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## **ABSTRACT**

of the dissertation for the degree of Doctor of Philosophy

# DEVELOPMENT AND APPLICATION OF COMPLICATION CONTROL METHODS IN OIL PRODUCTION WITH THE USE OF NEW INNOVATIVE COMPOSITIONS

Specialty: 2525.01 – "Development and exploitation of oil

and gas fields"

Field of science: Technical sciences

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#### GENERAL FEATURES OF THE WORK

It is very important to develop suitable technologies for ensuring the normal operation of wells and well bore equipment during oil production.

Pumping water at the final stage of development of oil and gas fields leads to a deterioration in the filtration properties of the porous medium and a change in the properties of the formation fluids. A sharp increase in the amount of asphalt-resin-paraffin, saline deposit, corrosion products in the area around the well and in the well bore of the reservoir takes an intensive form. The deposition of components in the fluid in the surrounding area of the well leads to the inhomogeneity of the flow profiles of the operating wells and to the decrease in the receiving capacity and permeability of the injection wells. As a result of the formation of deposits in the area around the well and on the surface of the tubing the inner diameter of the lifting pipes becomes smaller, the current production of the wells is reduced or cut off.

Even though numerous works have been carried out in the direction of eliminating these complications that have arisen in the wellbore field, the problem is still relevant.

# The purpose and tasks of the research

The purpose of the research is to develop and apply new methods for eliminating the complication that arises in the flow of fluid from the formation to the bottom of the well, extraction and well service during the well kill.

The task of the research is to develop new methods using innovative compositions for complication control in oil production

# Research methods

The problems were solved through theoretical, laboratory research, mathematical calculation and mining research.

#### The main issues in the thesis defense

- 1. New methods of contamination control in the well-bottom area;
  - 2. New methods of complication control in the well bore **The academic novelty**

- 1. The method of restoring the permeability of the area around the well bottom of the reservoir has been developed
- 2. The method of isolating the water flow to the well has been developed;
  - 3. Inhibitor of asphalt-resin-paraffin has been developed;
- 4. The well kill method with a foamy gel-based composition has been developed.

# Theoretical and practical significance of research

New methods have been developed with the use of innovative compositions for complication control in oil production and have been effective as a result of their application in field conditions.

The method of restoring the permeability of the area around the bottom of the formation was tested in wells No. 610 and 664 at Absheronneft OGPD, and as a result of its application, additional 86 tons of oil was produced from the wells.

The method of isolation of water flow into the well was tested in operational wells No. 1347, 1858, 2651 of Neft Dashlari OGPD. As a result of the application, additional 60.7 tons of oil was produced from the wells.

Three Eurasian patents were obtained for the developed methods: Eurasian patent No. 041274 for the invention "well kill method";

Eurasian patent No. 042573 for the invention "Method of acid treatment of the bottom hole zone of the terrigenous heterogeneous formation"

Eurasian patent No. 043725 for the invention "Method of isolation of water flow in a well".

# Work approval

The main provisions of the thesis were discussed at the following international conferences:

VI International scientific-practical conference "Bulatovskie chteniya", Krasnodar, March 31, 2022;

International Scientific and Practical Conference «Heydar Aliyev and Azerbaijan Oil Strategy: Advances in Oil and Gas Geology and Geotechnologies», Baku, 23-26 May 2023;

10<sup>th</sup> Annual SPE Caspian Technical Conference and Exhibition, Baku, 21-23 November 2023.

Publications. The main content of the thesis is reflected in 13 scientific works, including 7 scientific articles, 3 proceedings of the conference and 3 inventions.

Structure and scope of work. The thesis is composed of an introduction, 3 chapters, conclusions and proposals, 217 a list of cited literature, 2 appendices, 16 figure and 8 table.

Chapter I - 139876, Chapter II - 61905, Chapter III - 22828 signs, total - 228182 signs of the dissertation thesis.

#### **BRIEF CONTENT**

In the introduction, the relevance, purpose and summary of the main issues of the thesis are given and the practical significance of the work is indicated.

The thesis work is devoted to the development of new methods and compositions in the reduction of permeability of rocks of the well bottom area during oil production, water cut, deposition of asphalt-resin-paraffin sediments in the content of well product in the well and in the well bore and elimination of complex formations arising during the use of kill fluid.

In the first item of the first chapter of the thesis, the classification of complications arising during oil production is considered.

As a result of the use of various methods of oil displacement at the final stage of field development, fluid injection, cooling of the reservoirs, deterioration of the filtration properties of the porous medium and changes in the properties of the formation fluids occur. Complications during the operation of wells can include ARP deposits, salts, mechanical mixtures of the well and equipment, a decrease in the permeability of the well rock, well flooding, corrosion of equipment, formation of high - viscosity emulsions, hydrate formation and high gas factor. Most of these processes ultimately lead to complications in the well performance, which leads to a decrease in production, premature failure of well bore and surface equipment.

In the second item of the first chapter of the thesis, the issues of restoring the permeability of the area around the well bottom of the reservoir were considered. In the process of drilling and developing wells, the state of the rock surrounding the well undergoes significant changes as a result of the penetration of relevant technical fluids into the wellbore area and pollution of this zone. During operation, the deposition of inorganic salt, asphalt-resin-paraffin, and the removal of poorly cemented rock particles due to rock deformation and disintegration also change the properties of the wellbore area.

There are a large number of methods for influencing the area around the well. These technologies are conditionally divided into mechanical, physical and chemical methods.

As a result of impacting the wellbore area with various chemical compositions, methods of restoring the permeability of the wellbore area are widely used. The most appropriate technology for restoring the permeability of the wellbore area when the pores of the productive formation are blocked by sediments with high molecular weight organic compounds is the method of treatment with acid solutions. Acid treatment of carbonate reservoirs leads to the formation of highly permeable channels. Due to the low reaction rate, organic acids and chelating reagents are used.

The formic, acetic, citric and lactic organic acids are manily used in the oil and gas industry due to their ability to provide various technical conditions of use. Organic acids are weaker than HCl, react more slowly with reservoir rocks, and are less corrosive to metals.

The works conducted in the direction of water shuttoff in oil wells were investigated in the third paragraph of the first chapter. Water cut is observed at a certain stage of well operation in most oil fields. Product dilution not only causes numerous economic problems for oil producers, but also affects the productivity of production wells and reduces their service life. On the other hand, additional water removal increases salt deposition, corrosion and damage to oil field facilities in general. Produced water separation, purification and utilization from production requires serious expenses.

Water shut-off in the formation and wells can be carried out by chemical methods. The measures taken provides to the conforming control of the injection wells and closing of water-flooded areas. The goal is to isolate water ingress by reduction of permeability and mobilize water for oil displacement. The efficiency is achieved by increasing the viscosity of the injected fluid using chemical reagents, compression and, as a result, water removal is prevented.

A new generation of thermotropic compositions based on titanium coagulant has been developed. The derived gels are superior to gels of similar composition in their structural and mechanical properties (viscosity and durability). The composition of the TK-2 reagent, which is used in procedures for increasing the coverage of water injection and leveling oil production profiles, is significantly (1.4-2.2 times) superior the compositions  $\Gamma A J K A$ -C,  $T E P M O \Gamma O C$  and P B-  $3 \Pi$ -1 MC, which are widely used in Western Siberia, at 70-98 °C formation temperatures, in structural and mechanical properties, and T K-4 composition is superior to its analogues for formations with temperatures below 60 °C.

One of the ways for solvution of the problem of water shutoff is the use of cement slurry based on synthetic resins, for example compositions based on urea-formaldehyde resin (UFR), which have a number of advantages, such as high adhesion and durability, easely prepared, low toxicity, low cost, and a rich raw material base. Laboratory studies have been conducted on the development and use of quick-setting cement slurry (QSCS) for 20-100 °C formation temperature, with a setting time ranging from 15 minutes to 8 hours, on the basis of the UFR. The rheological properties were studied and the formulation of the QSCS composition and hardener was selected. The practical application of QSCS together with the Alkaline Polymer-Clay-Silica System (APCSS) was carried out at the well of the Yuzhno-Okhteurskove field to eliminate water inflow; decrease in water cut, increase in oil production was achieved, and the well operated effectively for more than two years. Total conducted tests for water shutoff in two highly flooded wells by injecting RPM (Relative Permeability Modifier) microgels in one of Abu Dhabi offshore fields. Microgels (Powelgel<sup>TM</sup>) consist of polymer chains connected in part by an organic binder, which allows the creation of a three-dimensional system. Microgels are preferred to conventional polymer gels due to their superior salinity, slip and H<sub>2</sub>S resistance. Laboratory studies were conducted to select the optimal microgel size and obtain initial data

for modeling near the wellbore (microgel adsorption, permeability reduction, absorption). The first results showed that additional oil production by 15%, and decrease in well flooding by 1% was obtained in well No. 1.

The fourth paragraph of the first chapter is devoted to the investigation of works conducted in sedimentation control in oil production. The deposition of paraffins, asphaltenes, resins and salts in formations, production pipes and transport pipes is one of the main problems in ensuring flow in the oil and gas industry. At the well bottom, the paraffin components are in a liquid state under high temperatures, which become cool while rising to the surface and exit out of the well, which leads to paraffin sedimentation in the production pipes. Deposits significantly reduce well productivity, and this in turn requires the search for optimal methods to reduce deposition formation.

Paraffin deposits settle mainly in well pumps, pipelines, injection lines, and oil field collection points reservoirs. Paraffin settles on the inner surface of well pipes, tubings and transport pipelines decreasing the diameter of the useful part of the pipeline and this causes an increase in line pressure, hydraulic resistance, corrosion during injection and other additional costs during the operation and maintenance of energy resources and equipment.

The currently widely used mechanical and thermal methods for ARP deposits control are ineffective in most cases. Thus chemical reagents are increasingly used to dissolve and destroy these deposits. Wax inhibitors help delay paraffin deposition and change the crystal morphology of the deposited paraffin particles.

The literature on the properties of chemical inhibitors, dispersants, depressants and paraffin crystallization modifiers was reviewed. A paraffin dispersant is a group of surfactants that adsorb on the surface of the tube wall, either changing the wettability of the tube wall or reducing the paraffin adhesion by forming a thin layer from which the wax crystals are easily separated. Depressants affect the structure of paraffin through co-crystallization under van der Waals forces, lowering the freezing point of crude oil.

Wax crystal modifier helps reduce the formation of three-

dimensional networks of wax crystals, thus reducing freezing point and viscosity of oil.

The "cold finger" analysis has been the standard test procedure for evaluating paraffin precipitation inhibitors in oil and gas production for the last 20 years. Challenges have arisen in the application of wax inhibitors with the advent of unconventional oil and gas production in reservoirs such as the Montney and Duvernay formations in Canada. Baker Hughes has developed a differential scanning calorimetry (DSC) method for the evaluation of wax inhibitors that demonstrates great advantages over "cold finger" analysis. DSC analysis is widely used in the oil and gas industry to determine the wax appearance temperature (WAT) of crude oil by defining the point at which wax crystals form.

Kill fluids to prevent complications in well repair were investigated in the fifth paragraph of the first chapter.

Back pressure is generated at the well bottom in well kill operation to eliminate the production of formation fluids. The fluids that can generate the required back pressure in the formation are used in well kill operations. Kill fluid shall have certain physical and chemical properties that meet the specified conditions: it shall be chemically inert to the rocks and formations, prevent irreversible clogging of the pores and fractures of the productive formation, and have not corrosive effect on the well equipment and field structures and be stable under certain thermobaric conditions for the implementation of measures for a period of time.

A variety of water-based, hydrocarbon-based, and foam-based kill fluids are available. Water-based kill fluids eliminate irreversible clogging of pores with solid particles, thus preventing decrease in reservoir permeability, and the use of hydrocarbon-based kill fluids prevents swelling of clay particles and corrosion of the equipment. Foam-based fluids are intended for use in formations with abnormally low formation pressure (ALFP). Well killing before workover is an important technological stage, one of the tasks of which is to preserve and restore the natural percolation properties of the bottomhole formation zone (BFZ).

Sealants are used to preserve the filtration properties of the

productive formation and prevent fluid losses in well kill operations in production wells.

The main feature of the selection of high-pressure oil well completion technologies in the fields of Bashneft" LLC is the use of reservoir water in the completion of wells.

However, there are a number of significant limitations. In the first place, sedimentation occurs when salt compositions based on calcium chloride are mixed with the field's reservoir water.

According to calculations conducted using the Oddo-Thomson methodology, the composition of the colmatant is complex and includes unresolved salts.

X-ray phase analysis method has revealed the presence of resolved chloride salts in the composition of the sediments. Considering the compliance information of the water obtained, the preparation of the maximum density brine solution is only possible by using fresh technical water.

In China, many old gas fields like Yakela, Dalaoba, Kekeya, and others are characterized by very low reservoir pressures. The reservoir pressure typically ranges between 0.6 and 0.9, making it prone to gas blowouts. Ordinary solutions easily seep into the reservoir, compromising well productivity. Alternative solutions are available for the prevention of blowouts in low-pressure wells, including foam, oil-based emulsion mud, and reduced-density kill mud containing agent. However, the density of these alternative kill fluids is primarily above 0.8 g/cm³, and if density reducing agents are used in large volumes to lower the density below 0.8 g/cm³, costs increase. The article presents nitrogen foam kill mud successfully used for sand cleanout operations in low-pressure gas collectors. Sodium dodecyl sulfate has been chosen as the foaming agent.

During the killing of oil and gas wells, non-metallic salts are widely used, which leads to intensive salt deposition and corrosion on metal surfaces in contact with oilfield equipment. Developing enhanced formulations of kill fluids by utilizing materials that can reduce the intensity of salt deposition and corrosion processes is currently a relevant issue.

The second chapter focuses on exploring new methods for

combating emulsions arising from the use of innovative composite compositions in oil production.

In the first paragraph of the second chapter, a method is proposed for restoring the permeability of the surrounding area of the wellbore.

During exploitation, the filter cake of the wellbore becomes contaminated due to interaction with components in the fluid composition, affecting the surrounding area of the wellbore. The condition of the wellbore area of the collectors is affected by salt and asphaltene-tar-paraffin deposits. When selecting an effective drilling fluid composition for cleaning the wellbore area, several parameters must be considered, such as the mineralogy of the mud, the rate of chemical reactions between the various minerals in the mud and the wellbore, the degree of dissolution of the mud, well temperature, the composition and properties of the drilling fluids, among others.

Drilling mud compositions are used to restore the permeability of the wellbore area. However, the quality of these operations is often compromised due to the high dissolution capability, high corrosion rate, insufficient penetration, and tendency to cause deposits of drilling mud compositions.

Emulsified solutions, foam systems, enhanced mud compositions, mud-additive reagents, organic solutions, and so forth are used to increase the reaction time of the drilling mud system with the formation <sup>1,2</sup>.

The reason limiting the use of citric acid in calcium-rich layers is the low solubility of calcium citrate. In laboratory research, it is shown that during the reaction of lemon mud with carbonate, the pH of the calcium citrate solution precipitates within a range of 2.7 to 3.2, and as the initial concentration of the mud increases, the pH value of the precipitation decreases.

<sup>&</sup>lt;sup>1</sup>Gurbanov, A. G., Rzayeva, S. D. Self-diverting organic acid system for processing terrigenous reservoirs // SOCAR Proceedings, - 2022, No. 3, - p. 45-53.

<sup>&</sup>lt;sup>2</sup> Gurbanov, A. G., Rzaeva S. D. Organic acid composition for processing terrigenous reservoirs // Bulatov Readings: collection of proceedings of the VI International Scientific and Practical Conference, Krasnodar, March 31, 2023. – p. 167-175

Due to the ability of precipitated calcium to chelate, the solubility of salts can be increased by mixing glycolic acid with these acids. When lactic acid is mixed with glycolic acid in stimulated calcite rocks, a significant improvement in the solubility of calcium lactate has been observed.

The possibility of applying the mentioned idea to other organic acids such as acetic, formic, citric, and glycolic and boric acids was investigated. Kern dilution results showed that the mixture of glycolic acid with acetic acid increases the solubility of the resulting calcium salt and allows the use of acetic acid at 15% by mass without the risk of precipitation of calcium acetate. When mixed with formic acid, minimal risk was observed at 1:7 ratio of glycolic to formic acids. This made it possible to use 12.5% by weight of formic acid without observing precipitation of calcium formate.

Thus, a new method has been developed for restoring the permeability of the wellbore area by enhancing the dissolution capability of calcium salts resulting from the reaction of organic acids with calcite.

A method of acid treatment of terrigenous inhomogeneous formation well bottom area was developed, which consists of sequential injection of sodium bicarbonate aqueous solution and binder (0.01-2 mass %), light oil and acid solution - citric acid mixture (0 - 8.0 mass %), polymer (0.01 - 1 mass %) and milk whey (CMW) (remaining). To prevent premature mixing of the solutions, light crude oil is injected beforehand. In the developed method, chromium potassium oxide (CPO) or aluminum potassium oxide (APO) is used as a binder. Carboxymethyl cellulose (CMC) or polyacrylamide (PAA) is used as a polymer.

During the treatment of the wellbore area with solutions, the solutions penetrate into highly permeable consolidated layers. The reaction between sodium bicarbonate and the mud results in the release of carbon dioxide gas (CO2), creating a stable foam system that will isolate the penetrated intervals in the formation. The addition of the polymer to the acid solution is carried out to increase the stability of the foam and thicken the acid solution. The constructed polymer gives the foam mechanical strength, ensuring the high stability of the foam

system. After the high permeability layers are closed, the next portion of the injected acid solution spreads in the direction of small permeability areas, which ensures an increase in the impact coverage area of the layer. Organic compounds such as acid (milk whey, citric acid) are used, which ensures a decrease in the rate of reaction of the solution with the formation rocks, and as a result, the solution penetrates deep into the rock.

As a result of the dissolution of carbonate minerals, the filtration properties of the formation are enhanced. In the method for restoring the permeability of the wellbore area using the new mud, the aggressiveness and corrosion activity of the mud are reduced. With the closure of highly permeable zones, the subsequently injected mud tends to migrate towards lower permeability areas saturated with oil.

The employed method has been tested through various experiments and compared with prototypes in laboratory trials. In one beaker, a mixture was prepared by adding various amounts of a binder to the aqueous solution of sodium bicarbonate and stirring. In another beaker, the mud solution was prepared: Citric acid and polymer are added to milk whey in a laboratory mixer with constant stirring until they are completely dissolved. Then the solution obtained in the second beaker was added to the solution in the first and the process of foam formation was observed. Foam volume growth and foam stability were determined. The results of the studies are shown in table 1.

Experiment 2. In the proposed method, the rate of reaction of acid solution with rock is determined by changes in the mass of rock particle samples, and 10 g of carbonate rock sample is placed in a flask and 60 cm<sup>3</sup> of prepared acid solution is added to it. After covering the flasks with a glass lid, they were kept in a thermostat at a temperature of 45 °C for 4 hours. The rock samples were then filtered and dried to a constant weight. The reduction amount of the rock sample fraction was calculated (table 2).

Laboratory tests have shown that:

- In comparison with the prototype, the volume increase of the foam in the proposed method has increased by 1.8 times, and its stability has increased by 3.3 times;
  - Polymer added curd whey (CW) dissolves up to 7% of

carbonate rock. Addition of citric acid to CW increases the dissolution of carbonate rock by 40%.

Experiment 3. The method was tested in laboratory conditions on a two-formation model. The model is filled with quartz sand of different fractions with the addition of carbonate powder (7-40%).

Table 1. Characteristics of the obtained foam system

Experiment number	The amount of scale inhibitor in the aqueous solution of sodium bicarbonate, %	Acid solution	Increase in foam volume, amount	Foam stability, sec.
1	CPO - 0,001	CMC - 0,01 mass.% MW	1,9	2,2
2	CPO -0,01	Citric acid -2,0 mass.% CMC -0,1 mass.% MW – remaining	1,8	2,1
3 CPO -0,1 Citri		Citric acid -3,0 mass.% CMC - 0,5 mass.% MW – remaining	2,0	3,0
4 CPO –1,0		Citric acid - 4,0 mass.% CMC -1,0 mass.% MW – remaining	2,2	3,0
13 APO –1,0 Cmas		Citric acid - 5,0 mass.% PAA - 0,01 mass.% MW – remaining	1,8	2,1
14 APO -1,3		Citric acid - 6,0 mass.% PAA - 0,1 mass.% MW – remaining	2,1	2,2
15 APO -1,7		Citric acid - 7,0 mass.% PAA - 0,5 mass.% MW – remaining	2,0	2,4

16	APO -2,0	Citric acid - 8,0 mass.% PAA - 1,0 mass.% MW – remaining	2,2	2,6
17	Regarding the prototype 1,2 0,9			0,9

Table 2. Solubility of the acid solution

	The	After the reaction, the	Amount of	
No	The composition of the acid solution	amount of CaCO <sub>3</sub> ,	dissolved CaCO <sub>3</sub> ,	
	acid solution	gr	%	
1	CMC - 0,01 mass.%	9,3	7	
1	MW – remaining	7,5		
	Citric acid - 2,0 mass.%			
2	CMC - 0,1 mass.%	8,92	10.8	
Ш	CMC – remains			
	Citric acid - 3,0 mass.%			
3	CMC - 0,5 mass.%	8,4	16.0	
	MW – remaining			
	Citric acid - 4,0 mass.%			
4	CMC - 1,0 mass.%	7,87	21,3	
	MW – remaining			
	Citric acid - 5,0 mass.%			
5	PAA - 0,01 mass.%	7,3	26.0	
	MW – remaining			
	Citric acid - 6,0 mass.%			
6	PAA - 0,1 mass %	6,905	30.95	
	MW – remaining			
	Citric acid - 7,0 mass.%			
7	PAA - 0,5 mass.%	6,281	36.2	
Ш	MW – remaining			
	Citric acid - 8,0 mass.%			
8	PAA - 1,0 mass.%	4,7	40.8	
	MW – remaining			

The porous medium is saturated with formation water, and then the formation water is displaced with oil. The permeability of the lowpermeability layer was 0.3 mkm<sup>2</sup>, and the high-permeability layer was 2.5 mkm<sup>2</sup>.

In the next stage of the experiment, an aqueous solution of sodium bicarbonate with a builder added in the amount of 10% of the pore volume of the model, light oil in the amount of 5% of the pore volume, and an acid solution selected depending on the carbonation of the porous medium in the volume of 10% of the pore volume were supplied from the outlet to the model. The injected ingredients first entered the high-permeability layer, where the reaction formed a stable foam and the foam closed the high-permeability layer. The next injected portions of the acid solution were directed to the porous medium with low permeability. Experiments on the prototype were conducted compare the also to results. The results of the research are shown in Table 3.

Table 3. Results of experimental studies

		Layer	rs	In an		The	final
Carbonation of the rock %		starting		aqueous		l	ability
_n		conduct	_	solution of		of	- 1
ıt n	Carbonation	mkm		sodium	composition	lay	
ner_	of the rock			bicarbonate		mk	
erir	%	TC 1	ICO	amount of	solution		
/xb(		Kln	K2n	builder		K1k	K2k
E				%			
				VV7	KMS -		
1	7	0,30	2,50	XKZ -	0,01 weight.%	1,12	0,81
				0,001	KSZ- res.		
					Citric acid -		
					2,0 weight .%		
2	11	0,31	2,52	XKZ - 0,01	KMS - 0,1	1,22	0,79
					weight.%		
					KSZ - res.		
					Citric acid -		
					3,0 weight.%		
3	16	0,30	2,51	XKZ - 0,1	KMS - 0,5	1,45	0,80
					weight t.%		
					KSZ-res.		

4	21	0,32	2,53	XKZ - 1,0	Citric acid - 4,0 weight.% KMS – 1,0 weight t.% KSZ - res.	1,56	0,78
5	26	0,32	2,49	AKZ- 1,0	Citric acid - 5,0 weight.% PAA - 0,01 küt.% KSZ - res.	1,64	0,81
6	31	0,29	2,48	AKZ - 1,3	Citric acid - 6,0 weight.% PAA - 0,1% KSZ - res.	1,82	0,82
7	36	0,30	2,50	AKZ - 1,7	Citric acid - 7,0 weight	2,12	0,79
8	40	0,30	2,51	AKZ – 2,0	Citric acid - 8,0 weight.% PAA – 1,0 weight t.% KSZ - res.	2,53	0,79
9	By prototype	0,31	2,51			0,82	1,50

It can be seen from Table 3 that the results obtained in the 8th experiment were more favorable. In the double-layer model, after processing with the proposed method, the conductivity of the low-conductivity layer increased by 8.4 times (3.1 times more than the prototype), and the conductivity of the high-conductivity layer decreased by 3.2 times (1.9 times less than the prototype). Method Received Eurasian Patent No 042573.

In the second paragraph of the second chapter, the development of the method of isolating the water flow to the well is shown.

Limiting the volume of formation water and increasing the oil recovery of formations is one of the actual problems in the oil extraction industry. A large number of compositions and methods have been developed and tested to limit the flow of water into wells. The complexity of the compositions, the high price of the components and the laboriousness of the measure, and the diversity of the geological conditions, taking into account the real processing of heterogeneous formations, reduce the efficiency of these compositions and methods, and it is necessary to continue research.

A new water shutoff method has been developed, which has the ability to increase the quality of water shutoff due to the closure of high permeability areas and the involvement of low permeability areas, as well as the ability to adjust the time and process of gel formation at the depth of the formation<sup>3</sup>.

The newly developed water shutoff method has the ability to adjust the gel formation process and timing during water shutoff water shutoff water shutoff. The developed method prevents the formation of sediment and allows the formation of the gel screen in full volume. To ensure thorough mixing of the method components and to prevent sedimentation, before injection into the well, a 1:1 volume of gelling agent solution is added to the gelling initiator solution and mixed until a homogeneous mixture is obtained. At certain concentrations of the gel-forming agent and the initiator of gel formation, the obtained pel-forming agent and the initiator of gel formation, the obtained homogeneous aqueous solution completely turns into a gel within a certain period of time, depending on the temperature of the formation.

In the developed method, after the gel is stored for the calculated time using the components of the composition in specified quantities, the oil formations are treated with acid. If there are carbonate rocks in the formation, then acid treatment is carried out by injecting an inhibited hydrochloric acid solution. If the formation contains

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<sup>&</sup>lt;sup>3</sup> Suleymanov, B. A., Gurbanov, A. G. Method of isolating water inflow into a well. Eurasian patent No. EA 043725, 2023.

terrigenous rocks, acid treatment is carried out by injecting a mixture of inhibited hydrochloric acid and hydrofluoric acid (clay acid) solution.

To justify the method developed in the laboratory, gel-forming compositions were prepared by adding a solution of the gel-forming agent to a solution of the gel-forming initiator. Figure 1 shows the dependence curve of the gel-forming agent solution pH on its concentration.

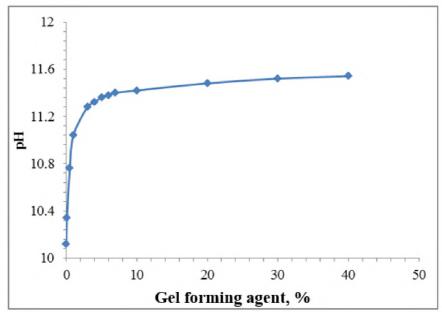


Figure 1. Dependence of pH concentration for a gelforming agent

The analysis of the results shows that the optimal concentration of the gel forming agent is 9-10%. The pH of the solution does not change with the increase in concentration.

In the second version of the experiments, the change in the pH of the mixture obtained by introducing gel-forming agent solution with a concentration of 0.5 to 12%, into gel formation initiator with a concentration 5; 10, 15 and 20% was studied concentration of 5; 10; 15 and 20% into the solution was studied (Fig. 2).

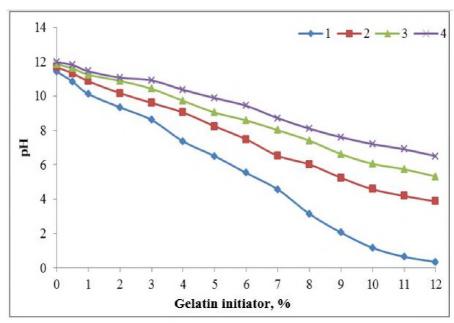


Figure 2. Dependence of the pH of the solution upon the introduction of the gel formation initiator into the 1-5%, 2-10%, 3-15%, 4-20% concentration solution of the gel-forming agent

It can be seen from figure 2 that when the gel forming initiator solution is added to the gel forming agent solution, gel formation begins and the pH of the mixture decreases to 1.5-2. When a 5% solution of the gel forming agent is added to the gel forming initiator solution, the pH of the mixture drops dramatically. The optimal concentrations of the components of the mixture are: 10-12% for the gel initiator and 9-10% for the gel-forming agent. In this case, the pH of the mixture is between 4 and 5, which is the most optimal option for full gel formation.

When a solution of a gel initiator is added to a solution of a gel forming agent, the formation of a gel-like residue is observed, but the gel formation is not complete. This situation is explained by the transfer of the gel formation initiator to the alkaline environment, which leads to the indicated course of the process. In this case, the density of the solution of the gel forming agent is about 1.3 times

higher than the density of the solution of the gel formation initiator ( $\rho \approx 1.39 \text{ g/cm}^3$  and  $1.05 \text{ g/cm}^3$ , respectively), and this does not allow quick and uniform mixing of the solutions.

When changing the order of the solutions, the gel-forming agent is introduced into an acidic environment, which prevents the early formation of a gel deposit, and a significant difference in the density of the solutions ensures their rapid and uniform mixing.

In laboratory conditions, the temperature dependence of the gel formation time of the mixture obtained by giving a solution (10%) of a gel-forming agent in a solution of a gel-forming initiator (10%) in a volume ratio of 1:1 was studied. (Figure 3).

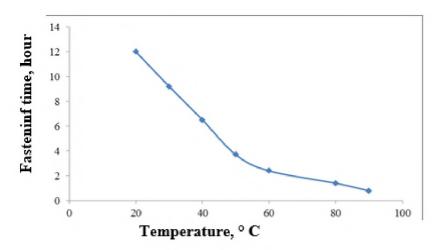


Figure 3. Dependence of the gel formation time of the mixture on the ambient temperature (formation temperature)

The time of gel formation decreases 5-6 times when the temperature increase from 20°C to 60°C, at temperatures above 60°C, the time of gel formation is 1-2 hours. Based on the results of laboratory studies, the formula for determining the time required for gel formation depending on the ambient temperature (layer temperature) is given:

$$t = 13 + 0.23T - 0.02T^2 + 0.0003T^3 - 1.42 \cdot 10^{-6}T^4$$

here: t – time required for gel formation, hours. T – ambient

temperature (formation temperature), °C.

Using a thermoactive gel-forming composition, the study of the displacement process of oil from the reservoir model was carried out in an experimental unit (Figure 4).

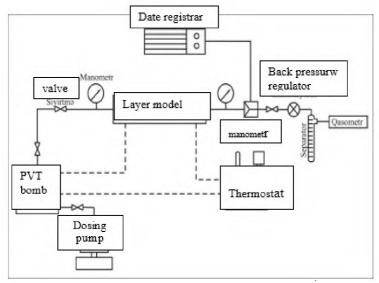


Figure 4. Schematic of the experimental facility

Experiments were conducted on carbonate and quartz sand models. In experiments conducted on carbonate and sand formation models, the best results are obtained by injecting the ready mix. Fairly results were obtained during the initial injection of gel formation initiator. The worst results were obtained with the initial injection of the gel forming agent.

The results of experiments on oil displacement showed that water shutoff method, based on the use of a thermoactive gel-forming mixture, was significantly preferable to known compositions in terms of technological efficiency

Eurasian Patent No. 043725 was obtained for the method.

In the third paragraph of the second chapter, the development of an inhibitor against the formation of ARP deposits was considered<sup>4</sup>.

Deposition of heavy hydrocarbon compounds asphaltene, resin, paraffin (ARP) sediments at the bottom of the well, in underground and surface oil mining equipment creates complications during the operation process. The high deposition rate of paraffin sediments communications, leads to a decrease in system productivity, the interrepair work period of wells, an increase in well operation and maintenance costs, a decrease in production and an increase in the cost of the product.

As it is known, the fight against ARP deposits in oil production processes is carried out in two directions:

- to prevent the formation of sediment;
- to clean existing sediments.

The first direction refers to the use of protective coatings, chemical exposure methods (solvents, cleaners, wetting agents, modifiers, depressants, dispersants), physical exposure methods (vibration, ultrasonic, electric and electromagnetic fields). The second direction mainly includes thermal methods (washing with heated oil or condensate, steam, electric heaters, induction heaters, reagents, exothermic reactions during interaction) and mechanical methods.

Various technologies and special equipment are used to prevent the formation of asphalt-resin-paraffin (ARP) deposits: wellhead and deep reagent dispensers, magnetic devices, heating cable lines, etc. The cleaning of deposits formed in wells is carried out with the help of pigs and heat carriers and by washing hydrocarbon solvents.

Effect with an inhibitor is a technological method, but the effect of inhibitors on asphalt-resin-paraffin (ARP) deposits is often not efficient enough, high reagent consumption is required for one ton of oil. Another disadvantage of such inhibitors is the high cost of raw materials. In this regard, the search and development of effective synergistic compositions of complex-acting inhibitors based on

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<sup>&</sup>lt;sup>4</sup>Gurbanov, A. G., Hajikerimova, L. G., Akbarova, A. F. A new inhibitor against asphaltene tar, paraffin and salt deposits// Scientific Petroleum, - 2023, No. 2, - pp. 41-47.

suitable raw materials is an relevant issue.

In the process of raising the oil flow from the bottom hole to the wellhead, the thermobaric conditions change and the chemical balance in the produced product is disturbed. At this time, ARP deposits is observed on the walls of the tubing (PCP). It should be taken into account that ARP deposits occur in complex hydrothermodynamic conditions, with the presence of oil components, gas phase and mechanical mixtures, which affects the intensity of the process, the nature and properties of the deposits formed both in the bottom hole zone of the formation and in oil field equipment.

It is known that the inhibitor contains dialkyldimethylammonium chloride as an active base, cataptin, gossypol resin and kerosene as a solvent. The disadvantage of the inhibitor is the low efficiency of paraffin deposition in flooded wells with a amount of exceeds 50% water in the well product and also, the increase of salt deposits in the medium.

Further studies were conducted to develop an inhibitor that effectively prevents paraffin deposits and simultaneously salt deposits in arbitrary mixtures of oil and formation water, and especially in cases where the relative amount of formation water exceeds 50%.

Amide as a condensation product of oleic acid in the presence of diethylbenzene in a ratio with triethylenetetramine as a solvent, Glycerin-based EO/PO block copolymers, isopropyl alcohol as a solvent, and the components of light phlegm of catalytic cracking in the following ratios by mass % new inhibitor was developed:

Stearic acid with triethylenetetramine	8-15
condensation product	0-13
Glycerin-based EO/PO block copolymers	5-10
Oxyethylenediphosphonic acid (OEDF)	3-5
Isopropyl alcohol	20-30
Light phlegm of catalytic cracking	residue

The triethylenetetraamine amide of stearic acid included in the inhibitor ensures the effectiveness of the paraffin precipitation inhibitor. Glycerin-based EO/PO block copolymers ensures the

penetration of the amide into the oil by providing deemulsification of the watered oil. Oxyethylenediphosphonic acid prevents precipitation of calcium and magnesium ions by forming a complex. Isopropyl alcohol is included as a solvent for block copolymers of alkylene and propylene oxide based on glycerin. The light phlegm of catalytic cracking diffuses to the surface of solid hydrocarbons in paraffin oil and provides a better effect of active substances.

In the fourth paragraph of the second chapter, the development of the method of well kill with a foamy gel-based composition was considered.

There are quite a lot of fields in the final stages of development in the oil and gas industry. In wells operated from these deposits, complications usually increase, as well as accidents and repair work to eliminate them. For the safe and accident-free maintenance of wells, kill fluids with special composition are used. There are special requirements for kill fluids.

One of the most important requirements for kill fluids is that they do not adversely affect the reservoir properties of the productive formations with which they are in contact, or that this effect is minimal. Improper selection of the kill fluids can lead to a decrease in oil flow and an increase in dilution of the well product due to the intensive absorption of the reagent into the formation.

Kill fluids should not create back pressure on the formation, should not negatively affect the collector properties of the productive formations, should be chemically compatible with formation fluids and technological fluids used during repair, should have an inhibitory effect on clay particles, should not allow them to swell and should not cause corrosion of repair and maintenance equipment.

Kill fluids differ in that they are based on water, hydrocarbons and foam. CaCl<sub>2</sub> and NaCl solutions are the most commonly used kill fluids. However, these solutions reduce the conductivity of bottom hole, increase water saturation and, when mixed with oil, lead to the formation of persistent high-viscosity emulsions.

The main problems associated with kill fluid injection are: intensive absorption, flooding and formation of emulsion in the bottom hole, damage to the formation or deterioration of flow

properties. Therefore, it is necessary to accurately determine the density of the kill fluid in order to prevent it from being absorption.

In the process of killing wells, sequential injection of a gel-like visco-elastic plastic mass based on an aqueous solution of sutural material a displacing fluid and an acrylic polymer into the well is used. The disadvantage of the method is that it is less effective in killing gas wells. The gel-like visco-elastic mass used in the method has a high density. To remove it from the well, special compounds are usually used to dissolve the split polymer systems, which reduces the efficiency of the method.

For this purpose, a method of killing wells with a new foamy gel-based composition based on sequential injection of a gel-like mass and displacing fluid into the well was developed in killing oil wells with gas show.

A water-soluble polymer is used as a foaming gel-like mass created by mixing builders, degassing agents, foaming agents and water. The required volume of foam gel injected into the well is determined by the height of the perforated interval of the well.

A foam gel is injected into the well, which is formed by mixing water-soluble KMS, builder, degassing, and defoaming agents and water. Salt solutions whose density (1200-1800 kg/m³) is selected based on the formation pressure of the well are used as the displacing fluid.

The required volume of injected foam gel v is determined according to the following formula:

$$v = \frac{\pi D^2}{4} \cdot h$$

where D – internal diameter of production casing, m;

h – is the height of the perforated interval of the well, m.

In oil wells operated by the Fontan and gas lift methods, after replacing the saline solution with a low-density working fluid, the foam gel is easily removed from the well under the influence of formation pressure. During the oil production in the mechanized operation method, using pumps of any construction, the foam gel can be easily pumped into and removed from the well.

To determine the density of the foam gel-based composition, its

components were prepared in laboratory conditions. Foaming gel, dry KMS powder, builder, gasifier, degassing and defoaming agents are prepared by adding the calculated volume to water and mixing continuously until completely dissolved in a laboratory mixer.

The density of the investigated components and the known composition at a temperature of 293 K is given in table 4.

As can be seen from Table 4, the density of foam gels according to the proposed method (530-810 kg/m $^3$ ) is much lower than the density of the prototype (1100-1800 kg/m $^3$ ) and can be easily removed from the well by pressure drop.

Table 4. Density of compositions at a temperature of 293°K

Components,	Content	Content	Content	Prototip
mass %	<b>№</b> 1	№2	<b>№</b> 3	1
KMS	KMS400	KMS600	KMS	1. Synthetic bifunctional
			1000	anionic copolymer
	2,0	3,0	5,0	"Ionomer BO-65".
Builder	0,5	1,5	3,0	2% aqueous solution-84.8
Gas separator	10	8,0	6,0	
Gas-	12	11	10	2. Chromium 3 sulfate
generating				Cr <sub>2</sub> (SO <sub>4</sub> )3·6H2O
Foam	0,5	0,1	0,01	3. (builder) 5% solution-
generating				0.2
agent				4. Barite BaSO <sub>4</sub> -15
Density,	530	720	810	1800
kg/m³				

Thus, a foam gel has been developed for effective kill of gas show well. Eurasian Patent No. 041274 was obtained for the method<sup>5</sup>.

In the third chapter, the results of the application of the methods developed in the fight against the complications formed during oil production in mining conditions - the method of restoring the permeability of the area around the bottom hole of the formation

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<sup>&</sup>lt;sup>5</sup> Suleymanov, B. A., Gurbanov, A. G., Baspaev, E. T. Well killing method. Eurasian patent No. EA 041274, 2022.

and the method of isolating the water flow into the well were considered.

In the first paragraph of the third chapter, the results of the tests of the method of restoration of the fluid conductivity of well were reviewed.

The developed method consists of essentially an aqueous solution of sodium bicarbonate and a builder (0.01-2 mass %), a light oil and acid solution - citric acid mixture (0-8.0 mass %), a polymer (0.01-1 mass %) and acid treatment of the bottom hole of the terrigenous heterogeneous layer by sequentially injecting milk whey (KSZ) (residue) into the layer. The light oil in the processed method serves to prevent premature mixing of solutions. Chromium potassium or aluminum potassium are used in the processed composition as a builder. As a polymer, carboxymethyl cellulose or polyacrylamide was used.

Solutions in the new method penetrate well into high flooded zone. The sodium bicarbonate reacts with the acid solution, the carbon dioxide formed as a result of the reaction penetrates the liquefied intervals in the CO<sub>2</sub> formation and creates a stable foam system. The polymer in the composition increases the stability of the formed foam and thickens the acid solution. The polymer provides high stability of the foam gel composition. The builder structures the polymer molecules, increases the stability of the foam system and gives the foam mechanical strength. In this case, after the high-permeability areas in the formation are covered by the foam, the next part of the acid solution no longer spreads to the high-permeability areas, but to the low-permeability areas, penetrating these areas. The new method ensures that the poorly permeable areas of the formation saturated with oil are treated with acid.

For rejuvenation of bottom-hole zone permeability of the well  $N_{2}610$  and  $N_{2}664$  in Absheronneft OGPU, the test was carried out with the composition of organic compounds and polymer consisting of curd milk whey and citric acid.

Histograms of wells were constructed on the basis of field data taken before and after application (Fig. 5, 6).

As can be seen from the histogram, the application of the new

method on both wells had a positive effect on the bottom area. Closure of watery areas with high permeability has been achieved. Thanks to this, water production in wells has decreased. Oil production has increased in areas with poor permeability. As a result of the application of the developed new method in two wells, 0.7 tons of additional oil was extracted during the day and 5.3 tons of water extraction was prevented. As a result of applying the method in the well, a total of 86 tons of additional oil was produced (Act is attached).

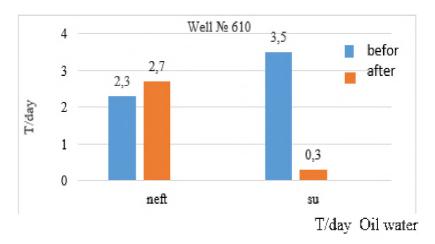


Figure 5. Production parameters for well № 610 before and after application

In the second paragraph of the third chapter, the application of the method of isolating the water flow to the well in field conditions was considered.

Mixtures of 9-10% sodium silicate and 10-12% solutions of hydrochloric acid are injected into the well in a 1:1 ratio. The solution mixture is injected into the bed with water and kept under bed conditions until a gel is formed. The arrival time is calculated by the formula given in the second chapter, depending on the temperature and the depth of the well.

First, a suitable solution of hydrochloric acid and then sodium silicate is injected into the well. After keeping the well until the gel is formed, an inhibited 12% solution of hydrochloric acid and 5% of hydrofluoric acid is injected into the well as an acid. Unlike other methods, this method creates a full volume gel screen in high permeability zones.

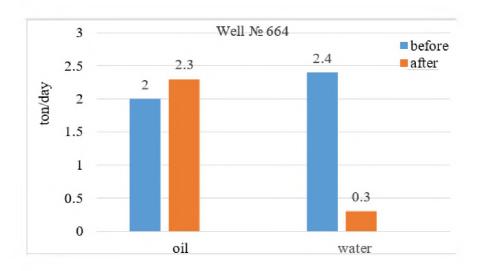


Figure 6. Production figures for well №664 before and after application

The method was applied in order to isolate high-permeability water areas in operational wells No. 1347, 1858, 2651 of Neft Dashlari OGPU.

In order to evaluate the effect of the composition, data were taken from operational wells No. 1347, 1858, 2651 of Neft Dashlari OGPU before and after application, and histograms of production parameters of the wells were constructed based on this data (fig. 7, 8, 9).

As can be seen from the figures, gel formation was ensured in the water-flooded parts of the bottom-hole zone and water was prevented from entering the well. 60.7 tons of additional oil were produced from the wells, and an average of 9.0 m<sup>3</sup> of water was prevented from entering the well from the bed during the day from the three wells (Act attached).

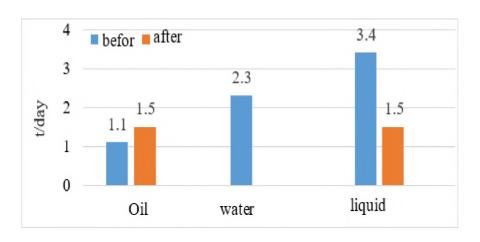


Figure 7. Production parameters in well No. 1347 before and after application

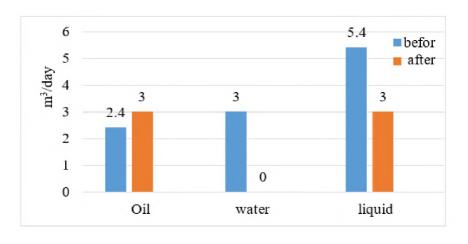


Figure 8. Production parameters in well №1858 before and after application

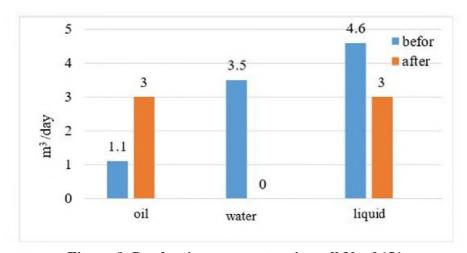


Figure 9. Production parameters in well No. 2651 before and after application

#### CONCLUSIONS AND RECOMMENDATIONS

- 1. The complications arising in oil production have been classified, the current state of complications control arising during rejuvenation of bottom-hole zone permeability of the well, the isolation of the water flow into the well, the formation of ATP sediments and the current situation of the fight against the complications arising during the killing wells has been studied and research directions have been determined;
- 2. A new method of rejuvenation of bottom-hole zone permeability of bed was developed. In the method, foam-forming and acid-based solutions are sequentially injected into the bottom of the well. As a result, foam is formed in the high-permeability formation, and the injected acid-based solution enters the low-permeability oil-filled formation, increasing its permeability and oil production.

The following results were obtained during the experimental studies of the method in the layer model:

- In comparison with the prototype, in the proposed method, the foam volume increased by 1.8 times, and its stability increased by 3.3 times:
- Polymer-added curd whey (KSZ) dissolves up to 7% of carbonate rock. Addition of citric acid to KSZ increases the dissolution of carbonate rock by 40%;
- In the double-layer model, after processing with the proposed method, the conductivity of the low-conductivity layer increased by 8.4 times (3.1 times more than the prototype), and the conductivity of the high-conductivity layer decreased by 3.2 times (1.9 times less than the prototype).

The developed method was successfully applied in field conditions and Eurasian Patent No. 042573 was obtained.

3. A method of isolating water flow to the well has been developed. In the method, by sequentially injecting a gel-forming and acid solution into the wellbore, high-permeability zones are isolated due to gel formation, and low-permeability zones are involved in processing. As a result, production increases and the percentage of water intrusion decreases.

The following results were obtained during the experimental studies of the method in the layer model:

- The optimal concentrations of hydrochloric acid and sodium silicate solutions were found to be 9-10% and 10-12%, respectively;
- On the basis of laboratory studies, a dependence was proposed for the calculation of gel formation time depending on the temperature and depth of the layer.

The developed method was successfully applied in field conditions and Eurasian Patent No. 043725 was obtained.

4. An inhibitor against the formation of ATP deposits has been developed. The gossypol resin contained in the inhibitor creates a "protective slippery" surface on the metal surface and prevents paraffin crystals from settling on the surface.

The following results were obtained during the study of the inhibitor in laboratory conditions with highly paraffinic oils:

- The freezing temperature of spent inhibitor paraffin oil is 50-300 mg/l;
- Reduces from  $+29^{\circ}$ C to  $-4^{\circ}$ C, 33°C exhibits additional depressor function;
- In studies with known inhibitors, the depressor additive effect was 21°C, with the freezing point decrease from +29°C to +8°C at the same doses.
- 5. The method of killing wells with foam gel was developed and researched in laboratory conditions. As a result of comparing the composition of the components prepared in different mass fraction with the prototype, the foam gel density (530-810 kg/m³) in the new method is significantly lower than the prototype (1100-1800 kg/m³), which indicates that it is easily removed from the well due to the pressure drop. Eurasian Patent No. 041274 was obtained for the method.
- 6. New methods have been developed with the use of innovative composites against complications in oil production and have been effective as a result of their application in field conditions. The method of rejuvenation of bottom-hole zone permeability of bed was tested in wells No. 610 and 664 at Absheronneft OGPU, and as a result of its

application, 86 tons of additional oil were produced from the wells. The method of isolation of water flow into the well was tested in operational wells No. 1347, 1858, 2651 of Neft Dashlari OGPU. As a result of the application, 60.7 tons of additional oil was produced from the wells (application acts are attached).

# The main content and results of the dissertation work are published in the following works.

- 1.Gurbanov, A. G., Baspaev, E. T. A new method of killing gas production wells // SOCAR Proceedings, 2022, No. 2, p. 28-34.
- 2.Gurbanov, A. G., Rzayeva, S. D. Self-diverting organic acid system for processing terrigenous reservoirs // SOCAR Proceedings, 2022, No. 3, p. 45-53.
- 3.Suleymanov, B. A., Gurbanov, A. G., Baspaev, E. T. Well killing method. Eurasian patent No. EA 041274, 2022.
- 4.Suleymanov, B. A., Gurbanov, A. G., Tapdygov, Sh. Z. Isolation of water inflow into a well with a thermoactive gel-forming composition // SOCAR Proceedings, 2022, No. 4, p. 21-26.
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- 10.Gurbanov, A. G., Hajikarimova, L. G. The application of the technology of selective isolation of formation water with decompression systems // Azerbaijan oil industry, 2023, No. 10. Accepted for publication.

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- 13.Rzayeva, S. C., Gurbanov, A. Q. Application of the method of restoration of permeability of the well bottom field // Azerbaijan oil industry, 2024, No. 1. Accepted for publication.

# Degree seeking applicant's personal contribution:

[1,2,7,8,10] setting the issue in scientific works, participation in conducting research and summarizing the results;

[3,4,5,6,9,11,12] participation in the setting of the problem and analysis of the results, performing laboratory and experimental studies.

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