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Article

Increasing the filtration characteristics of rocks in areas of high temperatures

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INCREASING THE FILTRATION CHARACTERISTICS OF ROCKS IN AREAS OF HIGH TEMPERATURES

One of the important problems of the oil and gas industry is the decrease in the production characteristics of wells in fields that are at the final stage of development. In addition, the drop in well production below their potential and the decrease in hydrocarbon recovery factors are often due to the deterioration of the reservoir properties of rocks in the process of drilling in productive formations, well workover, as well as the imperfection of production processes and means of their implementation.

The object of research is the technology of treatment of the bottomhole formation zone with non-acidic systems based on ammonium salts for the intensification of hydrocarbon production.

The paper considers a number of methods that allow solving the above problems, taking into account their complexity, efficiency and duration of the positive effect of processing. The main acid methods of influencing the bottomhole formation zone and their modifications are analyzed. The authors, using the results of the research and experience gained, proposed a non-acidic system of chemical treatment of oil and gas wells based on ammonium salts. Their influence on the rocks occurs more long-term and does not lead to the destruction of reservoirs.

During the research, physical, chemical, physicochemical methods and techniques developed by the authors for processing and analyzing field data, statistical methods for processing experimental studies were used. Modeling of deep processes was carried out on the installation developed and created by the authors.

The mechanism of interaction of ammonium salt solutions with terrigenous and carbonate rocks is revealed. Experimental studies have confirmed and theoretically substantiated the effectiveness of the use of ammonium salts to improve the filtration characteristics of reservoirs.

The effect of ammonium salt solutions on the change in the permeability of sandy and carbonate reservoirs in the Dnipro-Donetsk depression (DDD, Ukraine) has been studied. And also a mathematical model of the process of increasing the permeability of rocks during their dissolution by the studied chemical reagents was created. The mathematical model is available for its wide application in the practice of technological calculations and designing measures for the stimulation of oil and gas production.

Keywords: *production characteristics of wells, hydrocarbon recovery factor, solution of chemical compositions, carbonate and terrigenous reservoirs.*

1. Introduction

In the process of developing oil and gas fields, starting from well drilling and during operation, various factors appear that cause a decrease in their production characteristics. Well productivity is determined by the state of the bottomhole formation zone, its permeability, the deterioration of which is the result of various reasons: mechanical contamination of the bottomhole zone; physical and lithological, which lead to swelling of the reservoir cement when interacting with water; physical and chemical; thermochemical, etc.

To restore and increase the permeability of the bottomhole formation zone, various methods of acid action are widely used. An analysis of the mechanisms of acid stimulation in the form of summary data on the treatment of oil and gas fields is presented in [1].

In [2], the mineralogical, mechanical and physical reactions of acid with the rock matrix of several important North American shale formations were evaluated, and the effect of acids on the factors of productivity recovery was described.

When treating bottomhole zones (TBZ) of wells with acid compositions, the diffusion rate increases with increasing temperature. This leads to an acceleration of the reactions occurring between the acid and the rocks. The acid is quickly consumed, as a result of which part of the solution continues to penetrate into the formation, but the acid concentration in it decreases, and the content

of reaction products increases. This process reduces the depth of impact of the acid solution [3, 4].

The problem of treating reservoirs with acid solutions in areas of high reservoir temperatures above 70 °C causes certain difficulties due to the need to use special reagents to reduce the rate of acid-rock reaction, acid corrosion inhibitors and pH stabilizers. The authors of [5] in their studies use some alcohol components as retarding agents in acid operations in gas fields to reduce the rate of dissolution of limestones ($CaCO_3$) and dolomites ($MgCa(CO_3)_2$) by acid.
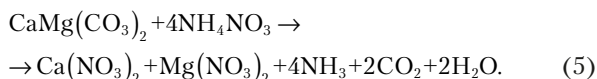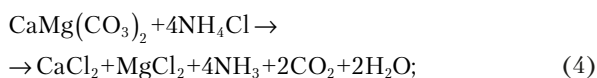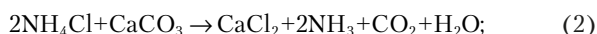
The authors of the study [6] proposed a complex composition consisting of the main treatment solution by the chelate mechanism, an acid solution and a salt squeezing solution for treating the bottomhole formation zone of high-temperature wells. The paper shows that the method of generating the formation of hydrofluoric acid based on chelate compounds and ammonium hydrofluoride is a simultaneous solution to the problems associated with high temperature and the formation of secondary precipitation. Due to the strong properties of chelate compounds, the part that is adsorbed on the surface of the formation of the bottomhole zone plays the role of an inhibitor of salt deposition and protects the bottomhole zone from contamination with inorganic salts for a long time.

However, among the chemicals there are other non-acidic reagents, aqueous solutions of which dissociate under conditions of high temperatures with the formation of active agents that easily dissolve rock components, for example:

$$NH_4Cl+H_2O \leftrightarrow NH_4OH+HCl. \tag{1}$$

The effect of such reagents on carbonate rock compounds is long-term and does not lead to reservoir destruction. They can be used to treat both carbonate and terrigenous reservoirs. Thus, the authors of [7] proposed a new approach to the choice of chemical reagents for treating carbonate and terrigenous formations in high temperature zones without the use of traditional acids. Such chemicals, due to complex chemical reactions, can effectively affect the permeability of the pore space. In this work, laboratory studies and field tests confirmed the effectiveness of the influence of non-acidic systems on increasing the filtration characteristics of the pore space of productive formations.
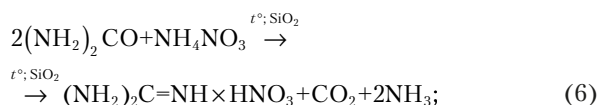
Under the conditions of a carbonate reservoir, non-acidic salt solutions dissolve the walls of the pore space according to the following schemes:

$$2NH_4Cl+CaCO_3 \rightarrow CaCl_2+2NH_3+CO_2+H_2O; \tag{2}$$

$$2NH_4NO_3+CaCO_3 \rightarrow Ca(NO_3)_2+2NH_3+CO_2+H_2O; \tag{3}$$

$$CaMg(CO_3)_2+4NH_4Cl \rightarrow$$
$$\rightarrow CaCl_2+MgCl_2+4NH_3+2CO_2+2H_2O; \tag{4}$$

$$CaMg(CO_3)_2+4NH_4NO_3 \rightarrow$$
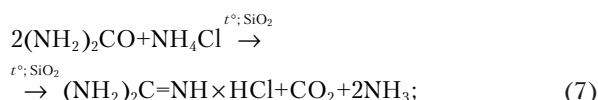$$\rightarrow Ca(NO_3)_2+Mg(NO_3)_2+4NH_3+2CO_2+2H_2O. \tag{5}$$

The resulting reaction products are substances that are highly soluble in water and are easily removed during well development, in contrast to the reaction products that are obtained when using acid systems based on mineral acids or their salts.

The treatment of terrigenous reservoirs in order to improve their filtration characteristics is most often associated with the use of hydrofluoric acid. However, for this type of formation, it is also possible to use non-acid salt reagents or chemical reagent compositions with a small amount of acids. Such reagents are mixtures of diaminocarbonic acid with ammonium salts. It should be noted that when these substances interact only at high temperatures and on the surface of silicon rock, reactions can occur with the formation of the corresponding guanidine salts according to the scheme [8, 9]:
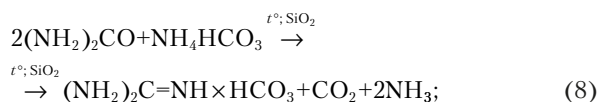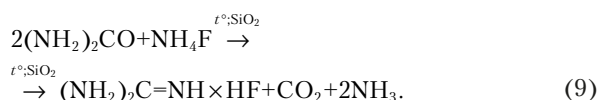
– guanidine nitrate:

$$2(NH_2)_2CO+NH_4NO_3 \xrightarrow{t°; SiO_2}$$
$$\xrightarrow{t°; SiO_2} (NH_2)_2C=NH \times HNO_3+CO_2+2NH_3; \tag{6}$$

– guanidine chloride:

$$2(NH_2)_2CO+NH_4Cl \xrightarrow{t°; SiO_2}$$
$$\xrightarrow{t°; SiO_2} (NH_2)_2C=NH \times HCl+CO_2+2NH_3; \tag{7}$$

– guanidine carbonate:

$$2(NH_2)_2CO+NH_4HCO_3 \xrightarrow{t°; SiO_2}$$
$$\xrightarrow{t°; SiO_2} (NH_2)_2C=NH \times HCO_3+CO_2+2NH_3; \tag{8}$$

– guanidine fluoride:

$$2(NH_2)_2CO+NH_4F \xrightarrow{t°;SiO_2}$$
$$\xrightarrow{t°;SiO_2} (NH_2)_2C=NH \times HF+CO_2+2NH_3. \tag{9}$$

As a result of continuous research on guanidines, scientists have developed various protocols and routes for the synthesis of these compounds, later they were tested for their possible use in various fields [10, 11].

The use of such reagents for the treatment of various types of collectors with prolonged exposure does not lead to their destruction. In addition, the reaction products are able to enter into further chemical transformations with other substances. For example, when carbonate salts of guanidine interact with higher fatty acids directly in the formation, salts of higher fatty acids can form, which in turn are simultaneously surface-active substances (surfactants) and carbon dioxide corrosion inhibitors. Therefore, if the treatment is carried out with the above composition of chemicals, which will include, for example, oleic acid, then as a result let's get a complex effect on the pore space of the productive reservoir:
– partial dissolution of pore walls;
– change in the wettability of its surface;
– reduction of surface tension;
– removal of asphalt-resin-paraffin deposits (ARPD);
– increase in permeability for the hydrocarbon phase.

Based on the performed analytical studies, the effectiveness of using non-acidic systems to improve the production characteristics of wells and intensify hydrocarbon production has been proven due to:
– absence of insoluble salts in the reaction products;
– soft dissolution of rock walls without their destruction and scree formation;

– the complexity of the use of compositions based on ammonium salts, which make it possible to increase the pore diameter, reduce the surface tension of the spent solution, unlike solutions with forced addition of surfactants, increase the wetting of rocks by hydrocarbons, preventing the swelling of clay minerals;
– absence of corrosive effect on downhole equipment and obstacles to contamination of the collector with iron salts.

Thus, *the object of research* is the technology of bottomhole formation zone treatment with non-acidic systems based on ammonium salts to improve the production characteristics of wells and intensify hydrocarbon production.

The aim of research is to determine the optimal parameters for the use of non-acidic salt systems in high temperature zones in order to formulate, within the framework of the complex of experiments, the main provisions that reflect the mechanism of their action on the porosity and porosity characteristics of a porous medium to improve the production characteristics of wells.

2. Research methodology

2.1. Methodology for experimental studies of the solubility of carbonate and terrigenous rocks. The authors conducted studies to determine the effectiveness of the use of the aforementioned chemicals. The dissolving abilities of these chemicals at different temperatures with respect to carbonate and terrigenous rocks were experimentally determined. For this, a special laboratory unit was developed and installed (Fig. 1).
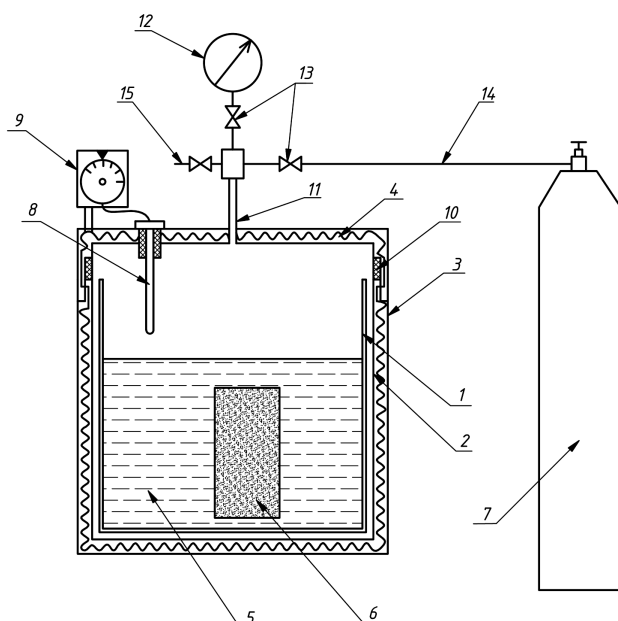
Fig. 1. Unit for studying the solubility of cores: 1 – container made of quartz glass or stainless steel; 2 – metal frame; 3 – temperature-controlled shell; 4 – cover; 5 – aqueous solution of the studied chemical reagent; 6 – core sample; 7 – gas cylinder; 8 – thermocouple; 9 – temperature sensor; 10 – seal; 11 – outlet tube; 12 – manometer; 13 – valves; 14 – gas injection line; 15 – gas bleeding line

An aqueous solution of the studied chemical reagent 5 and a core sample 6 were introduced into a container 1 made of quartz glass, which was inserted into a metal frame to prevent destruction 2. In order to maintain the temperature, the metal frame and cover 4 have all-round heating, which is fixed by a thermocouple 8 and controlled by a temperature sensor 9 with the possibility of setting the temperature up to 250 °C. Cover 4 through a system of silicone and copper seals 10 seals the test container and has an outlet tube 11 for supply 14 and discharge 15 of the gas. Thus, this setup makes it possible to study any acidic solutions (when studying hydrofluoric acid, the quartz container 1 is replaced by a stainless one) both at normal and elevated pressures.

The rocks that were used for the study had the following composition: carbonate – limestone with a clay content of 3.6 %, an average permeability of 1.27 μm^2; terrigenous – fine-grained quartz sandstone with a carbonate content of 3.2 % and clay content of 12.6 %, with an average permeability of 1.47 μm^2.

The time for studying the effect of these reagents on carbonate rocks was 1 hour, and on terrigenous rocks (sandstone) was 3 hours, since the dissolution is minimal until 2 hours, and only after that it is possible to record the weight loss of core samples.

2.2. Methodology for experimental studies of the solubility of carbonate and terrigenous rocks after treatment with chemicals. The influence and complex effect of ammonium salt solutions on the capacitive-filtration properties of reservoir rocks has been studied. Changes in the permeability of the pore space of carbonate and terrigenous rocks after treatment with the considered chemicals and compositions based on them have been studied. The experiments were carried out on a setup designed and built by the authors for modeling deep processes (Fig. 2) [12].

The difference of the unit is that one of the plungers of the core holder of the setup is equipped with a chamber with a vortex mixer for mixing the test liquids immediately before they enter the rock sample. In turn, the end part of the plunger contains a number of longitudinal holes for directing the investigated liquids through them into the rock sample.

The unit includes a core holder 1, inside of which plungers 2 and 3 are installed, between which a rock sample 4 is located. A press 8 is connected to the core holder 1 through pipeline 5, valve 6 and pipeline 7 to create hydrocompression, simulating rock pressure. The pressure of hydrocompression is controlled by a pressure gauge 9. The press 8 is connected to the intake tank 12 through pipeline 7, valve 10 and pipeline 11. A cylinder with compressed gas 13 and pressure gauge 14 through valve 15, pipeline 16 and valves 17, 18, 19 are combined with piston containers 20, 21, 22. Through the valves 23, 24, 25 and the pipeline system 26, 27, 28, the piston containers 20, 21, 22 are connected to the plungers 2 and 3 by the core holder 1. The plungers 2 and 3 are equipped with three longitudinal channels 29, 30, 31 hydraulically combined with the corresponding three radial channels 32, 33, 34 through the valve 35, 36, 37. The plunger 2 of the core holder 1 is equipped with a chamber 38 with a vortex mixer 39 and longitudinal holes 40, which are hydraulically connected to the rock sample 4. Through the pipeline 27, the valve 41 and pipeline 42, plungers 2 and 3 are connected to pressure regulator 43 to maintain reservoir pressure in core holder 1. Plungers 2 and 3 are equipped with pressure gauges 44, 45, 46, 47, 48, 49. At the outlet a measuring cylinder 50 is installed from the pressure regulator 43 to select and measure the volume of working fluids.
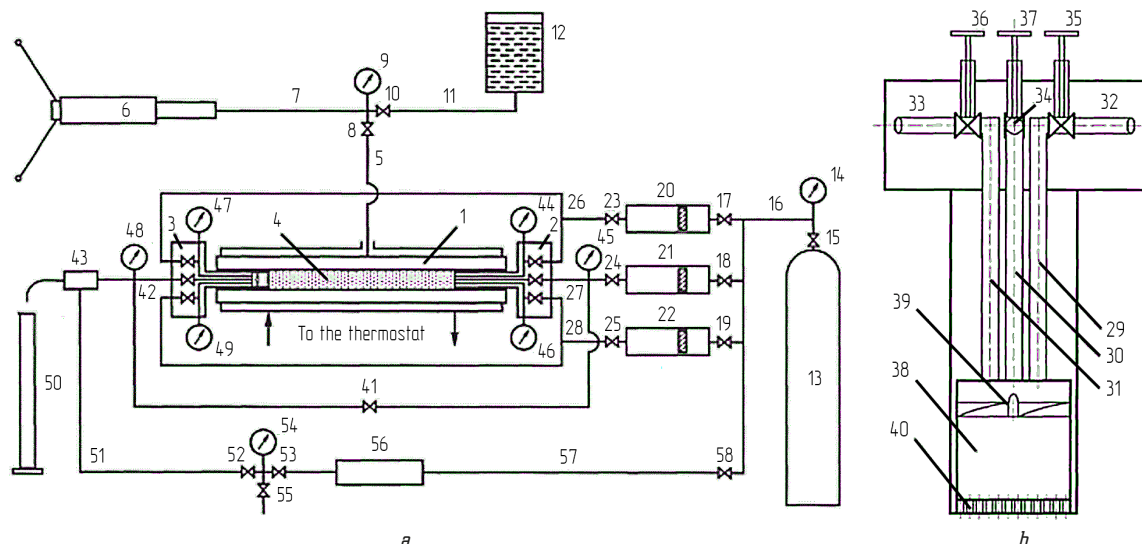
Fig. 2. Unit for studying the filtration properties of productive formations: *a* – a schematic diagram of the unit; *b* – unit plunger

The pressure regulator 43 through pipeline 51, valves 52, 53 with pressure gauge 54 and valve 55, buffer container 56, pipeline 57, valve 58, pipeline 16 and valve 15 is connected to a compressed gas cylinder 13. The required temperature in the core holder 1 is maintained by a thermostat (on diagram not shown). The entire installation, except for pressure gauges 9, 14, 44, 45, 46, 47, 48, 49, 54, press 8, intake tank 12, compressed gas cylinder 13 with valve 15 of measuring cylinder 50, is placed in a separate special thermostat, where reservoir temperature (not shown in the diagram).

The proposed unit for modeling deep processes allows exploring the filtration properties of productive formations of oil and gas wells when the bottomhole zone is exposed to various kinds of active chemicals. The use of a mixer in a plunger makes it possible to obtain more reliable data for the qualitative and quantitative assessment of the phenomena occurring in the bottomhole zone of productive formations during the technological processes of production stimulation.

Nitrogen, formation water ($\rho=1120$ kg/m^3) of these fields and gas condensate were successively filtered through a carbonate or terrigenous core sample from the productive strata of the Dnipro-Donetsk depression (DDD, Ukraine) with known data on the content of clay fractions. The condensate permeability was determined. The chemicals were then passed through five times the volume of the pore space at a rate of 3.2 ml/min.

Next, the reagents were removed by nitrogen purge and the condensate was filtered to determine the change in permeability.

3. Research results and discussion

3.1. Study of the solubility of carbonate and terrigenous rocks.
The results of studies of the solubility of carbonate and terrigenous rocks are given in Tables 1, 2.

An analysis of the data presented shows that aqueous solutions of these chemicals actually react with carbonate rocks, dissolving them (Table 1). In the process of research, the absence of destruction of the main skeleton of the rock was revealed, as evidenced by the absence of any sediment at the bottom of the tank.

Table 1

Study of the solubility of carbonate rock at temperatures of 70–150 °C for 1 hour

No. of experi-ment	Aqueous solutions of chemicals	Dissolution, %				
		70 °C	90 °C	110 °C	130 °C	150 °C
1	NH$_4$Cl	6	10	13	15	15
2	(NH$_2$)$_2$CO	0.01	0.05	0.07	0.09	0.09
3	NH$_4$NO$_3$	6	8	12	14	14
4	(NH$_2$)$_2$CO+NH$_4$Cl	12	13	15	18	18
5	(NH$_2$)$_2$CO+NH$_4$NO$_3$	10	12	13	16	16
6	NH$_4$NO$_3$+NH$_4$Cl	16	17	20	23	23
7	NH$_4$NO$_3$+NH$_4$Cl+(NH$_2$)$_2$CO	18	20	25	25	25

Table 2

Study of the solubility of terrigenous rock (sandstone) at temperatures of 70–150 °C for 3 hours

No. of experi-ment	Aqueous solutions in a ratio of 2:1	pH	Dissolution, %				
			70 °C	90 °C	110 °C	130 °C	150 °C
1	(NH$_2$)$_2$CO+NH$_4$F	4.8	7	9	13	15	15
2	(NH$_2$)$_2$CO+NH$_4$NO$_3$	4.1	3	3.1	3.2	3.2	3.2
3	(NH$_2$)$_2$CO+NH$_4$Cl	6.3	4	4.2	6	6.2	6.2
4	(NH$_2$)$_2$CO+NH$_4$HCO$_3$	11.2	16	18	21	21.5	21.5

Comparing the results of the studies, let's conclude that the considered compositions of chemical reagents, in order of increasing dissolving power of the carbonate rock, are arranged in the following order:

carbamic acid amide<ammonium nitrate<ammonium chloride<mixture of carbamic acid amide with ammonium nitrate<mixture of carbamic acid amide and ammonium chloride<mixture of ammonium nitrate and ammonium chloride<mixture of carbamic acid amide with ammonium nitrate and chloride.

The results of the study of the dissolution of terrigenous rock (Table 2) indicate that sandstone dissolves to

the maximum in a mixture of ammonium bicarbonate and carbamic acid amide (the main product of the reaction is guanidine carbonate). The minimum dissolving power of a mixture of ammonium nitrate with carbamic acid amide (the main product of the reaction is guanidine nitrate).

In the following, the names of the mixture of chemicals will be referred to by the final product of the reaction. The different dissolving ability of chemicals can be explained by the lithological composition of the studied core. So, in sandstone, clay minerals are better dissolved by alkaline compounds, in our case, by guanidine carbonate. Confirmation of this fact is the decrease in the content of clays in terrigenous rock, when before treatment $C_{cl} = 12.6$ %, and after $C_{cl} = 9.58$ %. The passage of the reaction is possible according to the scheme:

$$12(NH_2)_2 C = NH \cdot HCO_3 + Al_2O_3 =$$
$$= 2H_3 \left[Al \left((NH_2)_2 C = NH \right)_6 \right] + 12CO_2 + 15H_2O. \quad (10)$$
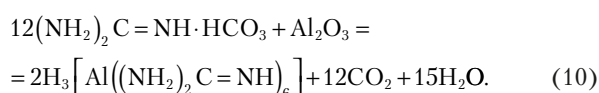
So, it has been proven that guanidine compounds dissolve silica, reducing the clay content of the rock. In addition, during the course of chemical reactions, CO_2 is formed, which contributes to an additional decrease in the viscosity of hydrocarbons.

The presence of guanidine salts was determined qualitatively according to the method [13]: an aqueous solution of a mixture of ammonium salts and diaminocarbonic acid in the presence of silicon oxide was placed in a thermostat and kept at a temperature of 150 °C for one hour. The reaction mixture was boiled with an alcoholic solution of picric acid. Upon cooling, yellow needle-shaped crystals formed, which, after drying, absorbed CO_2 and water. This fact confirms the formation of guanidine picrate. If necessary, the mass fraction of formed guanidine in solution can be determined gravimetrically [14].

Further laboratory studies consisted in determining the washing and foaming properties of the studied aqueous solutions. Guanidine salts were obtained in a reaction vessel at a temperature of 120–130 °C in the presence of pure silica gel, which is the reaction catalyst.

Further, 20 % solution of guanidine salts was introduced into formation water ($\rho = 1.17$ kg/m^3). 20 ml of the mixture was placed in a cylindrical vessel and sparged with air for 5 s. The height of the formed foam and the time during which the foam volume decreased by 50 % were recorded. According to formulas (11) and (12), the volume of foam V_f and its multiplicity K were calculated:

$$V_f = H \cdot \frac{\pi d^2}{4}; \quad (11)$$

$$K = \frac{V_f}{V_s}, \quad (12)$$

where V_f – foam volume, cm^3; H – foam height, cm; d^2 – diameter of the cylinder, cm; K – foam expansion; V_s – volume of the foaming agent solution.

The foam resistance U was determined by the ratio of the foam volume V_{30} or its height H_{30} to the initial foam volume V_f or the height H for 30 min. according to the formulas:

$$U = \frac{V_{30}}{V_f} \text{ or } U = \frac{H_{30}}{H},$$

where V_{30} – volume of foam after 30 min., cm^3.

The results of the study are presented in Table 3.

Table 3

Study of the foaming ability of the composition of chemicals with formation water

No.	Aqueous solutions	Foam volume V_f, cm^3	Multiplicity K	Foam resistance U	Foam bubble shape
1	$(NH_2)_2CO+NH_4F$	47	2.35	0.058	round
2	$(NH_2)_2CO+NH_4NO_3$	43	2.15	0.019	round
3	$(NH_2)_2CO+NH_4Cl$	54	2.7	0.034	round
4	$(NH_2)_2CO+NH_4HCO_3$	59	2.95	0.081	round

Thus, during the study, it was confirmed that guanidines are surfactants with sufficient foaming properties.

The study of the reaction products of ammonium salts showed the presence in the samples of biuret – $C_2H_5N_3O_2$, which has amphoteric properties and is simultaneously a surfactant. It is formed in the following way:

$$2H_2NCONH_2 \xrightarrow{t} (H_2NCO)_2NH + NH_3 \uparrow. \quad (13)$$

In order to confirm this assumption, a qualitative reaction for the presence of biuret was carried out. When a solution of copper sulphate was added to the reaction mixture, a violet-red color appeared, which qualitatively proves the formation of biuret [14].

Analyzing the results of the research, it was found that during the passage of the described chemical reactions, a mixture of new substances is formed that have a complex effect on the pore space of the reservoir.

3.2. Study of the solubility of carbonate and terrigenous rocks after treatment with chemicals. The results of studies of the solubility of carbonate and terrigenous rocks in solutions of these chemicals are given in Tables 4, 5.

Table 4

Results of experimental studies of changes in carbonate rock permeability under the influence of chemicals and their compositions

No. of experiment	Chemicals or chemical compositions	Average condensate permeability, μm^2	
		before exposure	after exposure
1	NH_4Cl	0.0175	0.02442
2	$(NH_2)_2CO$	0.0134	0.018938
3	NH_4NO_3	0.0162	0.0246
4	$(NH_2)_2CO+NH_4Cl$	0.0181	0.02638
5	$(NH_2)_2CO+NH_4NO_3$	0.016	0.02628
6	$NH_4NO_3+NH_4Cl$	0.0232	0.03228
7	$NH_4NO_3+NH_4Cl+(NH_2)_2CO$	0.024	0.03596

Table 5

Study of changes in the permeability of terrigenous rock (sandstone) after treatment with chemicals

No. of experiment	Chemicals	Average condensate permeability, μm^2	
		before exposure	after exposure
1	$(NH_2)_2CO+NH_4F$	0.0201	0.021
2	$(NH_2)_2CO+NH_4NO_3$	0.0145	0.0189
3	$(NH_2)_2CO+NH_4Cl$	0.0169	0.0184
4	$(NH_2)_2CO+NH_4HCO_3$	0.0157	0.0196

The results of the studies (Tables 4, 5) indicate that each of the considered chemicals contributes to an effective increase in the permeability of the pore space of natural reservoirs.

The effect occurs due to the dissolution of the carbonate and clay components of the rock, the cleansing of pores from technogenic pollution due to the presence of surface-active properties of the reaction solution, the change in the wettability of the rock and the decrease in the swelling of clay minerals. An increase in condensate permeability by an average of 1.4–1.6 times was recorded for carbonate rock (Table 4), and for terrigenous rock, by 1.05–1.3 times (Table 5).

The authors studied the effect of high temperatures on the change in the condensate permeability of the pore space of the carbonate (Fig. 3) and terrigenous (Fig. 4) core models during treatment with the considered chemicals.
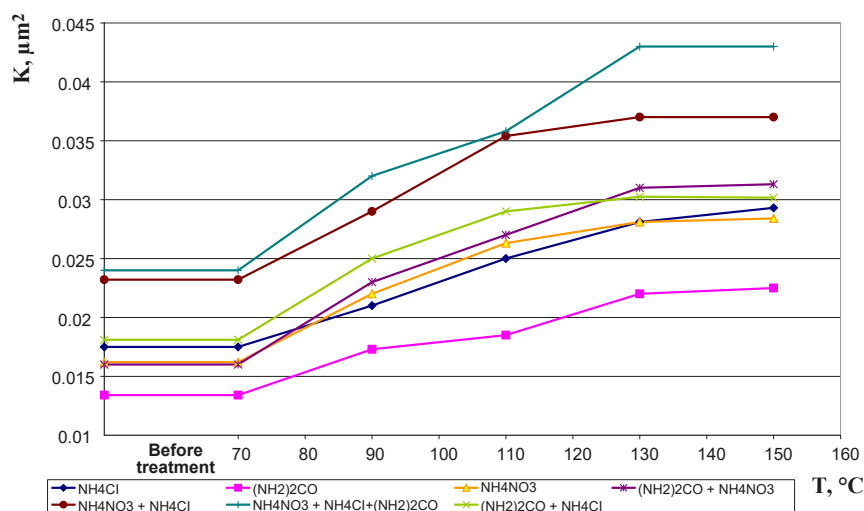
temperatures (above 70 °C). The maximum impact falls on the temperature range of 90–150 °C, while the permeability of the pore space increases for hydrocarbons by a factor of 1.15–1.32.

For mathematical representation of the process of increasing the permeability of rocks due to their dissolution by the above chemical reagents, an expression was obtained that follows from the following considerations. Let's assume that the pore medium corresponds to the capillary model, that is, it consists of n capillaries of radius r and length l (Fig. 5).

Fig. 5. Scheme of a capillary for modeling the process of increasing the permeability of the rock under the influence of chemical reagents

Fig. 3. The effect of temperature on the change in the permeability of carbonate rock for condensate during core treatment with chemicals
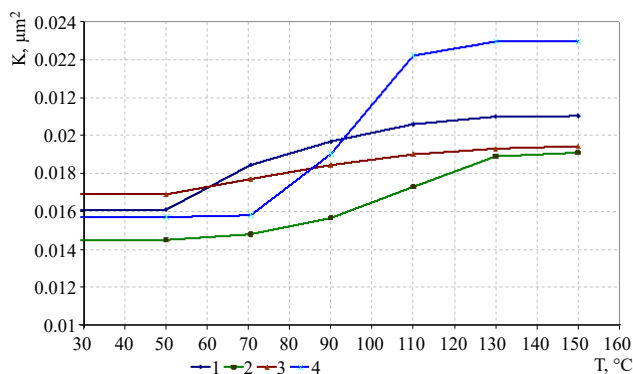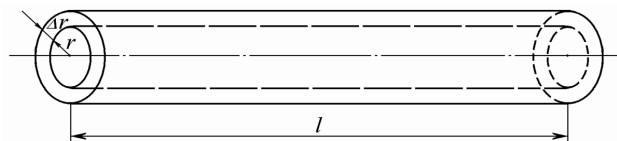

Fig. 4. Effect of temperature on the change in the permeability of terrigenous rock for condensate during core treatment with chemicals: 1 – $(NH_2)_2CO+NH_4F$; 2 – $(NH_2)_2CO+NH_4NO_3$; 3 – $(NH_2)_2CO+NH_4Cl$; 4 – $(NH_2)_2CO+NH_4HCO_3$

The research results indicate that after treatment with these chemicals at different temperatures, the permeability of the pore space of carbonate core models (Fig. 3) in the range of 70–130 °C increases by 1.5 times. A further increase in temperature does not significantly affect the reaction rate and the change in the permeability of the pore space. The results of the study of terrigenous reservoirs (Fig. 4) showed that the onset of the reaction is shifted to the zone of elevated

Let the capillary volume V_r, according to Fig. 5 is equal to:

$$V_r = \pi l r^2. \tag{14}$$

The capillary volume after exposure to its walls with chemical reagents $V_{r+\Delta r}$ and an increase in its radius by a value Δr is equal to:

$$V_{r+\Delta r} = \pi l \left(r^2 + \Delta r^2 \right). \tag{15}$$

The increase in capillary volume $V_{\Delta r}$ will be equal to:

$$V_{\Delta r} = V_{r+\Delta r} - V_r = 2\pi l r \Delta r + \pi l \Delta r^2. \tag{16}$$

According to Poiseuille's law [15], the volumetric filtration rate q of a chemical reagent in a capillary is described by the formula:

$$q = \frac{\pi \Delta p r^4}{8\mu l}, \tag{17}$$

where μ – the dynamic viscosity of the chemical reagent solution.

Let's assume that $\Delta p = \text{const}$ and $t° = \text{const}$ ($t°$ – the medium temperature). Then the volume of the chemical reagent V_r that has passed through the capillary in a very short period of time $\Delta\tau$ can be determined using the formula:

$$V_r = q\Delta\tau. \tag{18}$$

Here it is necessary to make an important assumption in further reasoning that the amount of rock dissolved by the chemical reagent is proportional to the volume of the chemical reagent that was filtered over a period of time $\Delta\tau$ according to the formula:

$$V_{\Delta r} = \psi V_r, \tag{19}$$

where ψ – dissolving power of a chemical reagent, fractions of a unit. The dissolving power of a chemical reagent ψ is a function of the concentration of the chemical reagent, the time of its interaction with the rock and temperature, i. e. $\psi = f\left(C_k, \tau, t°\right)$.

Taking into account formulas (17) and (18), expression (19) takes the form of the formula:

$$V_{\Delta r} = \psi \frac{\pi \Delta p r^4}{8\mu l} \Delta\tau. \tag{20}$$

Equating the right-hand sides of expressions (16) and (20) and passing to the limit, let's obtain the formula:

$$r^{-3}dr = \psi \frac{\Delta p}{16\mu l^2} d\tau. \tag{21}$$

Solving the resulting differential equation (21) under the boundary conditions $\tau=0$ and $r=r_0$ and taking into account that according to [16] $r^2=8k$, let's obtain equation (22) to describe the process of increasing the permeability k of the rock during its dissolution by chemical reagents:

$$k = \frac{k_0}{1-k_0 A\tau}, \tag{22}$$

where $A = \psi \frac{\Delta p}{\mu l^2}$.

From the resulting equation (22) it can be seen that the permeability of the rock k when exposed to chemical reagents increases inversely with the filtration time τ, that is, the process is mathematically described by a hyperbola (Fig. 6, 7).

Since the parameter A contains the parameters controlled in the experiment (μ, Δp, l), in addition to the coefficient ψ, which determines the process of rock dissolution by chemical reagents, it becomes possible to study the dependence of the latter on the properties of chemical reagents and the physical characteristics of the filtration process. This will ultimately allow a more complete study of the processes occurring under the influence of various kinds of chemical reagents on the bottomhole zone of the productive formation (Fig. 8, 9).
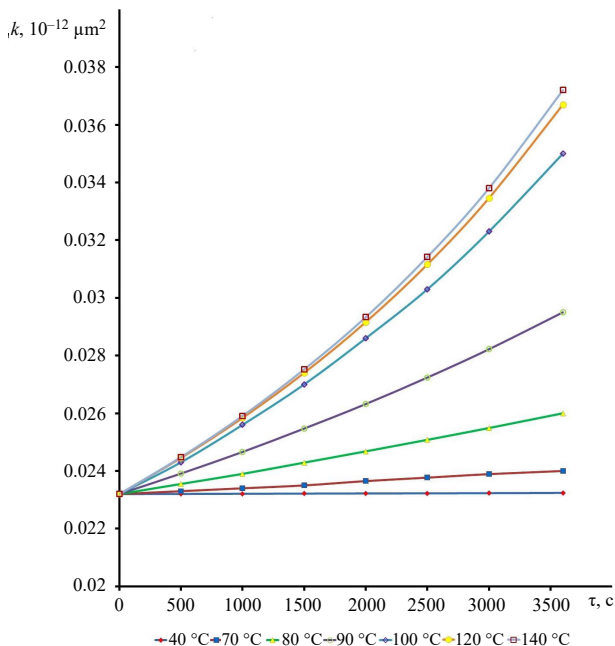

Fig. 6. Dependence of the change in the permeability of a sample of carbonate rock k in time τ of filtration of a solution of a mixture of nitrate and ammonium chloride at different temperatures t, °C
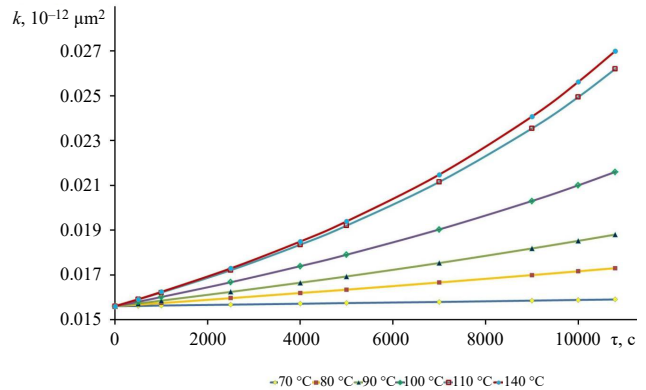
Fig. 7. Dependence of the change in the permeability of a sample of terrigenous rock k in time τ of filtration of a guanidine carbonate solution at different temperatures t, °C
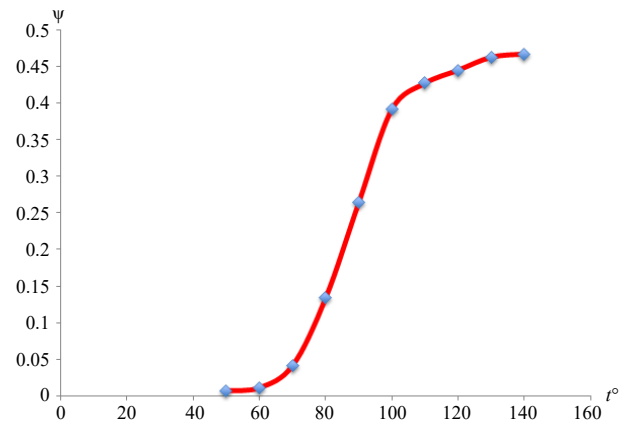
Fig. 8. Dependence of the dissolving power of the chemical reagent ψ on the temperature of the reservoir model t, °C for a carbonate reservoir when it is exposed to a mixture of ammonium nitrate and ammonium chloride
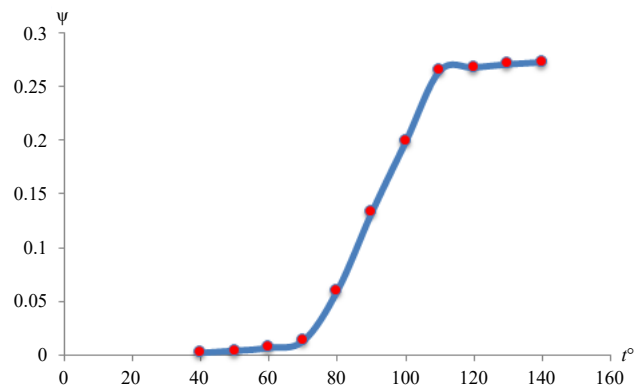
Fig. 9. Dependence of the dissolving power of the chemical reagent ψ on the temperature of the reservoir model t, °C for a terrigenous reservoir when exposed to guanidine carbonate

The good approximation properties of expression (22), as well as the understandable physical meaning of its coefficients, allow hoping for a wide application of this equation in the practice of technological calculations and designing measures to stimulate oil and gas production.

The technology of non-acid stimulation of the bottomhole formation zone using ammonium salts can be used in carbonate and sandy reservoirs in a wide range of reservoir temperatures. However, as practice has shown, the maximum complex effect on the bottomhole formation zone is recorded at temperatures above 70 °C, that is, in deep-seated formations above 3000 m. When using this technology, the concentration of active substances and their ratio, as well as

the pH of the medium, are essential. It has been established that the more clayed the reservoir, the higher the concentration of active reagents and the higher the pH should be.

The technology of complex, non-acidic action based on ammonium salts was successfully implemented in oil and gas wells of the DDD (Dnipro-Donetsk depression, Ukraine). At well 1 of the Ostroverkhivske GCF, after treatment with ammonium salts ($(NH_2)_2CO+NH_4Cl$), the gas flow rate increased from 46 thousand m^3/day up to 78 thousand m^3/day. Treatment of well 3 of the Zagorianske gas condensate field with $(NH_2)_2CO+NH_4HCO_3$ solution made it possible to restore the reduced flow rate from 12 thousand m^3/day up to 56 thousand m^3/day. The reaction to the shale reservoir of oil well 1 of the Natashynske field allowed increasing the flow rate from 2.3 tons to 5.1 tons of oil, as well as clean the reservoir from tar deposits and improve the rate of well development to self-flowing.

In the future, the authors plan to conduct a study of the effect of compositions based on ammonium salts on reservoirs with different content of clay components in wells with different degrees of stroke.

4. Conclusions

Summarizing the conducted laboratory studies and analyzing their results, the high efficiency of using compositions of chemicals based on ammonium salts to improve the filtration properties of productive carbonate and terrigenous reservoirs in high temperature zones was confirmed.

It has been proven that the treatment of productive formations with these chemicals does not lead to the formation of insoluble compounds, while increasing the efficiency of the physicochemical effect when removing reaction products from the pore space of the bottomhole formation zone. This is due to a decrease in the surface tension of the spent solution at the boundary with the rock.

The possibility of obtaining guanidine salts from diaminocarbonic acid and ammonium salts on natural silicates was proved, and a decrease in the content of clays in terrigenous rock by 1.3 times was recorded.

Experiments at the installation for studying the filtration properties of productive formations confirmed an increase in gas permeability of carbonate rocks in the temperature range of 70–130 °C up to 1.5 times and of terrigenous rocks in the temperature range of 90–150 °C up to 1.32 times. In addition, an increase in condensate permeability was recorded for carbonate rocks by 1.4–1.6 times and by 1.05–1.3 times for terrigenous rocks.

It has been established that the obtained reagents are surfactants that increase the removal properties of working solutions and reaction products from the pore space and bottomholes.

A mathematical model of the process of increasing the permeability of rocks under the influence of the investigated chemical reagents has been developed, which is described by a hyperbole and can be used in technological calculations and designing measures to stimulate oil and gas production.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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