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Features of natural gas hydrates formation of structures I and II in quartz sand with water and polymer solutions

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The relevance of investigation of a multicomponent gas mixture hydrate formation in quartz sand with water and polymer solutions is due to the risk of the hydrate formation in the pore space of surrounding rocks under the complex effect of a gas injection and water-polymer flooding in order to increase oil recovery at fields confined to the Nepa-Botuoba oil-and-gas bearing region (NB OGBR), which are characterized by abnormally low reservoir temperatures. These fields are located in zones of continuous and intermittent distribution of permafrost rocks, which, in combination with low values of heat flow and high heat capacity of the rocks composing their productive horizons, lead to abnormally low reservoir temperatures within 8–17 °C, which is 50–60 °C lower than the temperature calculated by the geothermal gradient. Thus, the reservoir conditions of oil occurrence at the NB OGBR fields are in the hydrate stability zone of reservoir gases, and the transition of the gas to the hydrate state is prevented only by the lack of a sufficient amount of salt-free water. In the research, natural gas from the the Srednevilyui field was used as a hydrate-forming gas. Hydrates of this gas were obtained in quartz sand samples with a grain size of 0.4–0.3 mm. The sand moisture content of 17.6% was set by distilled water and the following polymer solutions: 1 g/L polyacrylamide solution, 5 g/L sodium carboxymethyl cellulose solution, and 30 g/L polyethylene glycol solution. Phase transitions during the hydrate formation and decomposition in "the natural gas-sand-water/polymer solution" systems were investigated using thermal analysis. It was shown that hydrates with cubic structures I and II are formed in systems under study. The gas analysis in the hydrate of structure II was carried out by the method of gas-adsorption chromatography. It was established that during the hydrates formation of structure II, the hydrate phase is enriched with hydrocarbons C2-C4, which is the reason for the shift of the thermodynamic conditions of their formation to the region of high temperatures and low pressures.

Keywords: natural gas, hydrates of the crystal structure I and II, gas composition in hydrate, quartz sand, gas adsorption chromatography

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Introduction

Gas hydrates are non-stoichiometric crystalline compounds that form at low temperatures and high pressure from gas and water. During the gas hydrates formation, water molecules form a polyhedral framework with cavities that are occupied by gas molecules. The interest in studying gas hydrates is due to the following reasons: 1) the conditions of pipeline operation and oil and gas production can be favorable for the gas hydrate formation, which leads to pipelines blockage and causing of emergency situations; 2) huge deposits of hydrates discovered both under permafrost and on the sea shelf can serve as a source of natural gas; 3) gas hydrate is an attractive way to store large quantities of gas, such as hydrogen, carbon dioxide and hydrocarbon gases (Sloan, Koh, 2008).

The main drawback that prevents the large-scale dissemination of hydrate technologies in industry is the

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low rate of their formation. It is possible to stimulate the growth of hydrates through the use of porous media (Manakov, Stoporev, 2021). The increase in the intensity and completeness of the gas hydrates formation in porous media occurs due to the improvement of the conditions for heat transfer in the reaction medium, due to the occurrence of the exothermic process of hydrate formation, as well as due to the increase of the number of crystallization centers and the area of water-gas contact.

The first experimental investigations of hydrate formation in porous media began in the 60s of the last century. At present, the process of the hydrate formation of individual gases and gas mixtures has been studied quite well and there are a large number of publications on this topic (Makogon, 1974; Groysman, 1985; Troitsky et al., 2015; Buleiko et al., 2014; Seo et al., 2009; Kang, Lee, 2010; Pan, Schicks, 2023; Zaripova et al., 2021; Klapp et al., 2010; Chuvilin et al., 2002; Chuvilin, Kozlova, 2005; Chuvilin, Guryeva, 2009; Chuvilin et al., 2019; Chuvilin et al., 2022; Aladko et al., 2004; Linga et al., 2012; Zhan et al., 2018; Wu et al., 2022; Benmesbah et al., 2020; Wang et al., 2019; Yang et al., 2016; Wang et al., 2022; Khlebnikov et al., 2017; Qin et al., 2022; Zhang et al., 2023). These studies show that the porous medium affects the thermodynamic and kinetic characteristics of the hydrate formation. It is established that with a decrease in pore size (in the range < 100 nm), the equilibrium conditions of the gas hydrates formation shift to the region of higher pressures and lower temperatures, which is explained by a decrease of water activity in the pore space. In coarse- and medium-grained sand, the equilibrium pressures of hydrate dissociation are practically identical to those in the bulk water. In addition, compared to the hydrate formation in the bulk water, in a porous medium, the presence of water bound to the rock reduces the completeness of its conversion to hydrate. At the same time, there are still not enough publications devoted to the investigation of the gas composition in pore hydrates (Makogon, 1974; Buleiko et al., 2014; Seo et al., 2009; Kang, Lee, 2010; Pan, Schicks, 2023).

In nature, three crystal structures of gas hydrates are known (sI, sII and H), the most common of which are hydrates of the crystal structure I (sI) and II (sII), which have different sizes and shapes of polyhedral cavities. It is known that small gas molecules such as methane and ethane form hydrates of structure I, and larger molecules such as propane and butane form hydrates of structure II. Hydrates of the H structure are rare in the natural environment and were first discovered and described in a complex sample of the natural hydrate extracted from Barkley Canyon, located on the Pacific coast of Canada (Lu et al., 2007) before this, it was believed that they could only be obtained through artificial synthesis.

Natural gas is a mixture of the above-mentioned hydrocarbons and non-hydrocarbon components such as hydrogen sulfide, carbon dioxide and nitrogen. Each of these components has its own hydrate equilibria and structural characteristics (Wang et al., 2022). Therefore, the hydrates formation from a gas multicomponent mixture can lead to the coexistence of hydrate phases with different structures and compositions. Thus, in Barkley Canyon (Lu et al., 2007) the coexistence of H and sII hydrate phases was discovered. The occurrence of hydrates of sI and sII in the Chapopote asphalt volcano in the southern Gulf of Mexico and in the Qiongdongnan Basin in the South China Sea was reported in (Klapp et al., 2010; Kida et al., 2006; Wei et al., 2021).

Under laboratory conditions, coexisting hydrate phases formed from a multicomponent gas mixture in a porous medium were described in the works (Seo et al., 2009; Kang et al., 2010; Makogon, 1974; Pan, Schicks, 2023; Portnyagin et al., 2024). In the works (Seo et al., 2009; Kang et al., 2010), the hydrate-forming gas had the following composition, %: methane 89.86, ethane 6.40, propane 2.71 and isobutane 1.03, silica gel with a nominal pore diameter of 100 nm was used as a porous medium, its humidity was set by distilled water. They found that the enrichment of the hydrate with heavy hydrocarbon molecules is enhanced in the pores of silica gel, compared to this process in the bulk water. In addition, when heavy hydrocarbon molecules are depleted in the gas phase during the formation of a mixed hydrate, a methane hydrate of structure sI is formed instead of sII mixed hydrate structure, and both structures coexist together, which is also confirmed by 13C NMR spectroscopy. In the monograph by Yu. F. Makogon, the change of the gas composition in a hydrate was studied during stepwise hydrates formation of natural gas from the Srednevilyui deposit (ΣC2-C4 = 6.56 mol%) in wet quartz sand. It was established that during the natural gas hydrates formation, its heavier components are the first to pass into the hydrate form, forming a hydrate with the structure II. After the transition of heavy methane homologues to the hydrate phase, the gas above the hydrate was pure methane, which then formed the sI hydrate. A recent study (Pan et al., 2023) found that, as a result of the natural gas hydrates formation in natural sediments collected from the permafrost region of Qilian Mountain, in addition to the sII hydrate, another coexisting solid phase, amorphous gas hydrate, was observed.

In the work of the authors (Portnyagin et al., 2024), it was found that during the natural gas hydrates formation in samples of monodisperse quartz sand with a grain size of 0.3–0.4 mm, saturated with water, a mixture of hydrates with the crystal structures of sI and sII is formed, while the equilibrium conditions for the formation of sII hydrates are shifted to the region of high temperatures by 0.5–1 °C. The detected shift

from the equilibrium conditions of hydrate formation can lead to errors in calculating the risks of gas hydrate formation during the production of hydrocarbon raw materials. This is especially important for oil production at fields characterized by abnormally low reservoir temperatures, where alternating gas methods with water-polymer flooding is used to increase oil recovery, since in this case the probability of hydrate formation in the reservoir increases, which requires experimental studies of the processes of hydrate formation in porous media saturated with polymer solutions.

Thus, it was shown that during the hydrates formation from complex mixtures of hydrocarbon gases, methane homologues C1-C4, in a porous medium saturated with water, a mixture of hydrates with the crystal structure sI and sII is formed. Moreover, the equilibrium conditions of the sII hydrates formation are shifted toward low pressures and high temperatures relative to the calculated equilibrium curves of the hydrate formation of the original gas mixture. In this paper, one of the reasons for the shift in the equilibrium conditions for the formation of coexisting hydrate phases is the involvement of gas with a high content of methane homologues C2-C4 (ethane, propane, and butanes) in the hydrate of structure II compared to the equilibrium composition of the hydrates of the original natural gas. Thus, the objective of this work is to determine the composition of the gas in the hydrate with the crystal structure sII, during its formation from natural gas with a high content of heavy methane homologues in the pore space of wet quartz sand in the presence of polymer solutions.

Materials and methods

The objects of the investigation are natural gas hydrates obtained in quartz sand with water and aqueous solutions of the following polymers: 1 g/l polyacrylamide (PAA) solution (SNF Floerger brand "FP-207" (France)), 5 g/l sodium carboxymethyl cellulose (Na-CMC) solution ("Camcell – O" technical specifications (TU) 2231-002-50277563-00 (Russia)) and 30 g/l polyethylene glycol (PEG) solution (Norchem – 008.F01600 TU 2483-008-71150986-2006 (Russia)).

Natural gas from the Srednevilyui gas and condensate field (GCF) was used as a hydrate-forming gas. In terms of its content of methane homologues: ethane, propane, isobutane and normal butane (C2-C4), it is close to the reservoir gas of the oil fields of the Nepa-Botuoba oil-and-gas bearing region (NB OGBR) (Table 1).

The study of natural gas hydrates obtained in a sand sample moistened with water or a polymer solution was carried out on a specially assembled setup, the diagram of which is shown in Figure 1. The main element of the setup is a high-pressure autoclave made of stainless steel manufactured at the Institute of Inorganic Chemistry SB RAS (Novosibirsk) under the supervision of Dr. Sci. (Chem.) A. Yu. Manakov. The useful volume of the autoclave is 220 cm^3. During preparation for the experiment, the moistened sand sample was placed in the autoclave in a perforated glass made of inert polymer so that the temperature sensor was immersed in the sample. The gas pressure above the sample was measured by a "MIDA PI-51" pressure sensor. The set temperature was changed and maintained by placing the autoclave in a "MIR-256" dry-air thermostat brand "Sanyo" (Japan). Collection and processing of primary data from pressure and temperature sensors was carried out using a precision multi-channel temperature meter "MIT-8", equipped with a special software package and connected to a computer.

The porous medium used in preparing the sand sample was sieved quartz sand with a grain size of 0.4–0.3 mm, a mineralogical density of 2.65 g/cm^3, and a density of the compacted sand sample in dry and wet

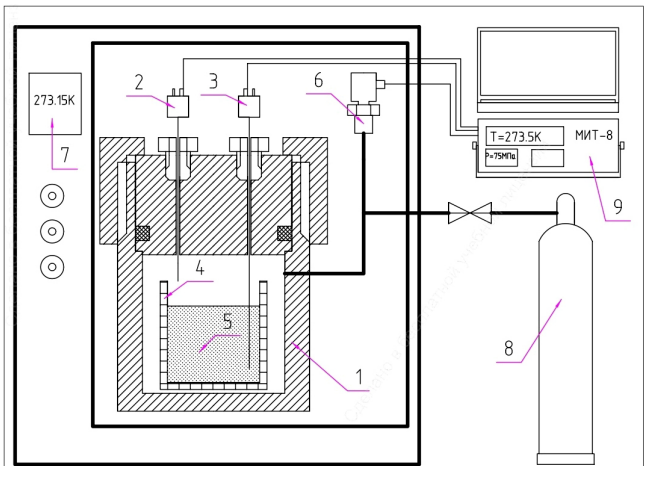

Figure 1. Schematic diagram of the setup for investigation the hydrates formation and dissociation processes in a porous medium and static isochoric conditions using thermal analysis: 1 – high-pressure autoclave, 2 and 3 – type K thermocouples; 4 – perforated glass made of inert polymer, designed to form a sample of the porous medium; 6 – MIDA PI-51 pressure sensor; 7 – air thermostat-incubator "MIR – 256" by Sanyo (Japan); 8 – cylinder with compressed natural gas; 9 – precision multichannel temperature meter "MIT – 8" with a computer connected to it

Content of components, mol.%							
CO_2	N_2	CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	n-C_4H_{10}	ΣC2-C4
0.032	0.57	92.32	5.43	1.37	0.144	0.134	7.07

Table 1. Component composition of natural gas from the Srednevilyui GCF

form of 1.44 and 1.60 g/cm^3, respectively. The porosity of the dry sand medium was 34.5%, and its filtration coefficient was 0.03 cm/s. To obtain a sand sample, 96.4 g of sand was mixed with 17 g of water or with an equivalent volume of polymer solution by the amount of water. The resulting mixture was placed in a perforated cylindrical cup, then the sand was compacted, while the degree of filling of the pores with water in the sample was 73.6%, and its weight moisture content (W) was 17.6%. The resulting wet sand sample was prepared using the method described above for all experiments and had the shape of a cylinder 3.8 cm high and 5 cm in base diameter. The characteristics of the porous medium sample and the experimental conditions are presented in Table 2.

The obtained wet sand sample was placed in a high-pressure autoclave so that the measuring part of the thermocouple (3) was located in the center of the sample volume. Then, in order to remove air from the free volume of the autoclave, it was purged with hydrate-forming gas by letting in gas to an excess pressure in the autoclave equal to 1 MPa and then bleeding it to atmospheric pressure. The purging procedure was repeated three times, after which the hydrate-forming gas was supplied until an excess pressure of 14 MPa was established. Then the autoclave was thermostatted at 20 °C until the specified temperature was reached in the sample. After that, the pressure in the autoclave was set equal to 13 MPa, while the amount of gas in the autoclave at the start of the experiment exceeded by 2 times its amount necessary for binding all the water contained in the prepared sample into hydrate. Then a special program consisting of three stages was started on the thermostat: cooling of the moistened quartz sand sample from 20 to –5 °C at a rate of 3 °C/h, its thermostatting for 8 hours at –5 °C and heating from –5 to 30 °C at a rate of 4 °C/h. Data collection of thermobaric conditions in the autoclave and the sample began at the moment the experiment program was started on the thermostat. The applied program of cooling and heating of the studied system was the same for all experiments.

Based on the experimental data on the sample temperature and free gas pressure in the autoclave, the pressure and temperature profiles of the formation and dissociation of the pore natural gas hydrate were constructed. A typical pressure and temperature profile is shown in Figure 2. It is shown that during the cooling of the moistened quartz sand sample, upon reaching point "A" on the pressure and temperature profile (Figure 2), an intensive formation of the pore hydrate occurs in the sample, accompanied by an increase in temperature as a result of the exothermic reaction and a decrease in pressure due to the binding of the free gas into the hydrate form. The most intensive hydrate formation was observed in the temperature range from 12 to 3 °C, depending on the hydrate formation medium. Upon transition to the region of negative temperatures, hydrate formation either did not occur (samples saturated with a PAA solution), or occurred less pronounced, without the manifestation of an exothermic signal on the thermograms (samples saturated with water and Na-CMC and PEG solutions).

The figure shows the thermobaric profile of the formation and dissociation of natural gas hydrate from water. The established decrease in the intensity of

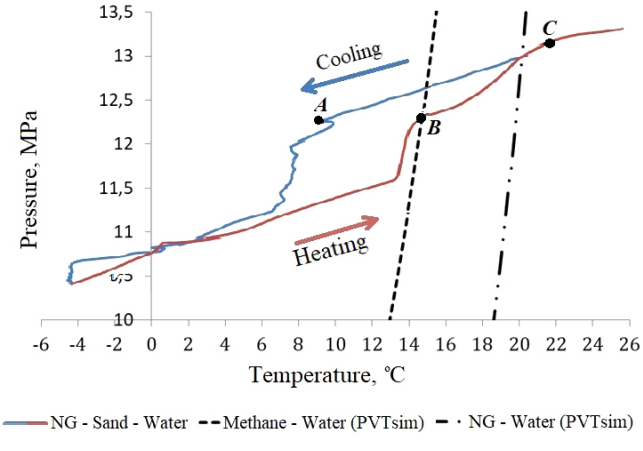

Figure 2. Typical pressure-temperature diagram obtained during an experiment on the formation and dissociation of natural gas hydrates in a wetted sand sample (W = 17.6%)

Hydrate formation medium	Mass of sand, g	Mass of solution, g	Moisture content by weight, %	Autoclave volume, ml	Initial temperature, °C	Final temperature, °C	Initial pressure, MPa
Water	96.4	17.00	17.6	220	20	–5	13
PAA solution, 1 g/l	96.4	17.02	17.6	220	20	–5	13
Na-CMC solution, 5 g/l	96.4	17.08	17.6	220	20	–5	13
PEG solution, 30 g/l	96.4	17.51	17.6	220	20	–5	13

Table 2. Characteristics of the porous medium sample and conditions for conducting experiments on the natural gas hydrates formation of the Srednevilyui gas and condensate field under static isochoric conditions

hydrate formation in the region of negative temperatures is consistent with the works (Chuvilin, Guryeva, 2009; Chuvilin et al., 2019). The greatest binding of gas into hydrate in the region of negative temperatures occurred in systems with water and PEG solutions. Probably, this nature of hydrate formation is associated with the kinetics of this process for different systems. Thus, in PAA solutions, hydrate formation ceases before the system passes into the region of negative temperatures, while in water and solutions of Na-CMC and PEG, the hydrate formation process is completed at the stage of thermostatting the system at –5 °C.

When the sample is heated, the reverse process occurs: dissociation of the formed hydrate. It is evident that the dissociation of the hydrate occurs in two stages, where at point "B" the dissociation of hydrates ceases, the equilibrium conditions of formation of which are in good agreement with the equilibrium conditions of methane hydrates formation, and at point "C" the hydrate dissociates, the equilibrium conditions of formation of which are shifted along the thermal scale relative to the calculated conditions of natural gas hydrates formation of the Srednevilyui GCF of the initial composition to the region of high temperatures (Portnyagin et al., 2024).

The composition of the gas in the hydrate was determined using two methods: experimental and calculation-experimental.

In order to determine the composition of the gas in the hydrate, gas samples were collected experimentally above the hydrate-saturated sample and from it. For this purpose, after the hydrate was formed in the sample of moistened quartz sand, at the thermostatting stage at –5 °C, a gas sample was collected from the free gas above the hydrate-saturated sample, then the remaining gas was released into the atmosphere until atmospheric pressure was reached, as a result of which the temperature inside the autoclave decreased to (–14)–(–18) °C due to the throttling effect, which slowed down the dissociation of hydrates at this stage. Then the autoclave was sealed and heated to 30 °C. During the heating process, all the pore hydrate dissociated into gas and water. The gas formed after the dissociation of the hydrates accumulated in the free space of the autoclave above the quartz sand sample, from where the next gas sample was collected. The composition of the obtained gas corresponded to the gas in the hydrate of both crystal structures. Next, the component composition of the gas in the selected samples was determined using gas- adsorption chromatography.

To determine the gas composition by the calculation-experimental method, points with a certain step on the temperature scale corresponding to the temperature change during the formation of pore hydrates in a sand sample were selected from the array of experimental data presented on the thermobaric profile (Figure 2). In this case, the discreteness of the selected points was 1 °C (Figure 3). For a correct comparison of the gas composition determined by the gas-adsorption chromatography method and the calculated composition by the method under consideration, empirical data on the temperature and pressure in the reaction system obtained in experiments on the formation of natural gas hydrates in samples of a porous medium, carried out with the selection of the studied gas samples above the sample and from the hydrate, were used in the calculations.

Next, based on the thermobaric conditions corresponding to the selected points, the amount of free gas in the autoclave not bound into hydrate (n) was determined for each point under consideration using the formula (Linga et al., 2012):

$$n = \frac{pV}{TRz}, \quad (1)$$

where p is the pressure of free gas (MPa), V is the volume of free gas (m^3), T is the gas temperature (K) and z is the gas compressibility factor.

The compressibility factor (z) was determined using a program specially developed at the Institute of Oil and Gas Problems of the Russian Academy of Sciences,

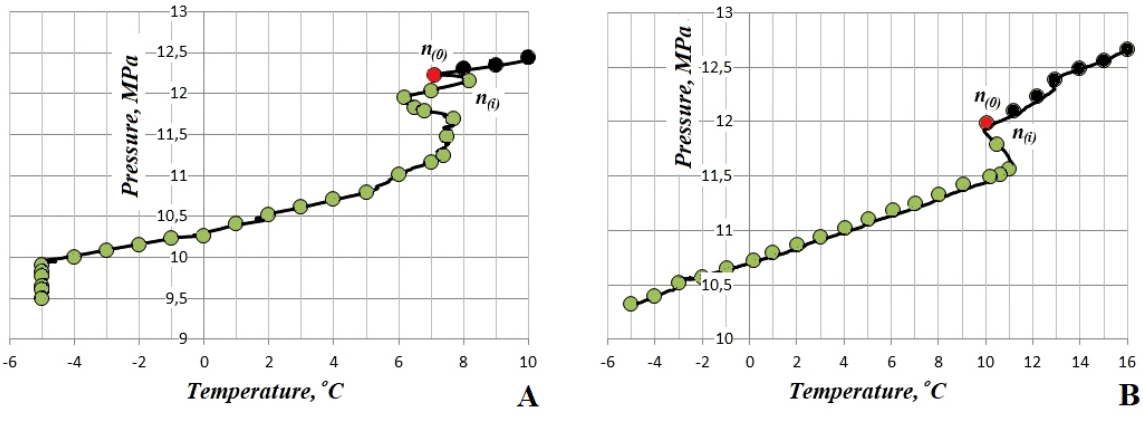

Figure 3. Experimental points selected on the curve of natural gas hydrates formation (highlighted in green) for calculating the component composition of gas in the pore hydrate during its formation in a sand sample saturated with water (A) and a solution of PAA (1 g/l) (B) (W = 17.6%)

taking into account the change in the composition of the hydrate-forming gas at each of the selected points in accordance with State Standard – GOST 30319.3-2015.

Then it was assumed that the amount of free gas at the point located before the onset of nucleation of hydrate particles, expressed by an exothermic peak accompanied by a decrease in gas pressure in the system, is equal to $n_{(0)}$ (red point in Figure 3), and the composition of the free gas above the hydrate is equal to the composition of the original natural gas. At the next point (i), the amount of free gas is $n_{(i)}$, and the amount of gas bound in the hydrate ($\Delta n_{(i)}$):

$$\Delta n_{(i)} = n_{(0)} - n_{(i)}. \quad (2)$$

$\Delta n_{(i)}$ for subsequent points (green points):

$$\Delta n_{(i)} = n_{(i-1)} - n_{(i)}.$$

Next, according to the thermobaric conditions corresponding to the i-th point, the composition of the gas in the hydrate was calculated using the PVTsim software product. The calculation also took into account the ratio of the amount of free gas $n_{(i)}$ to the amount of free water $n_{w(i)}$, calculated for the i-th point taking into account the amount of gas and water bound in the hydrate. The ratio of the amount of free gas to the amount of free water was calculated using the formula:

$$\frac{n_{(i)}}{n_{w(i)}} = \frac{100pVM_w}{TRzm_wW_{h(i)}}, \quad (3)$$

where M_w is the molar mass of water (g/mol), m_w is the mass of water (g) and $W_{h(i)}$ is the degree of conversion of water into hydrate at the point under consideration (%).

The water to hydrate conversion degree ($W_{h(i)}$) was calculated using the formula (Linga et al., 2012):

$$w_{h(i)} = \frac{\left(n_{(0)} - n_{(i)}\right) * N_{(i-1)} * 100}{n_{w(i)}}, \quad (4)$$

where $N_{(i-1)}$ is the hydration number, reflecting the number of water molecules required to form a hydrate cell, calculated using the PVTsim software product for the gas composition corresponding to point $i–1$.

Based on the gas composition in the hydrate calculated using the PVTsim software product, the composition of the free gas remaining in the system, which did not participate in the hydrate formation process, was calculated using the formula:

$$C\kappa_{G(i)} = \frac{\left(\left(n_{(i-1)} * C\kappa_{G(i-1)}\right) - \left(\Delta n_{(i)} * C\kappa_{Hd(i)}\right)\right)}{n_{(i)}}, \quad (5)$$

where $C\text{k}_{G(i)}$ is the molar concentration of the gas mixture component that did not participate in the hydrate formation process (mol%), $C\text{k}_{Hd(i)}$ is the molar concentration of the gas mixture component bound into hydrate (mol%), $C\text{k}_{G(i-1)}$ is the molar concentration of the gas mixture component that did not participate in the hydrate formation process, calculated for the previous point (mol%).

Then, using the PVTsim software product the composition of the gas that entered the hydrate at the next point ($i+1$), where the hydrate-forming gas was free gas with a composition equal to the composition of the gas determined for the i-th point was calculated. Thus, the change in the composition of the hydrate-forming gas, which will affect the composition of the gas that entered the hydrate at the following points, was taken into account.

The concentration of gas components involved in the hydrate after completion of the hydrate formation process (C_{Hd}, mol%) was calculated using the formula:

$$\text{C}_{Hd} = \frac{\Sigma_i(\text{C}_{Hd(i)} * \Delta n_{(i)}) * 100}{\Sigma_j \text{C}_{Hd(j)}}, \quad (6)$$

where $\Sigma_j C_{Hd(j)}$ is the total concentration of all components of the gas mixture (mol%).

If, the system based on the results of calculating the composition of the gas included in the hydrate, in the PVTsim software product reveals the formation of a mixture of hydrates with the crystal structures sI and sII, then formulas (5) and (6) will take the form:

$$\text{C}\kappa_{G(i)} = \frac{w_{sI}\left(\left(n_{(i-1)} * C_{G(i-1)}\right) - \left(\Delta n_{sI(i)} * \text{C}_{HdsI(i)}\right)\right)}{100 * n_{(i)}} + \frac{w_{sII}\left(\left(n_{(i-1)} * C_{G(i-1)}\right) - \left(\Delta n_{sII(i)} * \text{C}_{HdsII(i)}\right)\right)}{100 * n_{(i)}} \quad (7)$$

where w_{sI} and w_{sII} are the mass fractions of hydrates with the crystal structure I and II, $C_{HdsI(i)}$ and $C_{HdsII(i)}$ are the molar concentrations of the components of the gas mixture bound into hydrates with the crystal structure I and II (mol%), $\Delta n_{sI(i)}$ and $\Delta n_{sII(i)}$ are the amount of gas bound into hydrates with the crystal structure I and II (mol.):

$$\text{C}_{Hd} = \frac{\Sigma_i((\text{C}_{HdsI(i)} * \Delta n_{sI(i)}) + (\text{C}_{HdsII(i)} * \Delta n_{sII(i)})) * 100}{\Sigma_j \text{C}_{Hd(j)}}. \quad (8)$$

Thus, for each selected point, the component composition of free gas that did not participate in the hydrate formation process, as well as the component composition of gas that entered the hydrate, were calculated. Such calculations are necessary to understand the effect of the water to hydrate conversion degree on the change in the composition of free and hydrate-bound gas. The gas compositions in hydrates obtained by experimental and calculated-experimental methods are in good agreement with each other during the formation of natural gas hydrates in moistened samples of coarse quartz sand under thermobaric conditions that exclude the formation of methane hydrates. The determined gas compositions in hydrates formed under conditions that satisfy the methane hydrate stability zone, by the methods under consideration diverge due to a decrease in the content of methane homologues C2-C4 in the gas composition determined experimentally.

Research results

Earlier, it was shown in the works (Ivanova et al., 2023; Portnyagin et al., 2024) that a mixture of hydrates with the crystal structures I and II is formed in the samples of moistened monodisperse quartz sand from natural gas of the Srednevilyui GCF. Moreover, if the equilibrium conditions of the hydrates formation with the crystal structure sI were in good agreement with the equilibrium conditions of the methane hydrates formation of calculated using the PVTsim software product, then the equilibrium conditions of the hydrates formation with the crystal structure sII were shifted along the thermal scale to the high temperature region by 0.5–1 °C relative to the calculated conditions of the natural gas hydrates formation of the initial composition (Figure 4). This shift in the equilibrium conditions of the hydrates formation with the sII crystal structure is possibly associated with the difference in the composition of the gas involved in the pore hydrate from the equilibrium composition of the gas in the hydrate.

To study the dynamics of changes in the content of components C2-C4 in the gas that entered the hydrate and above it, their equilibrium compositions were determined at different stages of the hydrate formation process using the calculation method described above.

Calculations have confirmed that a mixture of hydrates with the sI and sII crystal structures (first and second stages, respectively) is formed in the natural gas – quartz sand – water system. Figure 5 shows the dependence of the content of methane homologues C2-C4 in the calculated composition of gas bound in the hydrate and in the composition of the gas above the hydrate on the water to hydrate conversion degree. It is shown that in the process of hydrate formation, the content of components C2-C4 decreases both in the gas that has entered the hydrate and in the gas above the hydrate. Such a course of the curves indicates that in the process of natural gas hydrates formation, a change in the composition of the free hydrate-forming gas occurs, which leads to a change in the composition of the gas in the hydrate. At the same time, the composition of the gas that has entered the hydrate with the sI crystal structure did not change significantly with an increase in the water to hydrate conversion degree.

Thus, it can be stated that natural gas in quartz sand (W = 17.6%) forms a mixture of hydrates with the sI crystal structure of constant composition and hydrates with the sII crystal structure of variable composition.

The composition of the gas in the hydrate with crystal structure II was determined by the calculation method using formula 9, where Δn_j is the amount of each component constituting the gas mixture bound into the hydrate, determined by the formula:

$$\Delta n_j = \frac{(C_{Hd(sI+sII)(j)} * (n_{sI}+n_{sII}) - C_{HdsI(j)} * n_{sI}}{100}, \quad (9)$$

where $C_{Hd(sI+sII)(j)}$ is the experimentally determined concentration of the j component of the gas from the hydrate (mol%), $C_{HdsI(j)}$ is the calculated concentration of the j component of the gas from the hydrate (mol%) with the sI crystal structure.

The amount of hydrates n with the structure I and II was determined experimentally.

The results of determining the component composition of the gas included in the hydrate by experimental and calculation methods are presented in Table 3.

Comparison of the calculated and empirical data of the gas composition included in the mixture of the obtained hydrates in the system "natural gas – sand – water" showed that the calculated gas composition differs from the empirical one in the direction of increasing the content of methane homologues C2-C4 by an average of 26.12%. Such a discrepancy in the content

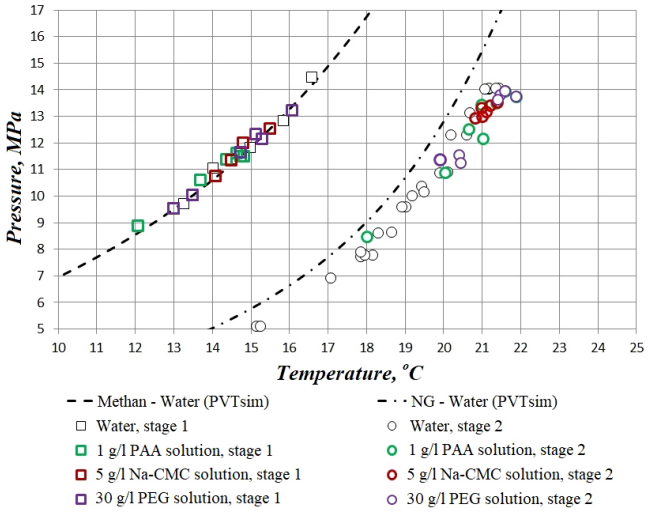

Figure 4. Experimental points of equilibrium conditions of the pore hydrate formation in the natural gas – quartz sand – water/polymer solutions system, as well as calculated curves of methane and natural gas hydrate formation in the water bulk (PVTsim) (Portnyagin et al., 2024)

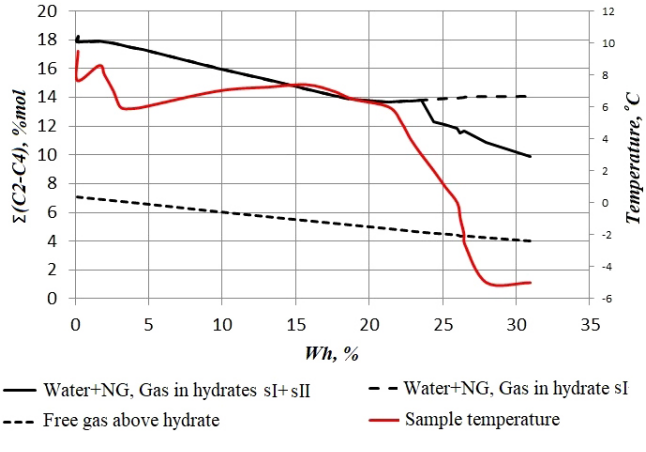

Figure 5. Dependence of the sum of methane homologues C2-C4 in the gas included in the mixture of hydrates with the crystal structure I and II and in the free gas, as well as the temperature on the water to hydrate conversion degree (Wh)

Components, % mol	Natural gas (NG)	Calculation method				Empirical method			
		In hydrate			Above hydrate	In hydrate			Above hydrate
		sI	sII	sI+ sII		sI	sII*	sI+ sII	
CO_2	0.032	0.029	0.052	0.051	0.028	-	0.089	0,070	0,094
N_2	0.57	0.201	0.187	0.19	0.65	-	0.38	0,32	0,70
CH_4	92.32	97.53	83.33	83.39	94.04	-	81.54	86,63	93,33
C_2H_6	5.43	2.24	12.37	12.31	4.10	-	12.73	9,39	4,68
C_3H_8	1.37	0	3.42	3.42	0.98	-	4.64	3,16	0,98
i-C_4H_{10}	0.144	0	0.359	0.359	0.103		0.414	0,282	0,101
n-C_4H_{10}	0.134	0	0.282	0.282	0.104	-	0.217	0,148	0,116
Crystal structure	-	sI	sII	sII	-	-	sII	sII	-
ΣC2-C4	7.07	2.24	16.43	16.37	5.28	-	18.00	12,98	5,87
n, 10^{-3}mol	-	8.73	166.84	175.57	-	56.50	120.91	177,41	-
n sII/ n sI	-	19.22		-	-	2.14		-	-

Table 3. Component compositions of gas in the pore hydrate with crystal structures sI and sII in a water-saturated sand sample (W = 17.6%), as well as the compositions of the free gas remaining after completion of the hydrate formation process. * – The composition is calculated based on the ratio of the amount of sII and sI hydrates

of components C2-C4 indicates a different content in the hydrate mixtures determined by the experimental and calculated methods of hydrates with the crystal structure I. It was found that in the composition of the mixture obtained by the experimental method, nsI is 6.5 times higher than in the calculated composition of the hydrate mixture. When a mixture of hydrates with such a ratio of the amount of hydrates of the sI and sII structures dissociates, a decrease in Σ(C2-C4) occurs in the gas from the hydrate, due to the dilution of the gas saturated with components C2-C4, released from the hydrate of the structure II, with a lighter gas from the hydrates of the structure I, as evidenced by the low values of Σ(C2-C4) in the composition of the gas from the hydrate obtained by the experimental method.

Comparison of the gas compositions in the hydrate with the crystal structure II, determined by the calculation and experimental methods, shows that in the studied system a hydrate is formed with a content of components C2-C4 that is 9.5% higher than in the calculated equilibrium composition. This indicates that from natural gas and water in quartz sand a pore hydrate with the crystal structure II of a nonequilibrium composition is formed, with a greater share of methane homologues C2-C4 than in the equilibrium composition.

The compositions of the free gas remaining in the system after the end of the hydrate formation process, obtained by calculation and empirical methods, agree quite well with each other, which confirm the redistribution of all the gas contained in the hydrate between hydrates with the sI and sII structures.

Thus, it can be stated that in the studied system a mixture of hydrates with crystal structures sI of constant composition and sII of variable nonequilibrium composition with an increased content of components C2-C4 is formed. This circumstance allows us to explain the shift of the equilibrium curve of the second stage hydrates formation (sII) by 0.5–1 °C to the region of high temperatures and low pressures relative to the calculated equilibrium curve of the initial natural gas (Figure 4).

The conducted studies of the natural gas hydrates formation in sand samples saturated with polymer solutions of given concentrations (Portnyagin et al., 2023, 2024) showed that, just as in the formation of hydrates in systems with fresh water, a mixture of hydrates with the crystal structure II and a hydrate with the structure I is formed (Figure 4). In this case, the content of sI hydrates in the mixture of hydrates formed from PAA solutions is more than 2 times lower than their content in the mixture of hydrates formed from fresh water, and in the mixture of hydrates formed from Na-CMC and PEG solutions, the content of sI hydrate is lower than this indicator for water by 93 and 67%, respectively (Table 4). However, in contrast to the data obtained experimentally, calculations of the composition of gas in natural gas hydrates formed from polymer solutions have not established the formation of hydrates with the sI crystal structure in these systems.

Based on the quantitative ratios of hydrates sII and sI crystal structures and the gas compositions included in the sI hydrates and the mixture of hydrates of both structures, the gas compositions in hydrates with the sII crystal structure were calculated using formula 9 (Table 4). It is evident that the content of C2-C4 in the experimentally obtained compositions is higher than this indicator for the calculated equilibrium compositions by

Components % mol	NG – Sand - Water		NG – Sand – 1 g/l PAA solution		NG – Sand –5 g/l Na-CMC solution		NG – Sand – 30 g/l PEG solution	
	Calculation	Empirical	Calculation	Empirical	Calculation	Empirical	Calculation	Empirical
CO_2	0.19	0.089	0.05	0.126	0,050	0,176	0,050	0,181
N_2	0.052	0.38	0.19	0.34	0,18	0,63	0,18	0,76
CH_4	83.30	81.54	82.32	77.18	81,72	78,12	82,02	78,62
C_2H_6	12.31	12.73	12.94	15.28	13,44	14,05	13,26	13,15
C_3H_8	3.51	4.64	3.81	6.41	3,90	6,23	3,80	6,44
i-C_4H_{10}	0.362	0.414	0.40	0.443	0,411	0,550	0,398	0,588
n-C_4H_{10}	0.282	0.217	0.29	0.203	0,297	0,243	0,294	0,262
ΣC2-C4	16.46	18.00	17.44	22.34	18,05	21,08	17,74	20,44
n sII/ n sI	19.22	2.14	-	4.45	-	4,15	-	3,57
Change ΣC2-C4, %	9.35		28.10		16.79		15.22	

Table 4. Calculated component composition of gas and composition of gas obtained experimentally in a hydrate with the sII crystal structure formed from natural gas in quartz sand with water and polymer solutions (W = 17.6%)

8.5–22%, which indicates the formation of hydrates of variable nonequilibrium composition in the dispersed medium from polymer solutions.

Discussion

The paper shows that a mixture of hydrates with the crystal structures I and II is formed in medium-sized quartz sand with water and polymer solutions from natural gas of the Srednevilyui GCF under static isochoric conditions. It is known that the formation of such a mixture of gas hydrates occurs as follows: first, during the formation of hydrates in a porous medium, methane homologues C2-C4, which have a higher equilibrium temperature compared to methane, are the first to pass into hydrate from natural gas, forming hydrates with the crystal structure II. The remaining unfilled small cavities of the hydrate framework are occupied by methane molecules, which have a high partial pressure in the natural gas under consideration. The preferential transition of the C2-C4 components of free gas into the hydrate form at a certain point in time leads to a decrease in their content in the gas over the hydrate-saturated sample at the next point in time. Thus, as the hydrate formation process proceeds, the composition of the hydrate-forming gas continuously changes, and, consequently, the composition of the gas bound into the hydrate, towards a decrease in the content of methane homologues C2-C4. This fact is confirmed by the results of the calculation of the change in the composition of free gas and gas bound into hydrate during the formation of gas hydrate (Figure 5).

Ultimately, the change in the concentration of components C2-C4 leads to the fact that pure methane remains in the free gas, from which methane hydrate with the crystal structure I is formed (Makogon, 1974). However, as established in the work, the composition of the gas above the hydrate-saturated sample after the completion of hydrate formation differs from the composition of the initial natural gas in the direction of a decrease in the content of methane homologues C2-C4, but their concentration is sufficient to form hydrates with the crystal structure II (Table 3). Also, this is confirmed by the calculations carried out, where the formation of methane hydrate occurs from a gas mixture of hydrocarbons with a total content of components C2-C4 equal to 13.7 mol. (Figure 5).

One of the important characteristics of the obtained hydrate mixture is its composition, expressed as the ratio of the amount of hydrates of the crystal structures sII to sI (nsII/ nsI). It was found that the distribution of hydrates of different structures in the mixture in the calculated (equilibrium) composition differs significantly from the composition of the mixture determined experimentally. Thus, the considered ratio in the equilibrium composition is 9 times lower than in the empirical one, which indicates the formation of hydrates with the crystal structure I in larger quantities than established by calculations. Similar results were obtained by the authors of the work (Seo, 2009), where in a porous silica gel medium the hydrate mixture contained 28% more sI hydrates than in the hydrate mixture obtained from the bulk water. This character of hydrate formation is related to the fact that during the formation of natural gas hydrates in quartz sand, hydrates sII of non-equilibrium composition with a higher content of components C2-C4 than in the calculated equilibrium composition are formed. Thus, Table 3 shows the composition of gas bound in hydrates sII, it is evident that the content of components C2-C4 in the gas composition in the hydrate, determined empirically, is higher by 9.5% than in the equilibrium composition. Thus, it has been established that in wet quartz sand from natural gas of the Srednevilyui GCF,

a mixture of hydrates of the crystal structures I and II is formed, where hydrates sII are hydrates of non-equilibrium variable composition.

A study of the composition of gas bound in hydrates obtained from polymer solutions in quartz sand has established that the content of components C2-C4 in the composition determined by the empirical method is 28.1, 16.8 and 15.2% higher than the content of these components in the calculated composition for PAA, Na-CMC and PEG solutions, respectively. Such a discrepancy between the empirical and calculated compositions indicates the formation of sII hydrates of a nonequilibrium composition. A decrease in the proportion of components C2-C4 in a series of polymer solutions from PAA to PEG is associated with a decrease in this series in the ratio of the amount of hydrates of sII to sI crystal structures by 6.7 and 14%, respectively, which is associated with a decrease in the content of sI hydrates (Table 4). At the same time, the formation of sI hydrates in the resulting hydrate mixture is not confirmed by the calculation method.

The decrease in the amount of sI hydrate is explained by the kinetic features of hydrate formation in these systems. Thus, in PAA solutions, the main stage of the hydrate formation process occurs at higher temperatures than in water, therefore, the formation of hydrates with the sI crystal structure in this system has not been confirmed by calculations. At the same time, the content of components C2-C4 in the gas from the sII hydrate, determined experimentally, is higher than this indicator for water by 24.11%, since at higher temperatures more components C2-C4 pass into the hydrate than at low temperatures (Figure 6).

Hydrate formation in Na-CMC and PEG solutions is characterized by lower values of the pore water conversion to hydrate degree, at which the concentration of methane in the gas above the hydrate is insufficient for the formation of hydrates with the sI structure. Thus, the water conversion to hydrate degree in Na-CMC and PEG solutions is 19.8 and 25.2% lower than this

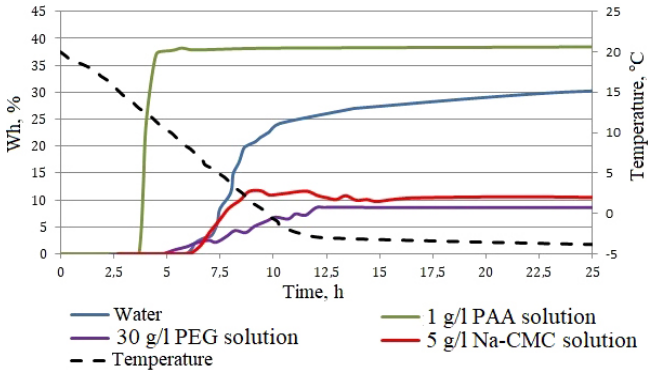

Figure 6. Dependence of the water conversion to hydrate degree (*Wh*) on time during the formation of natural gas hydrates in quartz sand with water and polymer solutions

indicator for fresh water at comparable or lower values of the hydrate formation rate. This is probably due to a decrease in the intensity of the hydrate formation when the reaction system passes into the region of negative temperatures. At a low the water conversion to hydrate degree, there is no significant decrease in the content of components C2-C4 in hydrates due to the low degree of depletion of these components in the gas above the hydrate, as a result of which the content of components C2-C4 in hydrates obtained in these systems is higher than in water by 17.11 and 13.55%, respectively, and are in good agreement with each other. Based on the analysis of the kinetic parameters of the hydrate formation in systems with polymers, it can be summarized that PAA solutions exhibit the properties of a kinetic promoter of the hydrate formation, and Na-CMC and PEG solutions can be classified as kinetic inhibitors of this process.

Thus, it can be concluded that at fields of the NB OGBR located in the zone of continuous permafrost distribution and characterized by low reservoir temperatures, with joint or sequential injection of reservoir gas and oil-displacing agents based on the considered water-soluble polymers into the reservoir, there is a risk of natural gas hydrates formation in the reservoir rock. Moreover, the use of PAA solutions is undesirable, since these solutions exhibit the properties of a kinetic promoter of the hydrate formation.

Conclusion

As shown by the experimental and calculated results of the investigation of the natural gas hydrates formation in sand samples saturated with water and polymer solutions at their weight moisture content equal to 17.6%, a mixture of hydrates of the structure I and hydrates of non-equilibrium variable composition with the structure II is formed. It was found that the content of components C2-C4 in the obtained hydrates of the structure II in all the studied systems is 8.5–22% higher than in the calculated equilibrium composition. This indicates that a pore hydrate with the sII crystal structure of non-equilibrium composition is formed from natural gas in quartz sand, with a greater proportion of methane homologues C2-C4 than in the equilibrium composition.

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Особенности образования гидратов природного газа со структурами КС-I и КС-II в кварцевом песке с водой и растворами полимеров

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Актуальность исследования гидратообразования многокомпонентной газовой смеси в кварцевом песке с водой и растворами полимеров обусловлена риском образования гидратов в поровом пространстве вмещающих пород при комплексном воздействии на них закачкой газа и водополимерным заводнением с целью увеличения нефтеотдачи на месторождениях, приуроченных к Непско-Ботуобинской нефтегазоносной области (НБ НГО), которые характеризуются аномально низкими пластовыми температурами. Данные месторождения располагаются в зонах непрерывного и прерывистого распространения многолетнемерзлых пород, что в сочетании с низкими значениями теплового потока и большой теплоемкости пород слагающих их продуктивные горизонты, приводят к аномально низким пластовым температурам в пределах 8–17 °С, что на 50–60 °С ниже температуры, рассчитанной по геотермическому градиенту. Таким образом, пластовые условия залегания нефти на месторождениях НБ НГО находятся в зоне стабильности гидратов пластовых газов, а переходу газовой части месторождений в газогидратное состояние препятствует лишь отсутствие достаточного количества свободной от соли воды. В работе в качестве газа-гидратообразователя использовался природный газ Средневилюйского месторождения. Гидраты этого газа были получены в образцах кварцевого песка с размером зерен 0,4–0,3 мм. Весовая влажность песка в количестве 17,6% задавалась дистиллированной водой и следующими растворами полимеров: 1 г/л раствор полиакриламида, 5 г/л раствор натриевой соли карбоксиметилцеллюлозы и 30 г/л раствор полиэтиленгликоля. Фазовые переходы при образовании и разложении гидратов в системах «природный газ-песок-вода/раствор полимера» исследовались методом термического анализа. Показано, что в исследуемых системах образуются гидраты с кубическими структурами КС-I и КС-II. Анализ газа в гидрате КС-II проводился методом газо-адсорбционной хроматографии. Установлено, что в процессе образования гидратов КС-II происходит обогащение гидратной фазы углеводородами С2-С4, что является причиной смещения термодинамических условий их образования в область высоких температур и низких давлений.

Ключевые слова: природный газ, гидраты кристаллической структуры КС-I и КС-II, состав газа в гидрате, кварцевый песок, газо-адсорбционная хроматография

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