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Use of synthesised ultradispersed substances in technological systems

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Ultrafine calcium carbonate was synthesized by the exchange reaction and carbonation method with crystallite size of 7-44 nm. The size, polymorphic modification, and morphology of the crystallites were confirmed by X-ray diffraction analysis and scanning electron microscopy. The main attention is focused on development of methods for the synthesis of ultrafine calcium carbonate directly at the sites of well depressurization (microcracks) and the basics of technology for eliminating or preventing fluid manifestations in oil and gas wells. Depending on the intensity of gas occurrences, gas migration paths, the size of gas pipeline channels, the location of depressurization areas, thermobaric conditions, as well as the technical and operational condition of wells, it is proposed to perform sealing in one of two effective ways.

The first method involves sealing microscopic gas flow channels by transporting highly mobile low-viscosity solutions containing chemical reagents in a colloidal state to the depressurization sites, followed by creating conditions for their reaction and the formation of solid or gel-like sealants. To implement this method, one inverted microemulsion is prepared, the internal phase of which is an aqueous solution with the ionic reagent $CaCl_2$, and the second – with the ionic reagent Na_2CO_3, which are injected together under stirring by the "jet to jet" method to form $CaCO_3$ crystallites and are pressed by carbon dioxide into the depressurized areas. The second method of sealing microscopic gas flow channels involves transporting a low-viscosity solution containing one of the reagents in a colloidal state and the other reagent in a gaseous state to the depressurization sites, followed by creating conditions for their reaction and the formation of solid or gel-like sealants. The technical result of this method is achieved by the interaction of calcium hydroxide contained in the polar phase of the inverted micelle with carbon dioxide, which is pre-filled into the well. The permeability of CO_2 through the membrane-like adsorption-solvent shell of biosynthetic surfactants around the calcium hydroxide facilitates the formation of $CaCO_3$ and the pushing of ultrafine calcium carbonate by carbon dioxide into the gas-fluid channels. The well is treated using the "sliding tamping" method in the repression-depression mode.

***Keywords*:** ultradispersed calcium carbonate, polymorphic modification, sealing, microcracks, oil and gas wells

Introduction

Researchers are now paying increased attention to ultradispersed nanoscale substances and compositions containing them. These are carbonate, metal and oxide nanoparticles, carbon nanotubes, graphenes for drilling processes, hydrocarbon stimulation, elimination of inter-column and annulus gas flow in wells, etc. [1-4].

The objects of nanotechnology research also include ultradispersed systems, such as aerosols, micellar colloidal solutions, polymeric ashes, and gels [2]. Thermodynamically stable dispersed systems are heterogeneous, and their micelles can be considered effective nanoreactors for the synthesis of ultrafine substances with a narrow size distribution, morphology, and polymorphic modification [5-6].

An important advantage of using nanotechnologies is their high efficiency with a low content of ultrafine substances in the technological system [5]. The effectiveness of nanotechnology in oil and gas processes is associated with the known pattern of high rheological properties of nanodispersions stabilized with ultrafine substances in a wide range of temperatures and pressures with increased thermal conductivity, thermal stability, and reduced filtration losses [1, 2].

The advantages of nanosystems in various technological processes are due to some basic properties of nanoparticles [2, 7]:

1. Due to their small size (<1 μm), nanoparticles can easily penetrate porous media, which allows for effective changes in the physical and chemical properties of the formation, as well as easily penetrate the intercolumnar and annular space of wells, which will help restore well integrity.

2. Nanodispersions are characterized by high stability, as surface forces exceed gravity.

3. Due to the reduction of capillary forces, respectively, the interfacial tension between hydrocarbons and the pore medium.

4. The size, polymorphic modification, and morphology of nanoparticles can be adjusted during the synthesis process to provide the required properties.

5. The chemical properties of the nanoparticle surface can be easily modified to impart high hydrophilicity or hydrophobicity, or other properties.

Several studies have shown that emulsion systems containing nanoparticles are more efficient and stable in the process of hydrocarbon displacement compared to similar formulations without nanoparticles [8-14].

It is important to synthesize dispersed calcium carbonate, which exists in crystalline modifications such as calcite, aragonite, and vaterite, as well as in the form of an amorphous material. The most stable of these is calcite, and the least stable is vaterite [5-6]. Equally important is the use of calcium carbonate dispersions as technological systems in places of well depressurization (microcracks) and their elimination or prevention of fluid manifestations in oil and gas wells.

One of the reasons for intercasing gas flows during well operation is poor quality cementing of production strings, leaky packers and threaded connections, and high thermobaric loads on the production string. The combination of these factors, combined with constant dynamic loads, leads to the formation of microcracks in the cement stone itself and at the boundary with the production casing or rock, and the radius of solid particles that could move into the depth of depressurized areas should not exceed 1-2 microns [8, 15-16]. The use of well-known water-based emulsion sealing systems is often accompanied by their penetration into the perforated zone of a productive formation, which leads to colmatation of the pore environment, or creates a threat of chemical contamination of drinking water through penetration into aquifers [15]. At the same time, they have a limited sealing capacity, and high filtration losses (4-26 cm^3/30 min) because complications associated with the formation of hydrates in the tubing. The use of high-viscosity sealant solutions, which are pumped under pressure into the defect zone, also does not have a long-term effect. Polymeric materials do not penetrate deep into the depressurized channels, as the films formed on the surface of the pipes are gradually destroyed by gas condensate, condensation, and formation water, peeled off due to pipe corrosion, and brought to the surface. Even temporarily plugging reservoir compositions based on chemically deposited calcium carbonate, which is formed directly in the wellbore, does not provide sealing. This is because in aqueous solutions, ionic reactions are very fast and the resulting insoluble salt molecules instantly form aggregates with a diameter of more than 3 microns [1].

To eliminate these shortcomings, the authors of [16] proposed approaches based on the use of organic-based solutions. According to the developed method, the sealing of gas flow channels is achieved by pumping low-viscosity sealing systems into the annulus, the integrity and retention of which are maintained by a gel plug with high cohesive strength, which is a suspension of a finely dispersed water-swelling polymer in a gel solution of water-soluble polymers (polyacrylamide, carboxymethyl

cellulose, hydrolyzed polyacrylonitrile, lignosulfonates) or a structured invert emulsion based on oil and fat concentrates. The sealing compound is pumped in a liquid and hot state at a temperature of 80-90 °C, in the form of a solution of saponified talcum pitch in diethylene glycol or its waste analog and 0.5-2.0 % of a nonionic surfactant (from the group AF_9-(4÷6), ES-2, twin-80, ripox-6, savenol-NWP, savenol-SWP, petrochem-1, phosphatidine) or cationic type (from the group of cationic fat, oleodin) with subsequent purging with gas and injection of an aqueous solution of calcium or magnesium chloride into the annulus until the sealing mass hardens.

For a selected group of wells (not disclosed to protect commercial secrets), a two-component sealing was performed to eliminate intercasing and annulus gas flow in wells by the method of "sliding tamping" with an 11-25 % water-alcohol solution of saponified talcum pitch in ethylene glycol, diethylene glycol or in their mixture with a water content of 8-25 %, followed by hardening and film formation of the sealant by crosslinking it with concentrated aqueous solutions of calcium chloride or bischofite. A distinctive feature of well sealing was the introduction of a surfactant [17] into the compositions, which is soluble in both water and hydrocarbons and improves the seepage of the water-glycol solution.

The results of pilot tests of this method of restoring well integrity with solutions of saponified talus pitch in diethylene glycol confirmed their effectiveness. In several wells, the company managed to eliminate or reduce gas inflow from the interstitial space, reduce the interstitial pressure in the wells to a safe level, and put the wells into operation.

The disadvantage of the above composition, as well as the previous ones, is still the unsatisfactory penetration ability into depressurized migration channels. In addition, in most gas fields with reservoir temperatures below 80 °C, pumping a relatively small (150-500 kg) viscous mass heated to 80-90 °C leads to its rapid cooling and loss of fluidity, which not only fails to seal the gas pipeline channels of rock and cement stone but also leads to complications due to thickening in the pipes and the bottom hole zone.

Further improvement of the quality of gas pipeline channels plugging and, as a result, an increase in the workover period to eliminate the wellbore and intercasing gas flow in wells was achieved by preliminary hydrophobization of the bottom hole formation zone and gas flow channels with a hydrocarbon solution of cationic surfactants – oleodin, dorad [18]. The actual sealing is achieved by pumping through perforations into the formation zone and gas flow channels of the sealing composition, % wt., of phosphatide concentrate (65.00-95.00), cationic surfactant (0.1-1.5) and hydrocarbon solvent (4.9-33.5).

The tests carried out with this method made it possible to eliminate gas leakage in all cases to safe operating levels and to extend the overhaul period to 1-6 months. The short-term effect is likely to be due to the surface sealing of the gas pipeline channels and the rapid destruction of the resulting hard film. Before that, repeated treatments did not yield any results.

After a systematic analysis of the results of the good surveys, it was found that it is possible to improve the quality of gas pipeline channel sealing by increasing the permeability and penetration depth of sealing systems by using ultradispersed materials such as calcium carbonate, which are formed in emulsion systems, directly in the depressurized gas pipeline sections.

Therefore, the aim of the work is to develop methods for the synthesis of ultrafine calcium carbonate directly at the sites of well depressurization (microcracks) and the basics of technology for eliminating or preventing fluid manifestations in oil and gas wells.

Experimental

Materials

For the synthesis of biosurfactants, concentrated phosphatides (PC), a waste product from sunflower oil refining was used. The physicochemical properties of this raw material are described in [19-20]. Also used monoethanolamine (99.5 %), sodium carbonate, Na_2CO_3 (99.3), and calcium chloride, $CaCl_2$ (95.4).

General methods

The chemical modification of concentrated phosphatides by transamidation of fatty acids with monoethanolamine in the presence of calcium hydroxide as a catalyst was carried out, with a molar ratio of PC : monoethanolamine : $Ca(OH)_2$ of 0.1 : 0.3 : 0.04. The synthesis and isolation of the product was performed similarly to the method outlined in [19-20]. A complex mixture of biosynthetic surfactants (bioFAA) was obtained, the active base of which is fatty acid alkanolamides and calcium glycerolphosphatides.

In terms of physical state, biosurfactants are oil-like substances of brown color with improved solubility in organic non-polar solvents and a surface tension of 35-36 mN/m. The synthesized bioFAA were used to create microemulsion compositions.

The synthesis of ultradispersed calcium carbonate was carried out using two methods.

The first method is microemulsion: intermicellular interaction of two microemulsions, one with an aqueous solution of sodium carbonate, the other with an aqueous solution of calcium chloride. Then they were mixed in an equimolar ratio and incubated for one day. A dispersion of calcium carbonate was obtained. To isolate calcium carbonate crystallites, the dispersed system was centrifuged at 3000 rpm for 15 min. The calcium carbonate crystallites were washed several times with ethyl alcohol and distilled water, and then dried. The dispersion medium is ethyl ester of higher fatty acids. The molar ratio of surfactant:isopropyl alcohol : (aqueous solution of Na_2CO_3 or aqueous solution of $CaCl_2$) is 0.02 : 0.4 : 0.1 (sample 1) and 0.04 : 0.4 : 0.1 (sample 2), respectively [4, 21].

The second method is based on the carbonation reaction: the interaction of calcium hydroxide, $Ca(OH)_2$, dissolved in the internal phase of the microemulsion at a concentration of 0.4 M, with carbon dioxide, CO_2, at a molar concentration of bioFAA (sample 3) of 0.04 M [22, 23].

The carbonation was carried out in a reactor equipped with a thermometer, a stirring device, a CO_2 supply tube and a reflux condenser. The microemulsion was loaded into the reactor, heated to 50 °C and CO_2 was supplied with intensive stirring. The CO_2 flow rate was measured with a manometer. The reactor is equipped with a hatch for loading reagents, which is hermetically sealed during the carbonation stage. The reaction vessel during the carbonation stage is connected to the atmosphere via a reflux condenser and a glycerine seal. The carbonation process was terminated when the absorption of carbon dioxide by the reaction mass ceased and the pressure in the system increased. A dispersion of calcium carbonate was obtained. To isolate calcium carbonate crystallites, the dispersed system was centrifuged at 3000 rpm for 15 min. The calcium carbonate crystallites were washed several times with ethyl alcohol and distilled water, and then dried.

Analytical methods

The phase identification of the products was examined under X-ray diffraction (XRD) using the MiniFlex 300/600 diffractometer (Rigaku, Japan). The diffraction patterns were recorded using Cu-Kα radiation (λ = 0.15418 nm), the operating voltage of 40 kV and a current of 15 mA. XRD pattern of samples was obtained in the 2θ range between 2° and 100° with a step of 0.02°. The scanning electron microscopy (SEM) images were taken using Zeiss Evo-10 (Carl Zeiss Microscopy, USA) microscope

working at 20.0 kV. The IR spectra of products were recorded on the surface of the diamond prism of the IR-spectrometer with Fourier transform Shimadzu IRAffinity-1Sn (Japan) with ATR-console Speacac GS 10801-B.

Results and Discussion

X-ray diffraction phase analysis

Figures 1 a, 2 a, and 3 a show XRD patterns of the synthesized samples (1, 2, 3) of calcium carbonate crystallites. It can be seen that with an increase in the concentration of bioFAA, the polymorphic modification of $CaCO_3$ crystallites changes with size from 7-15 to 32 nm for vaterite (Fig. 1 a, method 1), 15-44 nm for calcite (Fig. 2 a, method 1) and 7-39 nm for calcite (Fig. 3 a, method 2).

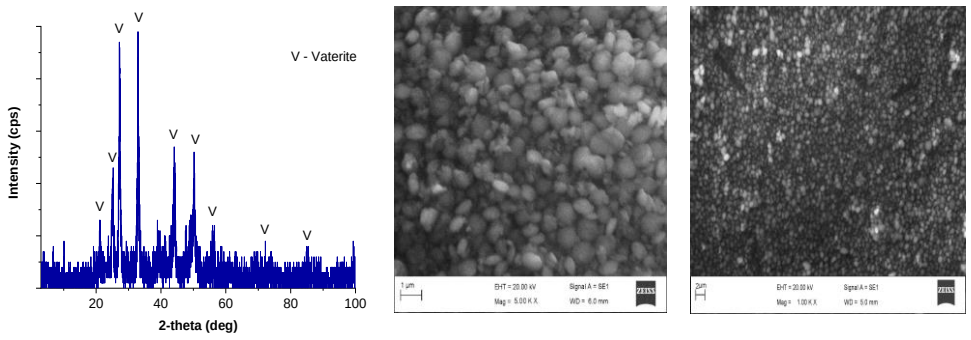
Scanning electron microscopy

Scanning electron micrographs Figures 1 b, 2 b, 3 b and in diminished view − Figures 1 c, 2 c, 3 c illustrate dispersed calcium carbonate in ellipsoidal, cubic, and spherical shapes.

The study of the properties of nanoparticles is one of the most important areas of physical chemistry, the development of which is associated with the development of simple and affordable synthesis methods that allow for the production of objects of a certain shape and a given size. The use of microemulsions with an internal aqueous phase in which the starting reagents are dissolved makes it possible to produce new substances and materials with dimensions down to 100 nm. Due to the nanoscale, the starting materials are actively involved in Brownian motion, during which they continuously collide, coalesce, and break up again. This makes it possible to carry out a variety of chemical reactions between substances contained in the polar phase and forming insoluble ultrafine substances in it, such as $CaCO_3$.

The size of $CaCO_3$ crystallites decreases after the addition of surfactant salts to aqueous solutions as emulsifiers-stabilizers. bioFAA, adsorbed on the surface of crystallites, facilitates their dispersion and simultaneously prevents their growth. The smallest size is achieved when a saturated monolayer of bioFAA molecules forms around the particles. An important tool in controlling the modifications and size of solid nanoparticles is the change in surfactant concentrations, the nature of bioFAA and co-bioFAA, the ratio of water/surfactant concentrations, the type and concentration of reagents, the properties of the aqueous and hydrocarbon phases, etc.

Using our own developments and information from the literature, we propose to develop dispersions of calcium carbonate that can be used as technological systems in places of depressurization and elimination of intercasing gas manifestations in oil and gas wells [1, 8, 19].



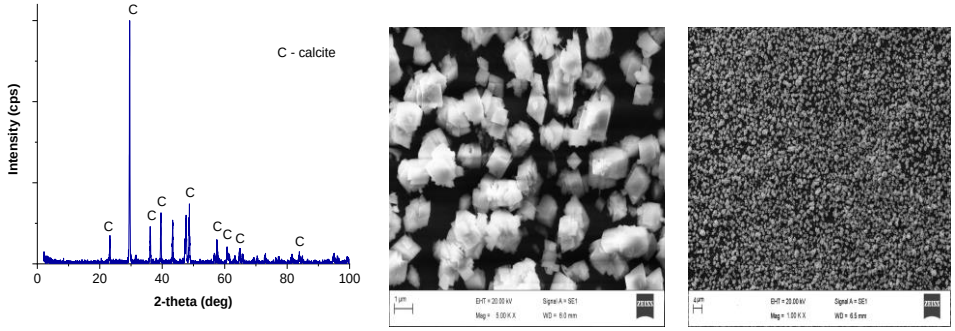
a b c

Fig. 1. XRD pattern (a) and SEM image (b), diminished (c) of $CaCO_3$ crystallites at a surfactant concentration of 0.02 M (method 1)

Depending on the intensity of gas occurrences, gas migration paths, and the size of gas pipeline channels, as well as the location of depressurized areas, thermobaric conditions, and the condition of the wells (technical, operational, etc.), it is proposed to perform sealing in the following ways:

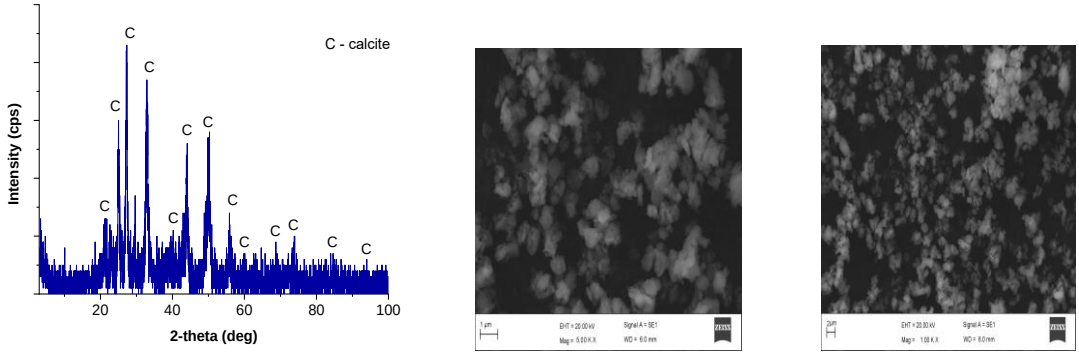
1. Transportation of highly mobile, low-viscosity solutions containing chemical reagents in a colloidal state to depressurization sites, followed by the creation of conditions for their reaction and formation of solid or gel-like sealants.

2. Transportation of a low-viscosity solution containing one of the reagents in a colloidal state and the second reagent in a gaseous state to the depressurization sites, followed by creation of conditions for their reaction and formation of solid or gel-like sealants.



a b c

Fig. 2. XRD pattern (a) and SEM image (b), diminished (c) of $CaCO_3$ crystallites at a surfactant concentration of 0.04 M (method 1)



a b c

Fig. 3. XRD pattern (a) and SEM image (b), diminished (c) of $CaCO_3$ crystallites at a surfactant concentration of 0.04 M (method 2)

To implement the first method, one inverted microemulsion is prepared, the internal phase of which is an aqueous solution with the ionic reagent $CaCl_2$, and the second with the ionic reagent Na_2CO_3 (Method 1), which are injected together under stirring by the "jet to jet" method to form $CaCO_3$ crystallites and are forced by carbon dioxide into depressurized areas [4, 8, 24]. The size of $CaCO_3$ crystallites is 7-44 nm.

The adsorption-solvent layer of the bioFAA performs a dual function. On the one hand, it prevents the instantaneous interaction of ionic reagents, and on the other hand, it prevents the growth of crystallites and allows controlling these processes in the desired direction at the stage of reagent transport and, in fact, during well-sealing.

At a constant ratio of the aqueous phase to the hydrocarbon phase, the properties of the emulsion systems change viscosity – from 0.15 to 0.44 Pa·s; density, kg/m^3 – 950-1070; resistance to phase

separation in time from 4 days to 12 months; electrical stability – 125-340 V; thermal stability at 80 °C – more than 9 days. The hydrocarbon phase is ethyl esters of higher fatty acids of oils. Due to the use of raw materials of plant origin in biosurfactants and dispersed systems, the environmental indicator, biodegradability, is 83-87 %.

To implement the second method of sealing microscopic gas flow channels, the technical result is achieved by the interaction of calcium hydroxide contained in the polar phase of the inverted micelle with carbon dioxide, which is pre-filled in the well (Method 2). The permeability of CO_2 through the membrane-like adsorption-solvent shell of biosynthetic surfactants around the calcium hydroxide facilitates the formation of $CaCO_3$ and the pushing of ultrafine calcium carbonate by carbon dioxide into the gas-fluid channels. The well is treated using the "sliding tamping" method in the repression-depression mode [4, 22-23]. Subsequently, an increase in the CO_2 concentration leads to emulsion degassing, and an increase in the rate of formation and growth of $CaCO_3$ crystallites with the corresponding sealing of the intercasing and annulus spaces.

The high CO_2 concentration and prevention of natural gas emissions into the atmosphere are achieved by pre-filling the well with a 2-fold volume of carbon dioxide and subsequent tamping of gas pipeline channels with an inverted microemulsion under carbon dioxide pressure not exceeding the production string pressure. An important feature of the process is a gradual increase in CO_2 with a simultaneous decrease in each repression-depression cycle of the microemulsion volume by 5-10 % and a holding time of 10-15 min to form a highly dispersed sealing emulsion-suspension system in the gas flow channels [8, 16-18].

The developed dispersed calcium carbonate systems can be used to develop high-temperature complex lubricants with improved tribological properties and increased oxidation stability.

Conclusions

Dispersed calcium carbonate systems with $CaCO_3$ crystallite size of 7-44 nm have been developed for use in well depressurization sites and the elimination or prevention of fluid manifestations in oil and gas wells. Depending on the intensity of gas occurrences, gas migration paths, the size of gas pipeline channels, the location of depressurization areas, thermobaric conditions, as well as the technical and operational condition of wells, it is proposed to perform sealing in one of two effective ways. The first method of sealing microscopic gas flow channels involves transporting highly mobile low-viscosity solutions containing chemical reagents in a colloidal state to the depressurization sites, followed by creating conditions for their reaction and the formation of solid or gel-like sealants. The second method of sealing microscopic gas flow channels involves transporting a low-viscosity solution containing one of the reagents in a colloidal state and the second reagent in a gaseous state to the depressurization sites, followed by creating conditions for their reaction and the formation of solid or gel-like sealants.

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Використання синтезованих ультрадисперсних речовин в технологічних системах

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Синтезовано ультрадисперсний карбонат кальцію реакцією обміну та методом карбонатації з розміром кристалітів 7-44 нм. Розмір останніх, поліморфну модифікацію та морфологію підтверджено рентгенофазовим аналізом та скануючою електронною мікроскопією. Основну увагу сфокусовано на розробленні способів синтезу ультрадисперсного карбонату кальцію безпосереднього в місцях розгерметизації свердловин (утворених мікротріщин) та основи технології ліквідації чи попередження ними флюїдопроявів в нафтогазових свердловинах. Залежно від інтенсивності газопроявів, шляхів міграції газу, величини газопровідних каналів, положення розгерметизувальних ділянок, термобаричних умов, а також технічного та експлуатаційного стану свердловин, пропонується проводити герметизацію одним із двох ефективних способів. За першим способом герметизації мікроскопічних газоплинних каналів здійснюється шляхом транспортування в місця розгерметизації високорухливих малов'язких розчинів, що містять хімічні реагенти в колоїдному стані, з подальшим створенням умов для їх реагування та утворення твердих або гелеподібних герметиків. Для реалізації даного способу готують одну інвертну мікроемульсію, внутрішня фаза якої є водний розчин з іонним реагентом $CaCl_2$, другу − з іонним реагентом Na_2CO_3, які разом закачують при перемішуванні методом «струмина в струмину» з утворенням кристалітів $CaCO_3$ і протискуються вуглекислим газом в розгерметизовані ділянки. За другим способом герметизації мікроскопічних газоплинних каналів відбувається транспортування в місця розгерметизації малов'язкого розчину, що містить один з реагентів в колоїдному стані, другий реагент в газоподібному стані, з подальшим створенням умов для їх реагування та утворення твердих або гелеподібних герметиків. Технічний результат даного способу досягається взаємодією гідроксиду кальцію, що містяться у полярній фазі інвертної міцели, з вуглекислим газом, яким попередньо заповнюють свердловину. Проникність CO_2 через мембраноподібну адсорбційно-сольватну оболонку біосинтетичних поверхнево-активних речовин навколо гідроксиду кальцію сприяє процесу утворення $CaCO_3$ і протискування ультрадисперсного карбонату кальцію вуглекислим газом в газоплинні канали. Обробка свердловини проводять методом «ковзаючого тампонування» в режимі репресія-депресія.

Ключові слова: ультрадисперсний карбонат кальцію, поліморфна модифікація, герметизація, мікротріщини, нафтогазові свердловини