Розроблено інноваційну технологію комплексного водневого термобарохімічного впливу (КВТБХВ) на продуктивний пласт нафтових (газових) свердловин з метою інтенсифікації видобутку вуглеводнів. В основу цієї технології покладено інтегроване використання аномальних властивостей водню в умовах багатостадійного термогазохімічного хіміко-технологічного процесу (ХТП). Підвищення ефективності технології потребує суттєвого покращення керованості базового ХТП.

Створено експериментальний комплекс для дослідження кінетики термобарохімічних процесів та фізичного моделювання комплексного впливу, в тому числі водневого, на зміну фільтраційно-ємнісних характеристик та проникності гірської породи. Комплекс дозволяє відтворювати технологічні особливості здійснення хіміко-технологічного процесу, забезпечує його протікання в умовах, максимально наближених до реальних пластових.

Експериментально доведено, що шляхом додавання до базових технологічних рідин активаторів та інгібіторів хімічних реакцій можна одержувати різні за характером протікання типи процесів та їх окремих стадій. Показано, як використання гідрореагуючих речовин на основі алюмінію дозволяє одержувати водень та підвищувати проникність гірської породи на низькотемпературній стадії процесу. Також введення полімерного нітрилу параціану активує та утримує протікання високотемпературної стадії процесу, на якій відбувається гідрокрекінг важких вуглеводнів.

Запропоновано та опрацьовано методику визначення найбільш ефективного хіміко-технологічного процесу технології КВТБХВ. Методику засновано на порівняльному аналізі результатів впливу різних за характером протікання ХТП на відновлення проникності закольматованих кернів гірської породи.

Створена методика досліджень дозволяє експериментально визначати найбільш ефективний ХТП технології КВТБХВ для використання на свердловинах з різними причинами зменшення продуктивності

Ключові слова: свердловина, інтенсифікація видобутку, термобарохімічний процес, керн, проникність, привибійна зона

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IMPROVING THE CONTROLLABILITY AND EFFECTIVENESS OF THE CHEMICAL-TECHNOLOGICAL PROCESS OF THE TECHNOLOGY FOR HYDROGEN THERMOBARIC CHEMICAL STIMULATION OF HYDROCARBON RECOVERY

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1. Introduction

The productivity of oil, gas and gas condensate wells is determined by the qualitative state of the bottom-hole formation zone (BFZ), which is characterized mainly by its permeability, that is, the ability to filter hydrocarbons to the bottom of the well. Almost all the layers are rocks such as sands, sandstones, carbonates, dolomites, clays, at the same time they have a sufficiently high porosity and low natural permeability. Therefore, through such rocks, it is possible to filter, as a rule, only gas, and then only at high reservoir pressure. The natural permeability of the productive formation significantly deteriorates even at the stage of the initial opening of the well (drilling and casing), at which mechanical mudding of the bottom-hole formation zone of the well with drilling and cementing muds occurs. During the entire life of the well, the BFZ formation damage is taken place by the products of formation destruction and asphalt-resin-paraffin wax deposits (ARPWD), which leads to a further decrease in the permeability of the productive formation and a decrease in well production, respectively.

These factors affect the quality of the BFZ filtration properties, violate the hydrodynamic connection of the reservoir with the well, resulting in reduced productivity.

The solution to the problem of increasing production and increasing the hydrocarbon extraction coefficient is seen in the creation and implementation of technologies, during the implementation of which an integrated multifactor physical and chemical effect on BFZ is realized. Moreover, this influence should be aimed at eliminating during one treatment all the main causes of clogging, as well as improving the filtration capacity of the reservoir. To increase the effectiveness of such technologies, it is necessary to study all the features of chemical-technological processes that occur both in the casing of the well and in the porous medium of its bottom-hole formation zone.

An innovative hydrogen thermobaric chemical technology is developed for stimulating hydrocarbon production from oil and gas wells. The basis of this technology is the integrated use of the anomalous properties of hydrogen in a multistage thermal-gas-chemical chemical-technological process (CTP). Further improvement of the technology requires a significant increase in the controllability of the basic chemical-technological process.

Improving the controllability of the specified chemical-technological process is an urgent task and one of the main directions of increasing the efficiency and competitiveness of this technology, its relevance to implementation.

2. Literature review and problem statement

Modern technologies for increasing oil and gas production, including from non-traditional sources (shale gas, coalbed methane), based on various types of physical and chemical effects on the productive formation. These are mechanical, thermal, acid, alkaline treatments, or combinations thereof. Recently, there has been a trend towards the creation and production of technologies that have a comprehensive focus on solving several problems of decreasing well flow rates at once [1]. Moreover, one of the significant roles is played by advanced chemical methods that integrate with thermal and mechanical.

So, for the development of deposits by heavy oil and natural bitumen, the technology of steam gravity drainage (SAGD) is quite effectively applied [2]. The physical meaning of this technology is to inject a large volume of high-temperature steam through paired horizontal wells, one of which is at a distance of up to 5 meters above the second. The energy of the phase transition is spent on heating the rock and fluid. After heating, steam is continued to be pumped into the upper well, and oil is produced from the lower well, the viscosity of which is significantly reduced compared to the initial one. SAGD technology and its advanced version of HI-SAGD [3] are characterized by a rather high oil recovery coefficient. However, increasing the efficiency and economy of this technology was achieved precisely by combining heat treatment with chemical. In ES-SAGD technology, steam and hot solvents of hydrocarbons are on duty [4]. It should be noted that these technologies are very difficult to implement, require large material, primarily energy costs. Steam injection with circulation to the beginning of drainage lasts several months. The method does not work in vertical wells; it requires special pair drilling of horizontal wells. These technologies are not used for the renovation of working wells, which are currently the vast majority.

One of the most effective methods of mechanical impact on the pay horizon is the hydraulic fracturing (HF) of formation and its varieties. The method is based on the injection of a special fracture fluid (gel) into the productive horizon under a pressure higher than the formation pressure to the appearance of a crack in the reservoir, which significantly increases the area of fluid inflow. In this case, it is not possible to talk about restoring or increasing the natural permeability of the rock, but rather about increasing the well supply area. Multistage HF along with horizontal drilling made it possible to produce gas from tight sandstones and shales [5]. The implementation of HF technology is well developed, it is carried out using modern modeling methods that can optimize the process and create the design of the future fracture [6]. But in the case of HF, this technology becomes more effective when combined with chemical methods [7]. Thus, the use of special thermochemical fluids initiates microexplosions in the formation, forms additional cracks, and lowers the threshold of rock mechanical strength.

At the same time, HF technologies have limitations in use associated with the presence of high paraffin content in the fluid, the proximity of aquifers, which creates a high threat of a further increase in water cut in the formation and the like. In addition, a large amount of water is required for HF, after which it needs to be cleaned (and this is thousands, and in the case of multistage HF, tens of thousands of cubic meters). The technology is difficult to implement, requires the participation of many units of special equipment. Use in wells with small flow rates is impractical.

Another modern direction of processing the bottom-hole formation zone of a well with the aim of stimulation is the use of chemical energy sources to create both mechanical and thermal effects on the formation. The use of propellants (components of rocket fuels) [8], which are ignited in the bottom-hole zone of the well, can be quite promising. During combustion, a large number of gases are formed that break the formation. But energy is spent mainly on mechanical cracking with little heating. Cracks are not fixed, there is a possibility of BFZ destruction.

An interesting thermobaric chemical technology is the stimulation of hydrocarbon production, in which the high-temperature influence of hydroreactive agents is carried out on the bottom-hole formation zone of the well [9], and their combustion in the casing together with combustible and oxidizing mixtures leads to chemical treatment of the formation and mechanical fracturing. The process is accompanied by thermal cracking-pyrolysis of high molecular weight hydrocarbon compounds. Hydrogen, which in this technology is released from boron-based compounds (in particular, isopropyl meta-carborane) is used only at the high-temperature stage of the process. The pyrolysis temperature (about 800 °C) leads to the formation of pyrolytic coke and various resins in the formation. If it is not possible to organize in-situ combustion in the presence of oxygen, these substances can become bridging agent and further reduce the permeability of the formation. This approach has one more drawback – the lack of effective factors influencing the increase in the permeability of the reservoir on the low-temperature phase of processing, as well as the difficulty of controlling the cracking process, which in some cases can lead to the destruction of the reservoir. Studies on saturation of cores with activated hydrogen at elevated temperatures and pressures have confirmed a decrease in their tensile strength. Serious drawbacks of this technology include the fact that organochlorine compounds are used as a buffer liquid (for delivering hydroreactive agents (HRA) to the reaction zone) [10], which are prohibited in many countries for use in the oil and gas industry. To date, no literature data has been found regarding mathematical modeling and the development of computer design for the thermochemical process implemented in this technology. It should be noted that computer and mathematical modeling has already become an indispensable toolkit for high-quality preparation for the industrial implementation of modern complex methods for stimulating production in real wells.

Scientific and practical foundations of innovative hydrogen thermobaric chemical technology [11] for the stimulation of hydrocarbon production have been developed. Its most effective modification, in which hydrogen is used at different stages of the chemical-technological process, is the technology of complex hydrogen and thermobaric chemical effects (CHTBCE) on the productive formation [12]. This technology is implemented by separately-sequential delivery of two process fluids into the bottom-hole zone of the productive formation, each of which represents a suspension from combustible-oxidative mixtures (COM) and hydroreactive agents. Mixing these liquids leads to a series of exothermic chemical reactions with the active formation of gases (H_2, CO, CO_2, NO, N_2O, NO_2), hot acids – hydrochloric, nitric and hydrofluoric. Fig. 1 presents a diagram of the implementation of the technological process and the main factors affecting the formation [11]. Hydrogen, which is released at the initial stage of the thermochemical process, improves the permeability of the reservoir and helps filter chemically active components into the formation, where their secondary reactions with the mineral part of the formation and bridging agent occur. At the high-temperature stage of the process (250–350 °C) under high pressure conditions, in the presence of active (atomic and molecular) hydrogen and catalysts, the process of ARPWD hydrocracking is carried out with the formation of gas and distillate fractions.

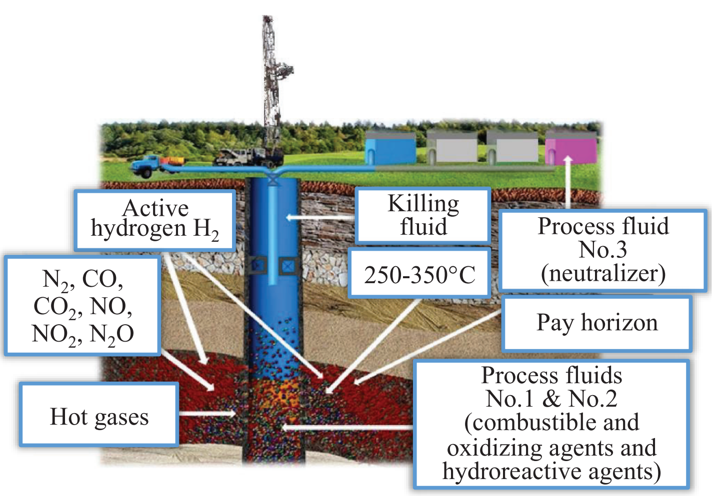

Fig. 1. Scheme of the implementation of the CHTBCE technological process and the main factors affecting the reservoir

Hot gases generated during the process are effectively involved in the processing process. In addition to heating the pore space, CO_2 reduces the viscosity of oil, NO_2 reacts with water, including formation water, and forms nitric acid directly in the BFZ, CO helps to improve the filtration properties of the formation.

HRA reaction with water reduces the BFZ water content leads to dehydration of the heterophase reaction medium and an increase in the concentration of nitric and hydrochloric acids formed during the reaction. A mixture of nitric and hydrochloric acids leads to the formation of aqua regia, the chemical activity of which is significantly higher than in each of these acids separately. This allows to effectively influence the solid phase of cementing and drilling muds, the mineral part of the reservoir of both terrigenous and carbonate reservoirs. The high-temperature effect on the treated horizon by reaction products leads not only to chemical treatment of the formation, but also to mechanical cracking due to high pressure and temperature gradients. Today, with the help of complex hydrogen thermobaric chemical technology, more than 100 wells have been processed in Ukraine, Georgia, Turkmenistan, China, Turkey, Russia, and India. The obtained results confirmed the high efficiency of this technological approach.

Expanding the possibilities of applying the CHTBCE technology, including for the stimulation of hydrocarbon production from non-traditional sources, and the growth of its demand, directly depends on the ability to provide the necessary levels of chemical and thermophysical factors affecting BFZ. This applies to each of the CTP stages, especially those at which hydrogen is generated. In this case, it is necessary to have mechanisms for controlling the duration of both the entire multistage thermobaric chemical process and each of its individual stages. Pilot research at the well is a valuable operation, during which very large funds are spent on materials, working mixtures, the use of equipment and human resources. In addition, errors in the preparation and conduct of work can lead to negative and sometimes irreversible results. Therefore, the mechanism for improving the controllability of the specified CTP and increasing the efficiency of technology implementation should be worked out in the laboratory. This requires a study of the kinetics of thermobaric chemical processes and physical modeling of the complex effect on the filtration-capacitive characteristics and permeability of the rock in conditions as close as possible to real well ones.

Currently, there are no experimental and technical means for conducting these studies. The mathematical model of the thermobaric chemical process is refined only taking into account the effect of hydrogen activation of diffusion [13]. In this case, neither the nature of the course, nor the staging of the chemical-technological process is taken into account.

Therefore, there is reason to believe that the lack of certainty of the mechanisms for improving the controllability of CHTBCE CTP makes it necessary to conduct laboratory studies by physical modeling.

3. The aim and objectives of research

The aim of research is increasing the controllability and efficiency of the chemical-technological process of multistage hydrogen thermobaric chemical effects on the pay horizons of oil and gas wells through physical modeling.

To achieve the aim, the following objectives are set:

– to create an experimental complex for studying the kinetics of thermobaric chemical processes and physical modeling of the complex effect on filtration-capacitive characteristics and rock permeability of productive horizons of oil and gas wells. In this case, the complex should reproduce thermobaric conditions as close as possible to the real past;

– to conduct experimental studies of the kinetics of chemical-technological processes, on which the CHTBCE technology is based, in conditions close to reservoir;

– to propose a methodology for determining the effectiveness of thermobaric chemical processes of a different nature;

– to analyze the results of experimental studies and give recommendations on their use to increase the controllability of the chemical-technological process and the efficiency of using the technology of complex hydrogen thermobaric chemical effects on the productive horizons of oil and gas wells.

4. Basic requirements for the experimental complex for studying the kinetics of processes and their influence on rock permeability

By controllability of a chemical-technological process is meant the possibility of ensuring a given duration of the process as a whole and of each of its individual stages. Also, the process of producing hydrogen at predetermined concentrations and ensuring the required temperature and pressure levels should also be guided at each stage, especially when the stage is limiting.

The analysis of literary sources shows that there are no research facilities and complexes in the world on which physical modeling of the indicated chemical-technological processes would be possible without significant modernization [11, 14–16]. This is due to the fact that the following technical requirements are put forward to the research complex:

– provide sequential mixing of two or more outlet liquids in a vertical extended cylindrical reactor at initial pressures and temperatures in it, close to reservoir;

– withstand temperatures up to 400 °C (short-term up to 600 °C) and pressures up to 50 MPa (short-term up to 70 MPa). It is such thermobaric parameters that characterize the CHTBCE CTP technology in reservoir conditions;

– in the modes specified in the previous paragraph, withstand the variable effects of aggressive media – from acid to alkaline;

– keep tightness, even in the presence of activated hydrogen, which has an abnormally high filtration and diffuse characteristics compared to all substances in nature;

– it should be possible to measure and fix temperatures and pressures during the CTP duration;

– the complex should determine the thermobaric and chemical effect of liquid and gaseous products of the COM-HRA reaction, including hydrogen, on the change of the filtration characteristics of rock cores. All these processes should proceed under thermobaric conditions close to reservoir ones.

5. The results of experimental studies to improve the controllability of the chemical-technological process of CHTBCE technology

5. 1. An experimental complex for studying the kinetics of thermobaric chemical processes and their influence on rock permeability

The scheme of the created research complex, which meets all the above requirements, is shown in Fig. 2. The complex consists of four experimental modules, each of which is indicated by a dotted line in the diagram and indicated by Roman numerals I–IV.

Experimental module I is intended for the physical modeling of thermobaric chemical processes and the study of their kinetics, which occur in BFZ under conditions as close as possible to the borehole ones. The main element of module I is a cylindrical reactor with an inner diameter of 62 mm and a height of more than 2.5 meters (item 1). The maximum allowable pressure inside the reactor is 70 MPa. The maximum temperature is up to 700 °C.

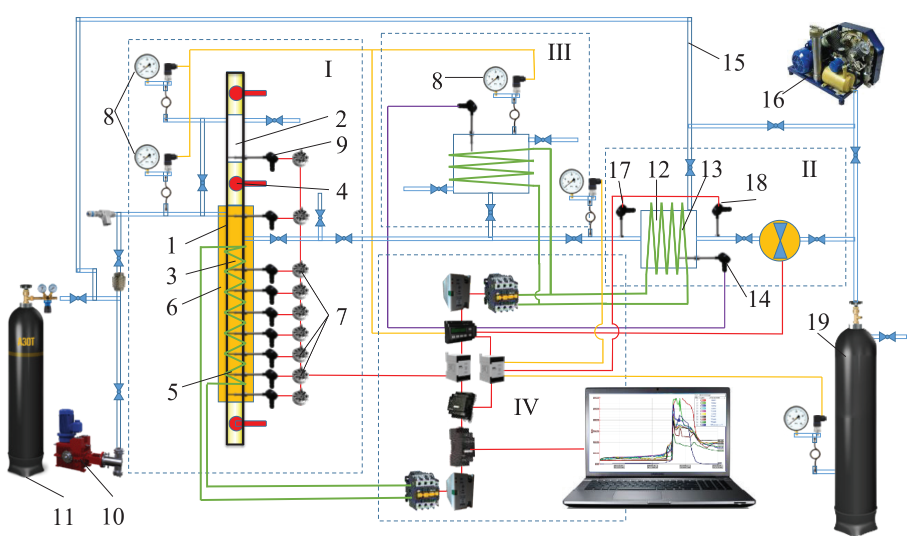

Fig. 2. The scheme of the research complex:
1 – reactor, 2 – upper reactor chamber, 3 – lower reactor chamber, 4 – ball valve, 5 – thermocable, 6 – thermocouple, 7 – temperature sensors, 8 – pressure gauges, 9 – temperature sensors, 10 – high pressure hydraulic pump, 11 – cylinder with argon or nitrogen, 12 – core sample holder, 13 – thermal cable, 14 – temperature sensor, 15 – high pressure line, 16 – high pressure compressor, 17, 18 – temperature sensor, 19 – receiver

The internal volume of the special ball valve 4 is divided into two parts 2 and 3, in which the process fluids for mixing are placed, in particular the liquid with a higher density in the upper chamber 2. The reactor is equipped with a pre-heating system 5 and thermal stabilization 6 and a unit for providing a given initial pressure in the reactor 10, 11, 16, which allows high-precision modeling of the course of thermobaric chemical processes under conditions as close as possible to reservoir. Thermometry is carried out by thermocouples 7, 9 located along the entire height of the reactor. Thermocouples in the lower chamber allow measuring the temperature without interruption in the chemical reaction zone, while others measure the temperature of reaction products, including gaseous ones.

The experimental module II is designed to study the filtration-capacitive characteristics and permeability of the rock. This module can be used as a standalone installation for research on purpose. But as part of the complex, it is with its help that it becomes possible to conduct studies of the thermobaric and chemical effects of liquid and gaseous reaction products that are formed during CTP in module I to change the filtration characteristics of natural or artificial rock core samples.

The key element of the II module is core sample holder 12. It houses the test sample of core sample material. The sealing material of the core sample holder and matrix is resistant to high temperatures of more than 250 °C and aggressive media such as concentrated acids and alkalis, hydrocarbons and concentrated brines. Its design provides reliable tight pneumatic or hydraulic compression of core sample material, which in turn provides filtering of the studied fluids through the core sample and eliminates lateral leakage during research. A high pressure line connected to the core sample holder is designed to compress core sample material to reservoir pressures (the unit is unified and the source of pressure can be a cylinder with compressed gas, for example, argon or nitrogen 11 or a liquid high pressure pump (up to 60 MPa) 10 or a pneumatic high pressure compressor 16.

The core sample is heated to a predetermined temperature using thermal cable 13. To fix the core sample temperature, a resistance thermometer 14 is mounted in the core sample holder.

A very important feature of the core sample holder design, which makes it possible to approximate the conditions for studying filtration in reservoirs, is the possibility of organizing back pressure at the outlet from the core sample, which is supplied from receiver 19. This allows to set real pressure drops per unit length of the core sample and prevent the process of boiling up of the liquid phase at the outlet heterophase flow of formation fluids and salting out of chemically active components. During filtration, thermocouples 17 and 18 measure the temperature of the medium at the inlet and outlet of the core sample, it is possible to study the temperature inside the core sample or on its side surface.

The complex also includes experimental module III, which is designed to study the effect of high-temperature reaction products of the COM-HRA reaction on the change in the properties of fluids that are in the internal pore space of a rock and impair its filtration properties. The results of these studies are not considered in this publication.

The hardware and software module of the IV complex allows measuring process parameters with high discreteness and accuracy, forming databases from them for further storage, and visualizing these parameters over time in the form of graphs.

Fig. 3, 4 shows photographs of experimental modules I and II, respectively.

Fig. 3. Module I for the physical modeling of thermobaric chemical processes and the study of their kinetics

Fig. 4. Module II for studying the thermobaric and chemical effects of liquid and gaseous reaction products on the change of rock filtration characteristics

The research complex, in addition to the hardware and software module IV, is located in the armored chambers with forced ventilation, and all the controls and the collection of current information are brought out. The recording, processing and visualization of research results are made using computers located in the premises for researchers.

5. 2. Experimental studies to improve the controllability of chemical-technological processes of CHTBCE technology

One of the effective ways to solve this problem is to improve the chemical composition of the COM-HRA system, first of all, by using new types of chemical activators or CTP inhibitors, which are added to the basic working mixtures [17].

Fig. 5–7 are graphs of temperature and pressure changes in the reactor during the course of the process, which were obtained by modeling thermobaric chemical processes with different contents of inhibitors and activators of reactions.

Fig. 5 shows a graph of the thermobaric process, the course of which is ensured by the reactions of the COM-HRA basic chemical system.

When mixing multicomponent chemical systems, the process begins with the interaction of nitric acid and sodium nitrite (sodium nitrite is one of the strongest reducing agents), which leads to an increase in temperature and the appearance of the first temperature peak on the graph. In this case, a mixture of nitrogen oxides begins to be released.

$$2NaNO_2+2HNO_3 \rightarrow 2NaNO_3+NO_2\uparrow+NO\uparrow+H_2O,$$

Q=443.11 kJ/kg.

With increasing temperature, nitrate begins to interact with sodium nitrite.

$$NaNO_2+NH_4NO_3 \rightarrow N_2+2H_2O+NaNO_3,$$

Q=4688 kJ/kg.

During the reaction, the $NaNO_3$ salt is released, which inhibits the rate of other reactions. In this case, the salts formed during the reaction act as inhibitors; therefore, a gradual increase in temperature occurs. Special inhibitors of the low-temperature stage of the process are also introduced. A sharp increase in temperature at this stage is also hindered by a sharp increase in the solubility of the granules, and also removes heat from the solution. Thus, by introducing special inhibitors, organizing the process with the formation of salts as reaction inhibitors and using granular substances, it is possible to slow down the onset of the active stage.

This type of process is advisable to use for processing oil wells with terrigenous pay horizons in the presence of injectivity. The duration of such a process in the reactor is about 30 minutes. At its low-temperature stage, which is accompanied by the evolution of hydrogen and lasts 17 minutes, there is a slight, but constant increase in temperature in the reaction zone to the level of 130–150 °C (green curve). This stage is necessary for preheating the pore space of the BFZ with a partial improvement in the filtration capacity of the reservoir, including due to the hydrogen action. The high temperature stage lasts approximately 10 minutes. The temperature increase in the reaction zone reaches 340 °C. The pressure does not significantly increase – up to 15 MPa (purple curve).

The second cycle of studies was devoted to the organization of the process, which would be identical to the previous thermobaric chemical process in terms of the parameters of the high-temperature stage. But it is necessary to significantly increase the duration of the low-temperature stage. Such a process is advisable to use in horizontal wells with a tight reservoir. The duration of the low-temperature stage with the evolution of hydrogen is due to the need to improve the filtration properties of the reservoir before the active high-temperature stage begins. At the same time, for the CTP quality flow, the technological procedure for processing horizontal or deviated wells using the CHTBCE technology requires the tubing to stay in the processing zone when process fluids are delivered to the bottom. It is necessary to have additional time for their removal from the reaction zone before the start of the CHTBCE high-temperature stage. Fig. 6 shows a graphical dependence of the course of the thermobaric chemical process. It is obvious that the duration of the low-temperature stage (up to 23 minutes) is significantly increased, and during its course there is an increase in temperature in the reaction zone only to the level of 60–70 °C. This time is enough to solve the requirements of technological regulations. Such a process is organized due to the addition of inhibitors of the low-temperature stage and the stage of the beginning of the active phase of reactions in the basic COM-HRA composition.

To organize a highly energetic effect on the formation with the maximum allowable temperatures and pressures (the latter are regulated by the rate of gas removal), it is necessary to accelerate the course of reactions and stimulate the combustible-oxidation process. Such a process is presented in Fig. 7. The duration of the thermobaric process is approximately 7 minutes; the low-temperature stage is 3.5 minutes. Moreover, the maximum values of temperature increase in the reaction zone reach 450 °C, and pressures – 25 MPa. Such a process is organized by using hydroreactive agents based on aluminum and sodium hydride as part of the COM-HRA system. At the low-temperature stage, during the exothermic reaction, they accelerate the flow of the chemical-technological process, dehydrate the medium and generate hydrogen, which in turn increases the initial permeability of the rock.

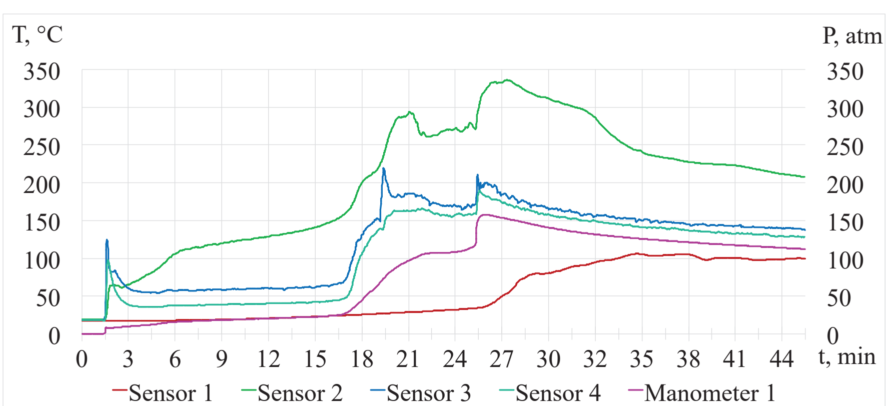

Fig. 5. Graphical visualization of the thermobaric chemical process with the basic composition of the components of the COM-HRA system

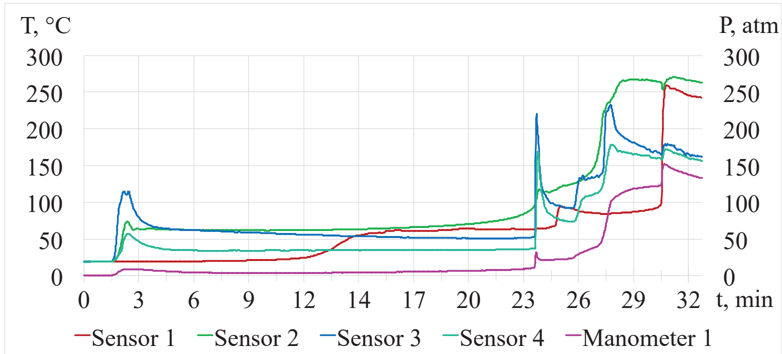

Fig. 6. Thermobaric chemical process with addition of inhibitors of low-temperature stage reactions in COM-HRA

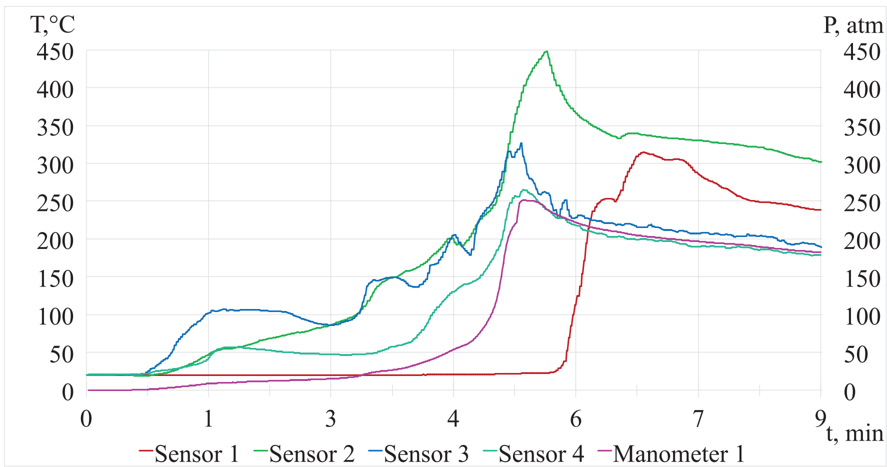

Fig. 7. Thermobaric chemical process with HRA and polymer nitrile activation

The acceleration of the combustible-oxidative process with increasing temperature was achieved by adding into the base composition of COM-HRA polymer nitrile paracyanogen in an amount of up to 1 % of the mass. Paracyanogen, which own synthesis technology was developed at IPMash NAS of Ukraine, is a very effective activator of combustion processes. The temperature of its combustion in oxygen reaches 3200 °C, and its presence in COM-HRA, even in insignificant amounts, makes the chain process [18, 19].

The release of paracyanogen begins at temperatures around 300 °C and already starting from 200 °C the reactions of thermal decomposition of urea and ammonium nitrate occur. Considering that at this point urea and ammonium nitrate remain in small amounts in the reaction zone, no significant energy release occurs. However, thanks to the paracyanogen, greater pressure is achieved, and a more gentle temperature drop.

Such a process can be used to treat reservoirs of both oil and gas wells, in which it is advisable to organize rapid processes with a sharp increase in temperature and pressure to increase permeability. With a packer installed, which cuts off the reaction zone from the main part of the casing, at a low injectivity, a significantly higher pressure level can be obtained, which allows not only the CHTBCE process, but also the fluid and gas micro fracturing of the formation.

5. 3. The methodology for determining the most effective chemical process

The presence in the experimental complex of a module for studying the filtration-capacitive characteristics of rock core sample allows not only to simulate various CTPs of CHTBCE technologies, but also to determine their effectiveness by the main criterion – the largest increase in core sample permeability. Effectiveness evaluation of processes is more convenient and correct to carry out by comparing relative indicators. Such a value is the permeability recovery coefficient, indicating the degree of permeability recovery after technological treatment of the bottom-hole formation zone and is determined in units or percent

$$\beta = k/k_0,$$

where β – the recovery coefficient of permeability; k – the permeability of the pore space after the technological operation to increase permeability, MD; k_0 – the initial permeability of the pore space to formation damage, MD.

During the research, the initial level of phase permeability of natural rock or synthetic core samples is measured by filtering oil from a specific field (or model oil). At the same time, natural core samples are preliminarily removed from water and hydrocarbon bridging agents by extraction, washing and drying according to a standardized method. Subsequently, the core samples are saturated with various formation damage fluids (ARPWD, water-oil emulsions, salt solutions, etc.), simulating the causes of permeability reduction in a real oil or gas reservoir, and the phase permeability is measured again when filtering model oil.

Further, in the research complex, under conditions close to reservoir conditions, liquid and gaseous reaction products that are formed during the course of the selected CHTBCE process are pumped through the core samples. After that, the final filtration rates of the model oil are already measured, and permeability restoration coefficients are calculated.

As an example of using the technique, Fig. 8 shows a diagram that shows the results of experimental studies to determine the effectiveness of the above CTP on the change in permeability and restoration of filtration-capacitive characteristics of three natural core samples from one layer of an oil well. The reason for the decline in productivity of this well was the filling of the pore space of the BFZ of the oil-water emulsion. The emulsion, samples of which were also taken from this well, is very stable and does not collapse even at high temperatures. The use of standard demulsifying agent is also ineffective.

In the diagrams (Fig. 8, from left to right), each 3 columns reflect the oil permeability of each of the three core samples that are studied, to saturation of the oil-water emulsion, after saturation and after processing using the CHTBCE process, which is sequentially described in section 5. All three core samples after preparation show approximately one level of initial phase permeability. The indicators practically do not differ even after the colmatage of an oil-water emulsion (12 mD). As for the phase permeability indices of the core after hydrogen thermobaric chemical treatment, in this case they already differ. So, the process with the basic composition of the components of the COM-HRA system is quite effective; almost complete restoration of the permeability of 88 mD – initial, 86 mD – after treatment was obtained. Permeability recovery coefficient $\beta=0.977$.

The thermobaric chemical process with the adding of inhibitors of the reactions of the low-temperature stage in the composition of COM-HRA in this case shows the worst result. This is, first of all, due to the fact that during the course of a long low-temperature stage, the thermochemical potential of the system is spent inefficiently, because the oil-water emulsion practically does not collapse at this temperature level. Hydrogen is also not used very effectively, because it is known that the greatest effect of hydrogen activation of diffusion and filtration is achieved with significantly lower initial rock permeability. Permeability value: initial 86 mD, after treatment – 78 mD. Permeability recovery coefficient – 0.9.

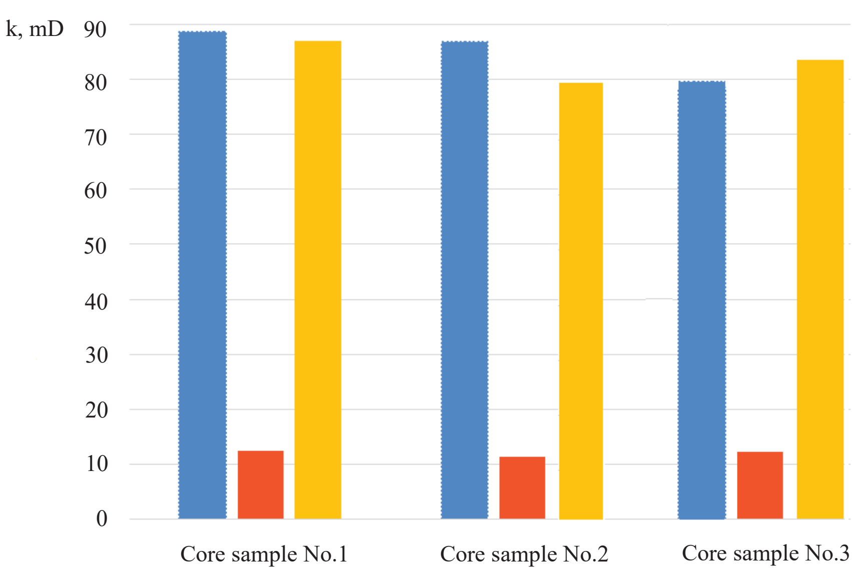

Fig. 8. Change in core sample permeability under the influence of various CHTBCE types: ■ – before saturation by the oil-water emulsion; ■ – after saturation by the oil-water emulsion; ■ – after CHTBCE

The best results in improving permeability (from 80 mD to 84 mD) are achieved after using a thermobaric chemical process with activation of hydroreactive agents and polymeric nitrile (Fig. 8, core sample number 3). Phase permeability is not only restored, but also becomes larger than the initial one. The permeability recovery coefficient is 1.05. This is explained by the maximum efficiency of using the hydrogen thermobaric chemical process in this case. The destruction of the oil-water emulsion begins already at the initial stage of the process. The increase in pressure leads to a more rapid filtration of working substances into the pore space of the rock. HRAs react with water inside the core sample to generate hydrogen, and hydrogen at this temperature level not only improves permeability, but also takes part in hydrocracking reactions of heavy oil fractions. A significant amount of hydrogen and temperature and pressure gradients lead to the formation of an additional microcrack system, which explains the increase in permeability compared to the initial one.

Thus, the most effective CTP for solving a specific problem has been experimentally determined.

The obtained absolute values of the core sample phase permeability after thermobaric chemical exposure are used to verify a 3D computer model of the CHTBCE process in the well and to refine the design of its processing.

6. Discussion of research results to improve the efficiency of the CHTBCE technology

The chemical-technological process that underlies the CHTBCE technology is very complex, the kinetic characteristics and the nature of its course are very dependent on pressure and temperature in the reaction zone. This is due to the fact that COM-HRA consists of many components, each of which is characterized by its physicochemical properties (phase transition temperature, thermal destruction parameters, chemical activity, etc.). Ammonium nitrate alone has nine thermal decomposition paths.

Therefore, for the first time under the thermobaric conditions, which are as close as possible to the reservoir conditions, the real experimental results obtained from the flow of chemical-technological processes of the CHTBCE technology are obtained at the created experimental complex. To this, the processes are investigated at maximum pressures of 70.0 MPa, which is significantly less than the borehole ones. A very important design feature of the core sample holder due to the organization of backpressure at the core sample exit, also makes it possible to approximate the conditions for studying filtration through the core sample in the reservoir. Firstly, this makes it possible to set real pressure drops per unit length of the core sample and to prevent the formation of a heterogeneous phase stream and salting out of chemically active components and formation fluids (oil, gas and formation water) under conditions of low or absent pressure at the outlet. Also, the unit ensures the identity of the main technological technique of CHTBCE technology, namely, mixing two output fluids in a vertical long cylindrical reactor, which simulates the bottom-hole formation zone of the well.

Therefore, the reliability of measuring the kinetic and thermobaric characteristics of the process is one of the main advantages of the created complex. Controlled modes with a long low-temperature hydrogen stage of the process and a regime with maximum levels of temperatures and pressures (stage of hydrocracking of heavy hydrocarbons) are obtained.

All these indicated rock features make it possible to determine the most effective CTP when introducing the CHTBCE technology.

So, taking into account the fact that core samples and water-oil emulsions that took part in the study are obtained from a specific problem well, CPT is selected for its treatment using the CHTBCE technology with the addition of activators in the HRA and polymer nitrile paracyan forms to the base working mixtures. The obtained permeability changes are used to refine the 3D computer model of the CHTBCE process in the well and to analyze the design of its technological processing.

The implementation result proves the high efficiency of the process, and the modeling results according to the revised methodology have small discrepancies with the results of industrial implementation. In particular, the real daily oil production rate after well treatment increased by 2 times, while the calculated indicator by the updated mathematical model is 1.73 times, and by the unspecified by 1.6.

A very promising direction of the use of CHTBCE technology is its application in horizontal and deviated wells. This is especially important when stimulating gas production of tight sandstones and shales, highly viscous oil, etc. New technological regulations have already been created and the first pilot tests of the technology have been carried out, which have yielded a positive result. But, if in vertical wells the process of mixing process fluids occurs due to the difference in their densities, then in horizontal wells such a process is impossible. It is supposed to squeeze one fluid into another at a given cost while moving the tubing or flexible pipe (when using coiled tubing) along the casing. However, the created experimental complex currently does not allow physical modeling of the course of these processes. To this end, the complex will be equipped with another experimental module being created, which will subsequently allow these important studies to be carried out.

7. Conclusions

1. An experimental complex has been created for studying the kinetics of thermobaric chemical processes and physical modeling of the complex effect, including hydrogen, of changing filtration-capacitive characteristics and rock permeability. The complex allows reproducing the technological features of the implementation of the chemical-technological process of the CHTBCE technology, ensures its flow under conditions as close as possible to the real reservoir.

2. The possibility of controlling the nature of the multistage thermobaric chemical process and its individual stages by adding activators and inhibitors of chemical reactions to the base process fluids has been experimentally proved. It is shown how the use of special inhibitors of chemical reactions and hydroreactive agents based on aluminum and sodium makes it possible to increase the duration of the low-temperature stage of the process, at which the resulting hydrogen acts as an activator of rock diffusion and filtration. Also, the presence of polymer nitrile paracyanogen in the chemical composition is defined, which activates and maintains the temperature level of the high-temperature stage of the process at which heavy hydrocarbons are hydrocracked. Moreover, paracyanogen, added to the system in an amount of less than 1 %, contributes to the maximum short-term temperature increase (up to 450 °C).

3. A method for determining the most effective chemical-technological process of the CHTBCE technology has been proposed and worked out by the example of solving a specific problem of restoring the core sample permeability hardened by a water-oil emulsion resistant to destruction. The methodology is based on a comparative analysis of the results of the impact of different types of CTP technology on the restoration of permeability and filtration-capacitive characteristics of plugged natural core samples.

4. The experimental complex and methodology created open up broad prospects for further research on improving the controllability and determining the effectiveness of the chemical process of the CHTBCE technology when it is introduced in oil and gas wells with various geological and technical characteristics, design features and reasons for the decrease in productivity. The obtained results on the permeability restoration will be used to refine the 3D computer model of the CHTBCE process in wells and to analyze the design of their technological processing.

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