoSAS technology in salt deposition control measures.

In the second paragraph of the second chapter, the selection of the optimal compositions of nanosystems developed against salt deposition was carried out [1]. Studies have shown that although metal nanoparticles have high surface active properties, they do not affect the surface tension of water. That is why the selection of a carrier medium for the transfer of metal nanoparticles to the object of study was important. An aqueous solution of sodium carboxymethyl cellulose (Na-CMS) with a degree of polymerization of 350 has been proposed as a carrier medium. Na-CMS increases the viscosity of the solution when dissolved in water, thus ensuring the distribution of copper nanoparticles in the system and the stability of the system. As a result of the research, it was determined that regardless of the amount of Na-CMS in the formation water, its effect on salt deposition has not been determined.

Hydrochloric acid, which is inhibited as an acid, has been added to the nanosystem designed to prevent salt deposition in order to affect carbonate and hydrocarbonate ions.

Numerous experiments have been conducted to determine the optimal composition of the nanosystem against salt deposition. The protective effect against salt deposition was studied with the additions of Alkan DE-202 B demulsifier in the range of 0.1%, Sulfanol in 0.3%, Na-CMS polymer in the range of 0.2-1.2%, inhibited hydrochloric acid in 0.1-0.3% concentration and copper nanoparticles with a size 60-80 nm in the range of 0.0005-0.005%. The results of numerous studies are presented in Table 2.

It should be noted that the protective effect against salt deposition was found to be in the range of 70.0-92.3%. The greatest protective effect of the agent at a consumption of 100 g/t is characteristic of two components:

First composition: 0.1% Alkan DE-202 B + 0.3% Sulfanol + 0.4% Na-CMS + 0.3% inhibited hydrochloric acid + 0.005% copper nanoparticles with a size of 60-80 nm and the rest is water;

Second Composition: 0.1% Alkan DE-202 B + 0.3% Sulfanol + 0.4% Na-CMS + 0.3% inhibited hydrochloric acid + 0.001% copper nanoparticles with a size of 60-80 nm and the rest is water.

For comparison, the protective effect against salt deposition of first and second compositions at a consumption of 100 g/t is 83.0% and 84.1%, respectively. The protective effect against salt deposition for the consumption of 150 g/t and 250 g/t of the second composition was 87.2% and 92.3%, respectively.

Thus, the optimal composition of the nanosystem, which allows to prevent salt deposition, is 0.1% non-ionic SAS, 0.3% ionic SAS, 0.4% Na-CMS, 0.3% inhibited hydrochloric acid, 0.001% copper nanoparticles with a size 60-80 nm and the rest is water. The composition contains Alkan DE-202 B as a non-ionic SAS, Sulfanol as an ionic SAS.

Table 2

Determination of the optimal composition of nanosystems preventing salt deposition

No	Contents of the reagent samples, %						Reagent consumption, g/t	Protective effect against salt deposition, %
	Alkan DE-202 B	Sulfanol	Na-CMS	Inhibited hydrochloric acid	Cu-nanoparticles with a size of 60-80 nm	Water		
1	0.1	0.3	0.2	0.1	0.0005	up to 100 %	100	70.0
2	0.1	0.3	0.4	0.1	0.0005		100	70.0
3	0.1	0.3	0.5	0.1	0.0005		100	70.0
4	0.1	0.3	0.8	0.1	0.0005		100	70.0
5	0.1	0.3	1.0	0.1	0.0005		100	70.0
6	0.1	0.3	1.2	0.1	0.0005		100	70.0
7	0.1	0.3	0.4	0.05	0.0005		100	66.4
8	0.1	0.3	0.4	0.2	0.0005		100	75.2
9	0.1	0.3	0.4	0.3	-		100	75.8
10	0.1	0.3	0.4	0.3	0.0005		100	80.3
11	0.1	0.3	0.4	0.3	0.001		100	84.1
12	0.1	0.3	0.4	0.3	0.005		100	83.0
13	0.1	0.3	0.4	0.3	0.001		50	76.3
14	0.1	0.3	0.4	0.3	0.001		150	87.2
15	0.1	0.3	0.4	0.3	0.001		250	92.3

It should be noted that the removal of salt deposits in formation water takes place in several stages. In the first period, nanosized crystals, which play the role of crystallization centers, and then microparticles are formed. Over time, these particles grow by association and accumulate on the surface of the equipment.

Nanoparticles added to the system in the composition of the complex reagent play the role of multiple crystallization centers, ensuring mass production of small nanosized salt crystals. The surface of the crystals formed as a result of the presence of surfactants in the used nanosystem is isolated by SAS molecules and the growth of the crystals together is prevented, small salt crystals are removed from the system by means of liquid flow.

Thus, the used nanosystem isolate the surface of the formed salt crystals and prevent their agglomeration, and the small-sized salt crystals are removed from the system through the liquid flow.

The third paragraph of the second chapter discusses the development and research of new generation nanosystems against salt deposition. Graphene, taunite and fullerene nanoparticles were used for this purpose. Initially, the protective effect against salt deposition of the composition of Sulfanol and Alkan DE-202 B reagents in a 3:1 mass ratio based on graphene, taunite, fullerene, carbon-based nanoparticles with a concentration of 0.001% for the consumption of 50 g/t and 100 g/t was studied. The protective effect against salt deposition of graphene, taunite and fullerene-based nanoSAS systems at 50 g/t is 58.8%, 59.8% and 61.3%, respectively; at 100 g/t consumption, the results were 63.9%, 64.5% and 66.4%, respectively. The protective effect against salt deposition of the composition of Sulfanol and Alkan DE-202 B SAS in a 3:1 mass ratio at a consumption of 50 g/t and 100 g/t is 48.0% and 55.3%, respectively. Analysis of the preliminary results shows that the protective effect against salt deposition of graphene and taunite-based nanoSAS systems is approximately the same, while in general, the protective effect against salt deposition of fullerene-containing nanoSAS systems is higher than others [6].

Studies have been carried out to determine the optimal composition of nanosystems against salt deposition based on graphene, taunite and fullerene. It is established that the nanoparticles on the basis of carbon are evenly distributed in the system at concentrations of 0.0005-0.001% and do not fall into the sediment over a specified period of time. Due to the small size of these nanoparticles, the surface area is large and they have a high protective effect against salt deposition. The protective effect against salt deposition of nanoparticles on the basis of carbon at concentrations of 0.0005% and 0.001% in the nanosystem is about the same. But the protective effect against salt deposition at a concentration of 0.0005% is high with a slight difference.

It was determined that when the amount of Na-CMS in the nanosystem exceeds the range of 0.4÷1.0%, it causes excess consumption of the composition and high viscosity of the solution. During the development of new generation nanosystems, it was noted that inhibited hydrochloric acid in the amount of 0.05-0.2% is more effective against salt deposition.

Thus, the optimal composition of the new generation nanosystem against salt deposition is 0.1% of non-ionic SAS, 0.3% of ionic SAS, 0.4-1.0% of Na-CMS, 0.05-0.2% of inhibited hydrochloric acid, 0005-0,001% of carbon-containing nanoparticles, such as graphene, or taunite or fullerene, and the rest is water. The composition contains Sulfanol as a non-ionic SAS, Laprol 4202 or Alkan DE-202 B as an ionic SAS. The analysis of the results shows that the presence of nanoparticles in the reagent in all cases leads to an increase in the activity of the system. Among these nanosystems, fullerene-containing nanosystem has a higher protective effect than others (92.8%) [14, 16].

The fourth paragraph of the second chapter deals with the development and study of the nanosystem that allows to increase the permeability of the bottomhole zone contaminated with ARP sediments [5, 11, 12]. Thus, organic solvents were initially selected and their effect was studied for the development of a nanosystem that allows to increase the permeability of the well bottomhole zone contaminated with ARP sediments. Condensate, kerosene, gasoline (80-180°C) diesel, and light pyrolysis resin were studied to select the primary component. The effect of the organic solvents used on the solubility of ARP sediments was determined by gravimetric method.

According to the results of studies conducted at different temperatures (20°C and 40°C), it can be said that the lowest effective organic solvent capable of dissolving ARP sediments was condensate. It should be noted that at 20°C and 40°C temperature the solution effiency of ARP sediments of condensate were respectively 1.11 % and 6.49 %. In contrast the most effective organic solvent capable of dissolving ARP sediments were diesel, and light pyrolysis resin. Thus, solution efficiency of ARP sediments of diesel and light pyrolysis resin at 20°C temperature accordingly were 21.49 % and 34.18 %. This indicators at 40°C temperature were 67.37 % and 78.85 %.

In order to increase the solubility of the solvents, a new system was obtained by adding SAS to its composition. Thus, Alkan DE-202 B demulsifier in the volume of 0.5-1.0% as SAS was added to each of condensate, kerosene, gasoline, diesel and light pyrolysis resin. The addition of high-efficiency SAS to the solvent not only increases its solubility, but also facilitates the penetration of the reagent into the micro-pores of the rock. It was found that in all cases, the addition of SAS to the organic solvent increased the efficiency of the system in resolving ARP sediments. Treatment of light pyrolysis resin with SAS allowed to achieve the most satisfactory solution efficiency depending on temperature at both 0.5% and 1.0% SAS concentrations. In addition, as a result of the conducted experiments, it was determined, that the efficiency of the systems obtained by adding Laprol 4202 to organic solvents for dissolving ARP sediments is approximately the same as the efficiency of the systems obtained by adding Alkan DE-202 B reagent.

To increase the efficiency of the obtained organic solvent-SAS system, aluminium nanoparticles with a size of 50-70 nm in small concentrations were added to it. The effectiveness of aluminium nanoparticle-based nanosystems to dissolve ARP sediments was studied, and the obtained results are presented in Figure 2.

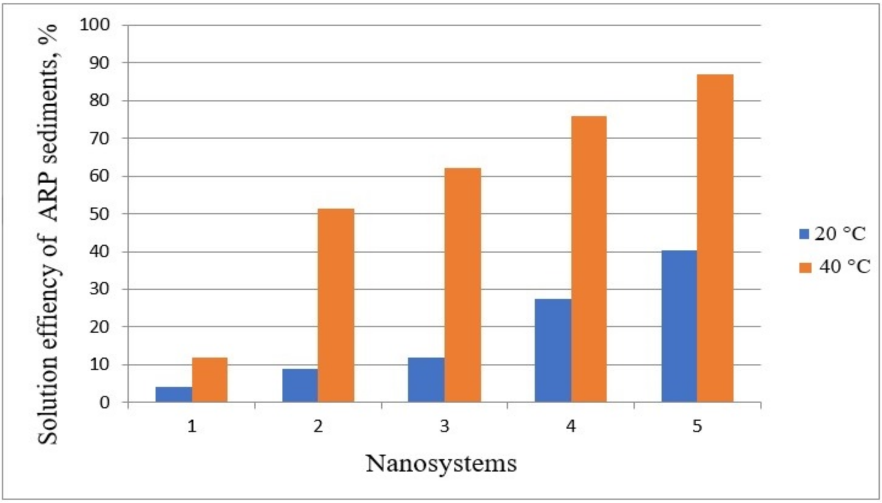

Figure 2. The solution efficiency of ARP sediments of the taken nanosystems at temperatures of 20°C and 40°C:
1–Condensate + 0.5 % SAS + 0.001 % Al (50-70 nm);
2–Kerosene + 0.5 % SAS + 0.001 % Al (50-70 nm);
3–Gasoline + 0.5 % SAS + 0.001 % Al (50-70 nm);
4–Diesel fuel + 0.5 % SAS + 0.001 % Al (50-70 nm);
5–Light pyrolysis resin + 0.5 % SAS + 0.001 % Al (50-70 nm).

As a result of the study of the developed nanosystems, it was determined that in all cases the presence of nanoparticles in the reagent leads to an increase in the activity of the nanosystem. However, nanosystem based on light pyrolysis resin, 0.5% SAS and 0.001% aluminium nanoparticles has the most effective ability to dissolve ARP sediments. Thus, if 40.25% solution efficiency was found at 20°C temperature, this indicator was 87.05% at 40°C temperature.

Thus, the optimal composition of the nanosystem, which allows to increase the permeability of the well bottomhole zone with a high solubility of ARP sediments, consists of 0.5% non-ionic SAS, 0.001 % aluminium nanoparticles with a size of 50-70 nm and the rest light pyrolysis resin. The composition contains Alkan DE-202 B or Laprol 4202 as a non-ionic SAS.

Taking into account the fact that the lithological composition of our deposits is composed of clay minerals, in the next stage of research, the swelling of clays in different dispersion media was determined. For this purpose, swelling of bentonite clay in fresh water, sea water, formation water, light pyrolysis resin, light pyrolysis resin in the medium of SAS addition and finally light pyrolysis resin in nanoSAS medium was studied. Studies conducted over a 24-hour period found that intense swelling persisted for the first 3-4 hours. This trend is particularly noticeable in fresh water, sea water and formation water environments. It was determined that the swelling of the formation water environment taken from the "Oil Rocks" OGPD was less than in the sea water and fresh water. Light pyrolysis resin with both SAS and nanoSAS has reduced the swelling of bentonite clay several times, which is one of the advantages of the proposed compositions. Thus, light pyrolysis resin, SAS and aluminium nanoparticle-based nanosystem does not create volume expansion without inflating clays in clay collectors and prevents the reduction of permeability. In addition, the transfer of the nanosystem to the well bottomhole zone ensures the development of this zone and, ultimately, dissolving of ARP sediments in the bottomhole zone [8].

The fifth paragraph of the second chapter considers the selection of a nanosystem to ensure the stability of clay rocks. The operation of the wells with low productivity makes it necessary to carry out measures to intensify the flow of oil, including increasing the permeability of the well bottomhole zone by processing it with a nanosystem (claystabilizer), and as a result, involving the oil reserves in the development.

The process of displacement of oil in the clay formation with water of different mineral content than the formation water, as well as the results of application of claystabilizer at the beginning and at a certain stage of the development, were studied. Treatment of the layer first with a claystabilizer leads to a sharp increase in the permeability of the layer. Then, the tendency of the permeability of the formation to decrease to its initial value is manifested, when the formation is exposed to low mineral water. It was determined, that the average conductivity of that zone increases proportionally with the increase in the amount of claystabilizer injected into the well bottomhole zone. Thus, the practical possibility of increasing the permeability of the formation to its original value after the injection of water with a lower minerality than the minerality of the formation water and treatment with a claystabilizer is identified.

It was found that after the application of nanosystem (claystabilizer), the effect of the process of displacement with low mineral water on the increase of oil flow rate and oil recovery factor is higher. Thus, low mineral water has a higher pH compared to formation water and the interfacial surface tension decreases.

Thus, the treatment of the clay-bearing layer with a claystabilizer after a certain period of development or at the final stage leads to the recovery of permeability and intensification of oil production. After treatment with claystabilizer, the technological parameters of the impact on the formation with low mineral water are characterized by higher values than with high mineral water [15].

The sixth paragraph of the second chapter is devoted to the development and study of nanoframe technology that allows to fix the well bottomhole zone [9, 10, 17]. Thus, the study of portland cements and their study in various nanoparticle environments, and ultimately the development of nanoframe technology with the required strength properties and permeability [[5]].

At the initial stage of research, RTM-75 brand portland cement mortar was prepared and studied. The density of portland cement mortar prepared in 0.5 "water-cement" factor and it was determined to be 1880 kg/m^3. To conduct a comparative analysis, PST-1-50 brand portland cement was also used, a cement mortar was prepared in that "water-cement" factor, and the density of this mortar was determined. So, this indicator was obtained 1840 kg/m^3.

Using the consistometer device, it was determined that the setting time for PST-1-50 brand portland cement is 4 hours 25

[5] Yusifzadeh Kh.B.Nanotechnologies in oil and gas well drilling / Kh.B.Yusifzadeh, E.G.Shahbazov, E.A.Kazimov,- Baku: Centralized topography of SOCAR, - 2014.- 176 p

minutes. This indicator was the same for expanding cement. As can be seen from these data, although in principle the same setting time was obtained, the densities of the solutions were obtained somewhat different.

The strength limit of cement stone made on the basis of RTM brand portland cement was determined and this indicator was compared with PST-1-50 brand portland cement. It was determined, that while the compressive strength limit for PST-1-50 brand portland cement stone was 6.4 MPa, this indicator was 7.9 MPa for expanding cement, which can be evaluated as another advantage of expanding portland cement.

Both PST-1-50 and RTM brand portland cement mortars were treated with aluminum nanoparticles with sizes of 50-70 nm and cement stone strength was measured. After the addition of nanoparticles, the strength of nanocement stone containing PST-1-50 decreased to 5.4 MPa, while in expanded portland cement, this decrease was observed very little, that is, to the limit of 7.6 MPa. As a result of the conducted research, it can be concluded, that the use of expanding portland cements in strengthening the well bottomhole zone can be considered more appropriate.

In the next stage of the experiments, a composition of the expanded portland cement mortar with fullerene in a 0.5 "water-cement" factor was prepared. The addition of 0.0035% fullerene practically did not affect the initial density (1880 kg/m^3) of the cement mortar. While the spread of RTM brand portland cement mortar without fullerene was 22.0 cm, the spread after fullerene addition was 21.5 cm. RTM expanded cement mortar set in 4 hours and 25 minutes. Due to the addition of fullerene, this indicator decreased by 15 minutes and was 4 hours and 10 minutes. While the strength of the sample without fullerene was 7.9 MPa, this indicator was 8.3 MPa after the addition of fullerene.

Subsequent experiments examined the combined effects of expanded portland cement with graphene. The addition of graphene slightly increased the density of the cement mortar and the density limit of 1885 kg/m^3 was achieved. The fluidity of graphene-treated portland cement mortar was measured in the AzNII cone and it was

23.0 cm. The setting time of graphene-treated portland cement mortar was 4 hours and 45 minutes. The compressive strength of graphene portland cement stone was 9.3 MPa. Thus, the increase in strength due to the addition of graphene can be considered as an advantage of graphene portland cement stone.

In other studies, the density, fluidity, and setting time of expanded portland cement mortar with the addition of taunite were determined and it was determined that these parameters remained practically constant.

The studies conducted with fullerene, graphene, taunite, as well as 50-70 nm aluminum nanoparticle additives have been systematized, and the results obtained according to the strength can be given as follows:

$$\sigma_{e.c.+graphene} > \sigma_{e.c.+fullerene} > \sigma_{e.c.+taunite} \geq \sigma_{e.c.} > \sigma_{e.c.+Al}$$

where $\sigma_{e.c.}$ - strength of expanded cement stone without additives, MPa;

$\sigma_{e.c.+graphene}$- strength of expanded cement stone with graphene addition, MPa;

$\sigma_{e.c.+fullerene}$- strength of expanded cement stone with the addition of fullerene, MPa;

$\sigma_{e.c.+taunite}$- strength of expanded cement stone with the addition of taunite, MPa;

$\sigma_{e.c.+Al}$- is the strength of the expanded cement stone with the addition of aluminium nanoparticles with a size of 50-70 nm, MPa.

The impacts on the strength of expanded portland cement in the co-modifications of nanoparticles such as fullerene, graphene, taunite with 50-70 nm aluminium metal nanoparticles were also studied by similar methods. As a result of the study, it was determined that there is no synergism of the above-mentioned nanosystems compared to the expanded portland cement stone. In other words, the resulting cement stones were found to be very brittle and not resistant to deformation.

Research was conducted to study the wettability of cube-shaped expanded cement samples without nanoparticles and with fullerene, graphene, taunite and 50-70 nm aluminium nanoparticles. The methodology of the study was that the masses of the cubes measuring 2x2x2 cm were defined, and then they were placed in a basin of solution filled with a special liquid. Saturated NaCl salt solution was placed in the liquid basin and the cement stones were soaked in this medium for 24 hours. It was determined that the sample with the best moisture absorption capacity consists of expanded portland cement and graphene nanoparticle (52.1%).

In the seventh paragraph of the second chapter, the study of the developed nanosystems on the basis of infrared spectroscopy method was considered [4, 7, 13]. Thus, infrared (IR) spectroscopy method from a series of analytical studies was used to assess the effects of nanosystems.

Nanosystems were studied by IR spectroscopy method on the Varian 640-IR FT-IR spectrometer. Initially, in different concentrations (0.001%, 0.005%, 0.01%, 0.05% and 0.1%) 50-70 nm aluminium, 60-80 nm copper and 90-110 nm iron nanoparticles were added to the 1.0% aqueous solution of Alkan DE-202 B and obtained these new nanoSAS systems were studied by IR spectroscopy method. It was found that at small concentration (0.001%) the intensities changed, at 0.005-0.1% concentrations new absorption bands appeared, and some disappeared. Destruction occurs when the concentration of aluminium nanoparticles exceeds 0.005%. A similar regularity was observed when 60-80 nm copper and 90-110 nm iron nanoparticles of different concentrations were exposed to a 1.0% Alkan DE-202 B solution.

IR spectroscopy study of new nanoSAS systems obtained with the addition of 50-70 nm aluminium nanoparticles at a concentration of 0.001÷0.1% to a 1.0% aqueous solution of Sulfanol reagent revealed that under the influence of aluminium nanoparticles at small concentrations (0.001% and 0.005%) nanostructuring, and at values of concentration greater than 0.005%, destruction is observed.

In subsequent studies, the effect of 60-80 nm copper nanoparticles in different concentrations (0.001%, 0.005% and 0.01

%) on a 1.0% aqueous solution of Na-CMS polymer with a degree of polymerization of 350 was studied. The formation of new absorption bands, the disappearance of some absorption bands and a decrease in intensity were observed as a result of the impact of copper nanoparticles at a concentration of 0.001% on a 1.0% Na-CMS solution. Under the influence of 60-80 nm copper nanoparticles at a concentration of 0.01% in the polymer solution, partial destruction of the structure was observed.

Thus, nanostructuring occurs in the system under the influence of nanoparticles in small concentrations, and destruction is observed at high concentrations.

The third chapter deals with the application and evaluation of the effectiveness of developed nanosystems. The first paragraph of the third chapter discusses the selection of wells for the application of the developed nanosystems. For this purpose, mining data containing the exploitation indicators of individual wells of different OGPDs were collected. So that, the interval between maintenance of wells, daily liquid (oil/water) production, physico-chemical parameters of oil and formation water, etc. indicators were analyzed.
Thus, based on the analysis of the collected mining data, well No. 2946, located at the "Bibiheybatneft" OGPD, for the application of the developed nanosystem against salt deposition, and for the mining tests of the nanosystem, which allows recovery the permeability of the well bottomhole zone by cleaning it from ARP sediments, is located in the “Oil Rocks” OGPD, located in the “Palchig pilpilasi” field well No. 1331, and well No. 1282, located in the “Palchig pilpilasi” field, was selected for the application of the developed nanosystem for recovery of swollen clay rocks and to ensure its stability.

The second paragraph of the third chapter examines the development of nanosystem manufacturing technology. Thus, the technological schemes that describes the techology of nanosystems preparation have been developed and interpreted.

The third paragraph of the third chapter examines the assessment of the economic benefits of the application. As a result of the application of the nanosystem that prevents scale formation, no complications were recorded during 147 days due to salt depositions, and the daily oil production increased from 0.7 tons to 1.0 tons. 482 tons of additional oil was produced within a year following the application of the nanosystem, which allows to increase the permeability of the well bottomhole zone contaminated with ARP sediments, in well No. 1331 of the "Palchig Pilpilasi" field of the "Oil Rocks" OGPD. After the application of the developed nanosystem to recovery the swollen clay rocks and ensure its stability in well No. 1282 of the "Palchig Pilpilasi" field, an increase of more than 1.25 times was observed.

Thus, as a result of the application of developed nanosystems, no complications were observed, the inter-repair period of the wells increased and additional oil production was achieved. These obtained results indicate that these developed nanosystems can be applied in other mining wells.

CONCLUSION

1. A nanosystem consisting of taken in different proportions surface-active substances, high-viscosity polymer, inhibited acid, copper nanoparticles with a size of 60-80 nm was developed against salt deposition process that occurs in the reservoir well system and field equipment. It has an efficiency of 80.3-92.3%, depending on the amount of agent consumed (100-250 g/t).

2. New generation nanosystems based on fullerene, graphene, and taunite nanoparticles have been developed, which allow preventing salt deposits in long-term operating fields. It was determined that these developed compositions have a protective effect against salt deposition of up to 92.8% at a consumption of 100 g/t, and the fullerene-based nanosystem shows a high efficiency compared to others.

3. In order to recovery the natural porosity and permeability of productive reservoirs made of clay rocks, a nanosystem consisting of organic solvents, surface-active substances, aluminium nanoparticles with a size of 50-70 nm has been developed and it is determined that it has an efficiency of up to 87.05%. The developed composition ensures the recovery of the initial permeability of the well bottomhole zone due to the cleaning of ARP sediments.

4. A method has been developed to ensure the stability of clay rocks and increase oil production by intensifying the development of oil reserves by applying a nano-based claystabilizer in the process of displacement of oil with water of a different mineral content than formation water.

5. Nanoframe technology containing expanded portland cement, various nanoparticles such as fullerene, graphene, taunite and is regulated on the basis of synergistic principles was developed, its properties of high permeability and strength properties were determined.

6. The developed nanosystem which against salt deposition was applied in well No. 2946 in “Bibiheybat” field, there was no complication associated with salt deposition within 147 days

following the application, and the oil production of the well was increased. The nanosystem, which allows to increase the permeability of the bottomhole zone contaminated with ARP sediments, was applied in well No. 1331 in the “Palchig pilpilasi” field. After the application of the nanosystem 482 tons of additional oil was produced for a period of one year. After the application of the developed nanosystem for the recovery of swollen clay rocks and its stability in the well No. 1282 of “Palchig pilpilasi” field, no complication was recorded and an increase of oil production more than 1.25 times was observed.

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The applicant's personal contribution

[3, 6, 11-13, 15-17] works were independently performed,

[1] statement of the problem, conducting research, calculating, and participating in the compilation of the article,

[2] conducting research, calculating, analyzing and summarizing the results, participating in the compilation of the monograph,

[4, 7, 8] statement of the problem, conducting research, analyzing and summarizing the results, participating in the compilation of the article,

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[14] conducting research and calculations, discussing of the results, summarizing, and participating in the compilation of the patent.

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