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# Study of methane hydrate dissociation under subzero temperatures

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**Abstract.** The use of cryolithozone resources is currently one of the priority issues on the agenda of scientific and technological and, consequently, economic development of the Russian Federation. The available research results confirm the possibility of using cryogenic processes and phenomena in engineering, agriculture, conservation of biological diversity and a number of other areas, such as, for example, for storing gas in a solid hydrate state. This paper presents the results of studies of methane hydrate dissociation obtained in systems with the presence of promoting additives in order to determine the conditions and efficiency of gas storage in a solid hydrate state. Dissociation of gas hydrates formed from liquid solutions or dispersed systems was carried out by experimental methods using a high-pressure reactor in the temperature range of 263–268 K, i.e. close to the temperatures of permafrost occurrence. Thus, it was shown that methane hydrates formed from liquid solutions of surfactants – soy lecithin and sodium dodecyl sulfate, has high porosity, as a result of which it is practically incapable of self-preservation and cannot be used in the implementation of gas hydrate technologies for gas storage. At the same time, the addition of water-soluble polymer polyvinyl alcohol in a concentration of 0.3 wt.% leads to the growth of a denser methane hydrate capable of self-preservation at a temperature of 268 K. The data obtained in the work can be used in the development of gas hydrate technologies for storing natural gas in a solid hydrate state.

**Keywords:** gas hydrates, dissociation at T<273 K, self-preservation effect, kinetic promoters, storage of natural gas in the cryolithozone, permafrost storage facilities.

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## Introduction

Permafrost soils cover vast areas of Russia, where the mean annual air temperature remains below freezing. These soils can be utilized for constructing underground storage facilities for oil and gas products, water, agricultural goods, thermal energy storage systems, and other applications. Such facilities serve as natural cryogenic reservoirs, reducing costs associated with construction, thermal insulation materials, and energy consumption during both the construction and operational phases (Kuzmin, 2023). In the 1960s–1970s, the northern regions of Russia saw significant development in cryogenic storage construction, with capacities ranging from 5 to 500 tons. These structures were primarily built in loose sedimentary deposits at depths of 10–40 meters. A 1967 monograph (Mironov, 1967) presents a zoning map for underground cryogenic storage construction (Figure 1), based on permafrost temperatures and the duration of subzero air temperatures. The permafrost regions are classified into three distinct zones based on thermal characteristics. Zone 1 represents areas with ground temperatures at or below 266 K, experiencing more than 100 annual days with air temperatures below 258 K, where natural cooling and freezing processes occur without requiring mechanical refrigeration systems. Zone 2 comprises territories with ground temperatures ranging between 266–268 K and over 100 days of sub-263 K air temperatures annually; these conditions enable seasonal product preservation during warmer periods through passive utilization of cold energy accumulated during winter months. Zone 3 consists of regions with persistently cold winters, maintaining ground temperatures of 268–271 K, where active refrigeration systems become necessary to sustain

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the required thermal regime of the frozen ground throughout the year.

The world's first underground cryogenic seed storage facility was constructed in Yakutsk in 2012, where the temperature regime is maintained exclusively using natural cryogenic resources – the cold of permafrost and outdoor air. The design of this facility is described in the article (Kuvaiev, Kuzmin, 2018). This structure is located within permafrost layers with a temperature of 270.6 K at the base depth of 11.0 m. The average temperature in the working chamber maintains approximately 265 K, with temperature fluctuations ranging from 256 K to 268 K.

The technological advancements by Japan's Mitsui Engineering & Shipbuilding have elevated gas storage and transportation in solid hydrate form to parity with conventional methods of transporting gas in gaseous and liquefied states. Gas hydrates constitute solid clathrate non-stoichiometric crystalline structures formed by water and gas molecules under low-temperature, high-pressure conditions. Natural gas hydrate storage and transportation technologies primarily exploit two remarkable properties: their capacity to concentrate up to 167 volumes of methane at standard conditions per unit volume of hydrate, and their ability for long-term atmospheric-pressure storage enabled by the self-preservation effect (Falenty et al., 2014; Takeya et al., 2012; Chuvilin et al., 2022). This self-preservation mechanism allows gas hydrates to maintain stability outside their thermodynamic stability zone at temperatures below 273.2 K through a unique process involving the formation of metastable water films during hydrate decomposition, followed by crystallization of these surface layers which creates a protective barrier significantly inhibiting further dissociation (Istomin, Yakushev, 1992; Chuvilin et al., 2018; Chuvilin, Kozlova, 2005; Kwon et al., 2008) has demonstrated the feasibility of gas hydrate technologies. Notably, Japan's Mitsui Engineering & Shipbuilding (Watanabe et al., 2008; Nakai, 2012) has developed an integrated technology for the production, transportation, and storage of natural gas in solid hydrate form. This comprehensive process involves: (1) natural gas hydrate formation at 277 K with an initial pressure of 5.5 MPa; (2) subsequent storage and transportation of the stabilized hydrate; and (3) controlled regasification at the destination point. The technology capitalizes on the unique properties of gas hydrates, particularly their high gas storage capacity and stability under moderate temperature-pressure conditions, while addressing key engineering challenges associated with large-scale hydrate production and handling, drying of the synthesized natural gas hydrate; granulation with preservation of the synthesized gas hydrate at a temperature of 253 K with a final hydrate content of 75% and ice content of 25% and a production rate of 5 tons/day, followed by pressure release to 0.1 MPa; transportation of hydrate granules over

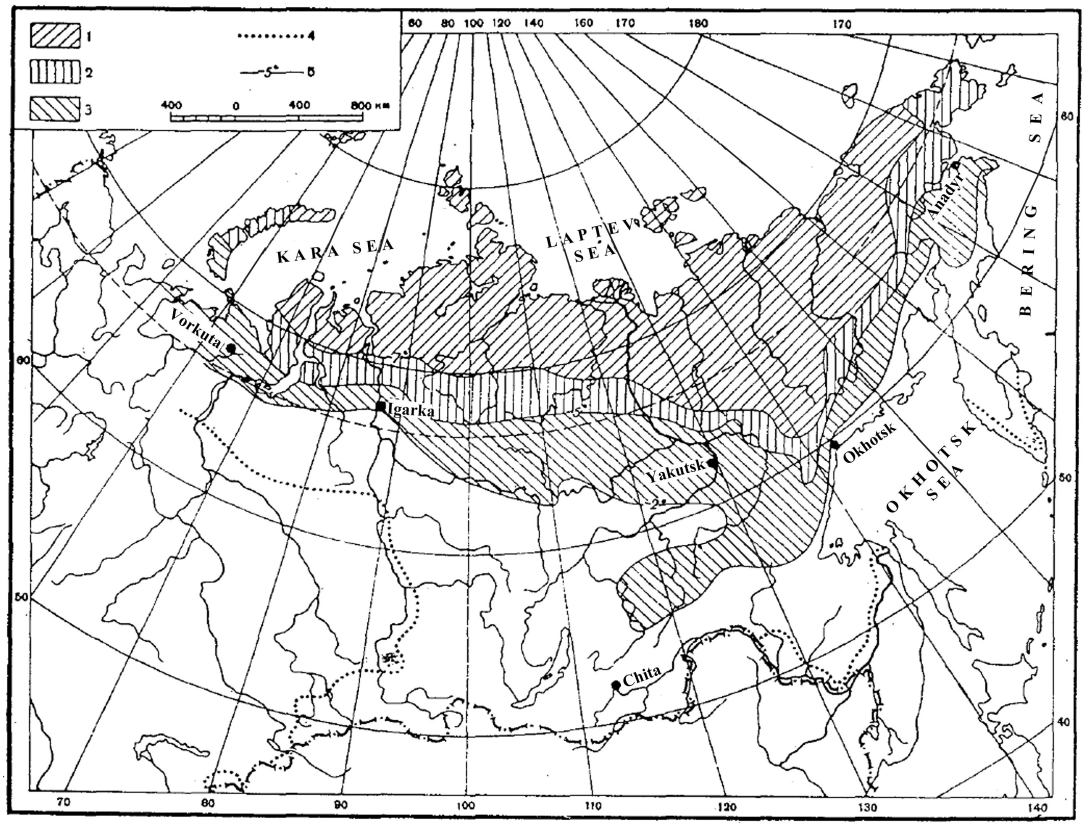


Figure 1. Zoning map for possible cryostorage facility construction (Mironov, 1967): 1 – Arctic and subarctic zones; 2 – temperate zone; 3 – zone of stable cold winters; 4 – boundary of the permafrost region; 5 – minimum rock temperature at the base of the layer of its annual fluctuations

a distance of 100 km within 2 hours at a temperature of 253 K and a pressure of 0.1 MPa in specially designed and constructed trucks; regasification carried out by circulating warm water at the bottom of the transport container. Additionally, the study (Watanabe et al., 2008) noted that during storage at 253 K, gas losses amount to less than 1% per day.

Moreover, in the late 1980s, the existence of relict gas hydrates under natural conditions due to the self-preservation effect was established (Ershov et al., 1991), which has also been confirmed in recent studies (Ershov et al., 2022). Russian scientists (Yakushev, 1988) were the first to study the self-preservation effect in laboratory conditions for methane hydrates synthesized from bulk water at temperatures of 274–278 K and pressures of 3–8 MPa. The obtained samples remained stable for a year at temperatures ranging from 255–270 K, showing almost no decomposition. The study (Istomin et al., 2006) presents data on the manifestation of the self-preservation effect in methane hydrates within a temperature range of 255–271 K and a pressure of 0.1 MPa. Additionally, it was shown that the degree of decomposition of a monolithic methane hydrate sample in the temperature range of 263–268 K was about 30% over 5 months. The study (Takeya et al., 2002) demonstrated that the dissociation rate of methane hydrates at atmospheric pressure within the temperature range of 198–268 K significantly decreases, indicating the manifestation of the self-preservation effect.

The study (Circone et al., 2004) demonstrated that the minimum dissociation rate of methane hydrate samples was observed at 268 ± 1 K, with subsequent confirmation of this effect under laboratory conditions provided in studies (Stern et al., 2003; Hachikubo et al., 2011; Takeya et al., 2013). Consequently, the authors' conclusion about the feasibility of storing methane hydrates under the temperature conditions of the Yakutsk cryogenic storage facility (specifically between 256 K and 268 K) is consistent with existing research by leading scientists on the methane hydrate self-preservation effect.

The literature contains information on the possibility of storing natural gas in solid hydrate form within rock pore spaces. Studies by researchers have evaluated the influence of rock porosity and permeability, as well as the uniformity of reservoir filling for gas storage in hydrate form, using both experimental and theoretical methods (Bondarev et al., 2015; Shagapov et al., 2008). The study (Rozhin, Argunova, 2022) presents results of mathematical modeling for natural gas injection and storage, including associated petroleum, greenhouse, and toxic gases in the form of gas hydrates in subpermafrost aquifers, aiming to assess the impact of reservoir properties on hydrate saturation. This study proposes an alternative storage approach – not in rock pore spaces, but in the air space of permafrost storage facilities at atmospheric pressure and natural temperatures below the ice melting point in hydrate form. For successful implementation of natural gas storage technology in solid hydrate form in cryogenic storage, several scientific and technological challenges must be addressed. One such challenge involves investigating the possibility of storing natural gas hydrates, produced using promoting additives, in a preserved state at subzero temperatures and atmospheric pressure.

It should be noted that the number of studies on the self-preservation effect of natural gas/methane hydrates obtained using various additives is currently limited. The study (Mimachi et al., 2016) investigated the self-preservation effect of methane hydrates formed from NaCl solutions with concentrations of 3 and 10 wt.%. The results revealed that the hydrate synthesized from the NaCl solution did not exhibit self-preservation. Kinetic promoters of methane hydrate formation were also examined for their ability to enable self-preservation of gas hydrates. For example, the study (Li et al., 2021) examined the effect of the most common additive, sodium dodecyl sulfate at a concentration of 0.05 wt.%, on the self-preservation phenomenon at atmospheric pressure and a temperature range of 253.15 to 268.15 K using high-pressure differential scanning calorimetry. It was found that methane hydrate remained stable throughout the entire studied temperature range for the full duration of the experiment (12 and 42 hours).

Moreover, the self-preservation capability of hydrates synthesized with thermodynamic promoters was investigated. It was found that a mixture of methane and tetrahydrofuran hydrates remained stable below the equilibrium curve at atmospheric pressure and 271 K for 2 years (Bhattacharjee et al., 2021). The study (Zhang et al., 2022) demonstrated the results of storing a methane-dioxane hydrate mixture outside the thermodynamic equilibrium zone at near-atmospheric pressure and 268.3 K for 120 days. The conditions examined in (Bhattacharjee et al., 2021; Zhang et al., 2022) correspond to the temperature conditions of permafrost existence. Thus, the aim of this work is to determine the influence of additives proven as effective promoters and systems on methane hydrate dissociation at temperatures below 273 K to identify a list of additives that do not increase the degree of dissociation. Sodium dodecyl sulfate, soy lecithin, polyvinyl alcohol, as well as the dispersed system "dry water" were used as promoting additives, since their effectiveness as hydrate formation promoters has been previously demonstrated by the authors (Mel'nikov et al., 2023; Molokitina, Drachuk, 2022; Podenko et al., 2018). Consequently, additives and systems that have proven to be effective promoters without increasing the methane hydrate dissociation rate can be recommended for use in the development and implementation of gas hydrate technologies for gas

transportation and storage. The study employed two experimental methodologies – isochoric and isobaric regimes at temperatures ranging from 263 to 268 K, approximating the thermal conditions of a cryogenic storage facility located in Yakutsk.

## Materials and methods

Table 1 presents the materials used in the study of methane hydrate dissociation formed in systems containing promoting additive substances. Methane (99.9 vol.% purity) was used as the hydrate-forming gas, being the main component of natural gas.

The investigation of methane hydrate dissociation in the temperature range of 263 K to 268 K involved the preparation of liquid solutions and dispersed systems containing various promoting additives to study their effect on methane hydrate's self-preservation capability. The component composition of the aqueous methane hydrate-forming systems is presented in Table 2.

*The methodology for preparing bulk and dispersed systems*

The procedure for preparing bulk samples of soy lecithin solutions and sodium dodecyl sulfate solutions was carried out at room temperature. The preparation process for liquid solutions of sodium dodecyl sulfate (SDS) and polyvinyl alcohol (PVA) involved dissolving PVA in a water bath (temperature approximately 353 K) with constant stirring, after which sodium dodecyl sulfate was added to the cooled PVA solution at a concentration of 0.05 wt.%.

The procedure for preparing ground frozen samples consisted of maintaining the solution at 258 K for at least 24 hours until complete freezing, after which the frozen solutions were ground at 258 K in a freezer (Teledoor, Germany) using a blender (Gemlux GL-BL1200G, China) at 20 000 rpm for 30 seconds. To increase the methane-water (ice) contact surface area, a fraction in the range of 80–140 μm was selected using fine analytical sieves (Molokitina, Drachuk, 2022).

The method for preparing "dry water" involved mixing distilled water with hydrophobized silicon dioxide nanoparticles (brand R202) in a household blender (Gemlux GL-BL1200G, China) at 20 000 rpm for 30 seconds at room temperature (Drachuk, 2018).

*Description of laboratory setup*

The schematic diagram of the laboratory setup for studying methane hydrate formation and dissociation is shown in Figure 2. This experimental setup consists of a programmable low-temperature cryostat (5) (KRIO-VT-11, Russia) using an aqueous propylene glycol solution as coolant; a high-pressure (HP) reactor (1) made of stainless steel with 60 $cm^3$ capacity and no stirring device, equipped with a pressure gauge (4) (DM5002M, accuracy ±16 kPa, manufactured by OAO Manotom, Russia) and either two thermocouples (3) (K-type TXA thermocouples, accuracy ±0.2 K, manufactured by PK Theseus, Russia) or temperature sensors (3) constructed from steel tubes with 2 mm outer diameter, containing a KD512A silicon pulse diode (operating range 228–373 K, accuracy ±0.1 K) soldered 3 mm from the active tip of the sensor.

The sensor data for pressure and temperature is recorded on a computer via an ADC. Before gas supply, air is evacuated from the reactor using a vacuum pump (6) (Value VE225n with 70 L/min capacity, China), after which methane charging is performed. A gas meter (Ritter TG0.5/5, Germany) was used in experiments studying methane hydrate dissociation under isobaric conditions (at atmospheric pressure).

The methane hydrate samples were synthesized under isochoric conditions without stirring at an initial pressure of 4.7–5 MPa and a temperature of 273 K in

| Material | Country, Manufacturer | Grade |
|---|---|---|
| Distilled water | Produced in the Laboratory | - |
| Polyvinyl alcohol (PVA) | Taiwan, Chang Chun | BF-14 |
| Hydrophobic Silica Dioxide | Germany, Evonik | R202 |
| Soy Lecithin (SL) | Germany, - | - |
| Sodium dodecyl sulfate (SDS) | Russia, Dia-M | - |

Table 1. Materials used in this study

| System | Substance | Concentration, wt.% |
|---|---|---|
| Liquid soy lecithin solution | Soy Lecithin | 0.5 |
| Liquid SDS solution | SDS | 0.05; 0.1 |
| Liquid SDS and PVA solution | SDS and PVA | 0.05 and 0.1; 0.2; 0.3 |
| Frozen powdered PVA solution | PVA | 0.5; 1; 2; 3 |
| "Dry water" | Hydrophobic Silica Dioxide | 3; 5; 10; 12; 15 |

Table 2. Composition of aqueous methane hydrate formation systems with promoter additives

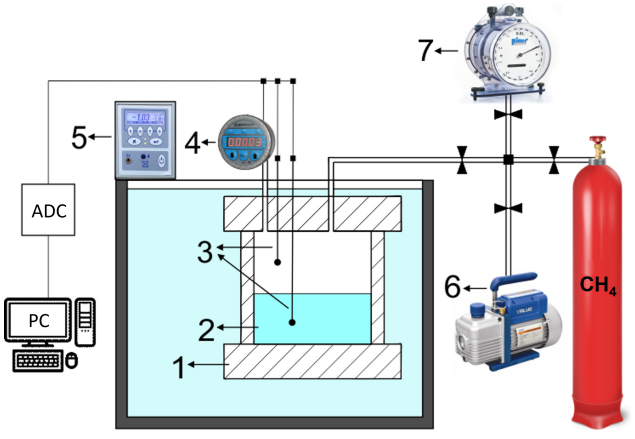


Figure 2. Schematic diagram of the laboratory setup for methane hydrate formation and dissociation studies: (1) 60 cm³ high-pressure reactor without stirring device; (2) sample containing promoter additives; (3) temperature sensors/thermocouples; (4) DM5002M pressure gauge; (5) programmable KRIO-VT-11 cryostat; (6) Value VE225n vacuum pump; (7) Ritter TG0.5/5 gas meter

bulk solutions and "dry water", and at 272 K in ground frozen solutions (Mel'nikov et al., 2023; Molokitina, Drachuk, 2022; Podenko et al., 2018).

Based on the experimental data obtained during methane hydrate formation in various promoter systems, the water-to-hydrate conversion ratios (the ratio of water mass converted to hydrate to the initial water mass in the sample) were calculated using the formula (Table 3):

$$\alpha = \frac{n \cdot M_{H2O} \cdot \Delta n}{m_0}, \quad (1)$$

where $n$ is the hydration number (according to the monograph by (Istomin, Yakushev, 1992), $n$ = 6 for methane); $M_{H2O}$ is the molecular mass of water (kg/mol); $\Delta n$ is the amount of gas converted to the hydrate state (mol); $m_0$ is the initial mass of the aqueous solution (kg).

*Experimental methodology for gas hydrate dissociation under isochoric conditions (without monitoring gas release during dissociation)*

The experiments studying ice-hydrate sample dissociation under isochoric conditions (with increasing reactor pressure) were conducted as follows: immediately after methane hydrate formation, the high-pressure reactor was cooled to 268–263 K. For temperature stabilization, the reactor containing pre-synthesized methane hydrate was maintained for at least 1 hour, followed by rapid pressure release to atmospheric through the reactor shut-off valve, which was then closed. The study assumed that pressure release only discharged the gas phase without losing gas absorbed in the methane hydrate. Gas release during methane hydrate dissociation was monitored via pressure gauge readings. To evaluate gas remaining in the hydrate phase after 22 hours of dissociation onset, the temperature was increased to 283 K for complete hydrate decomposition. Energy absorption during methane hydrate dissociation was not accounted for.

To evaluate hydrate decomposition, the degree of methane hydrate dissociation ($\Delta G$) was determined as the ratio of moles of methane released during dissociation at time $t_i(n_i)$ to the total moles of methane

| System | Concentration, wt.% | Water-to-hydrate conversion, % |
|---|---|---|
| Liquid Soy lecithin solution | 0.5 (268 K) | 70 |
| | 0.5 (265.5 K) | 72 |
| | 0.5 (263 K) | 62 |
| Liquid SDS solution | 0.05 | 84 |
| | 0.1 | 83 |
| Liquid SDS and PVA solution | 0.05 and 0.1 | 85 |
| | 0.05 and 0.2 | 78 |
| | 0.05 and 0.3 | 68 |
| Powdered frozen PVA solution | 0 | 95 |
| | 0.5 | 95 |
| | 1 | 95 |
| | 2 | 95 |
| | 3 | 97 |
| "Dry water" | 3 | 57 |
| | 5 | 71 |
| | 10 | 90 |
| | 12 | 95 |
| | 15 | 95 |

Table 3. Degree of water-to-hydrate conversion in methane hydrate samples for the studied systems at the onset of dissociation

released after complete dissociation of the ice-hydrate sample ($n$) (Podenko et al., 2018):

$$\Delta G = \frac{n_i}{n}. \quad (2)$$

*Methodology for investigating gas hydrate dissociation under isobaric conditions (with monitoring gas release during dissociation)*

Experiments on ice-hydrate sample dissociation under isobaric conditions (at atmospheric pressure) were conducted according to the methodology described below.

Immediately after methane hydrate formation, the high-pressure reactor was cooled to 268 K. The reactor pressure was then gradually reduced to a value 100 kPa above the ice-methane hydrate-methane phase equilibrium pressure (2180 kPa at 268 K (Sloan, Koh, 2007)). Following temperature stabilization in the high-pressure reactor, rapid gas venting was performed, after which the amount of gas released during dissociation was measured by a gas flow meter. Energy absorption during methane hydrate dissociation was not accounted for.

To evaluate hydrate decomposition, the degree of dissociation ($\Delta G$) of the ice-hydrate sample was determined similarly using formula (2).

## Results and Discussion

*Dissociation of ice-hydrate samples in promoter solutions at subzero temperatures*

Dissociation of the ice-hydrate sample prepared in 0.5 wt.% soy lecithin solution (Table 3) was investigated in the temperature range of 263–268 K under isochoric conditions.

Figure 3 presents the temporal evolution of the dissociation degree at 263, 265.5, and 268 K. At 268 K, the dissociation degree reached 77% within 1330 minutes, with 50% dissociation achieved within the initial 270 minutes of decomposition. Notably, after 1330 minutes, the dissociation rate showed no significant decrease, suggesting a complete absence of self-preservation effects.

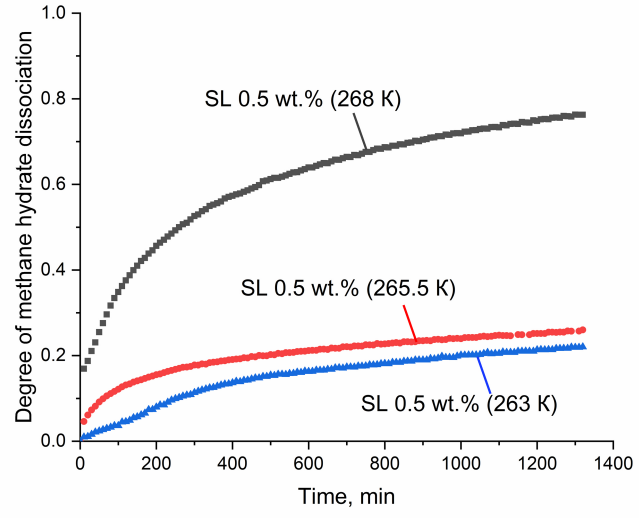


Figure 3. Degree of dissociation of ice-containing hydrate samples obtained from liquid solutions: soy lecithin (SL) – 0.5 wt.%. Dissociation in the temperature range: 263–268 K. Isochoric mode

When the temperature was lowered to 265.5 K, only 26% of the ice-hydrate sample dissociated over 1330 minutes. Here, the initial 200 minutes yielded 15% dissociation, after which the decomposition rate markedly decreased, indicating partial self-preservation of the ice-hydrate sample.

Further temperature reduction to 263 K resulted in an even greater decrease in dissociation rate, with the dissociation degree reaching 11% during the initial 300 minutes and 22% after 1330 minutes. Despite the significant slowdown of dissociation at 265.5 K and 263 K, complete self-preservation of the ice-hydrate sample was not observed during the 22-hour experiment, indicating the formation of an ice crust that permitted methane molecule diffusion.

Thus, it can be concluded that at temperatures below 265.5 K, partial self-preservation of the ice-hydrate sample formed in 0.5 wt.% soy lecithin solutions was observed, while further studies with longer exposure times are required. The dissociation of ice-hydrate samples formed in sodium dodecyl sulfate (SDS) solutions with concentrations of 0.05 and 0.1 wt.% and in binary solutions containing 0.05 wt.% SDS and 0.1–0.3 wt.% PVA (Table 3) was investigated at sub-ice melting temperatures under isobaric conditions. Figure 4 shows the temporal changes in dissociation degree at 268 K. Experimental data revealed that ice-hydrate samples formed in 0.05 and 0.1 wt.% SDS solutions already decomposed by approximately 25% within the first 50–100 minutes of dissociation, after which the dissociation rate decreased only slightly.

At the same time, the ice-hydrate sample formed in SDS solutions with the addition of polyvinyl alcohol at concentrations of 0.1 to 0.3 wt.% decomposed by approximately 10% during the first 50 minutes, which is 2.5 times less than for the ice-hydrate sample formed from pure SDS solution. It can be assumed that in pure SDS solutions, methane hydrate, growing along the reactor walls upward, has high porosity and a large surface area, leading to its complete decomposition outside the stability zone before the formation of an ice crust. In contrast, methane hydrate formed in SDS and PVA solutions has a denser structure, which promotes the formation of an ice crust capable of preserving the ice-hydrate sample.

This assumption is supported by the authors of the study (Istomin et al., 2006), which describes the influence of gas hydrate sample structure on their stability under identical conditions. Thus, it can be

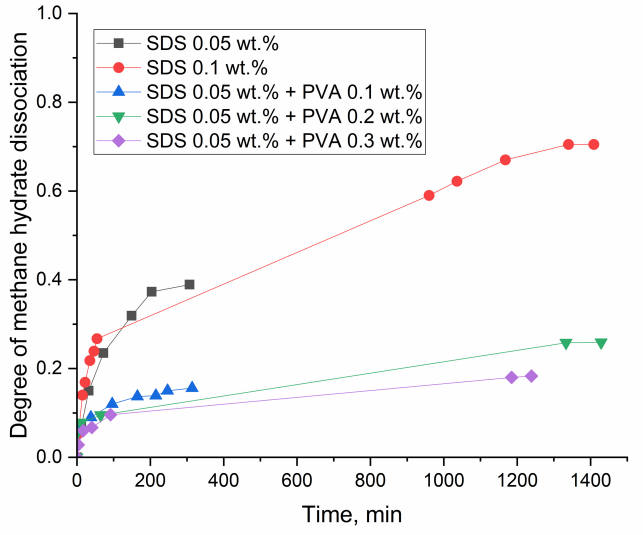


Figure 4. Degree of dissociation of ice-containing hydrate samples obtained in liquid solutions: SDS – 0.05 wt.%; SDS – 0.1 wt.%; SDS – 0.05 wt.% and PVA – 0.1 wt.%; SDS – 0.05 wt.% and PVA – 0.2 wt.%; SDS – 0.05 wt.% and PVA – 0.3 wt.%. Dissociation at a temperature of 268 K. Isobaric mode

concluded that the self-preservation effect is primarily influenced by the morphology (structure) of the methane hydrate/ice-hydrate sample. Specifically, gas hydrates formed in surfactant solutions exhibit high porosity, which complicates the formation of an ice crust on their surface, whereas the presence of additives leading to the formation of denser hydrates, conversely, promotes their preservation.

*Dissociation of ice-hydrate samples in dispersed systems containing promoters at subzero temperatures*

The dissociation of ice-hydrate samples prepared in dispersed systems – ground ice of 80–140 μm fraction and ground frozen PVA solutions with concentrations ranging from 0.5 to 3 wt.% (80–140 μm fraction, Table 3) – was investigated at sub-ice melting temperatures under isobaric conditions. Figure 5 shows the temporal changes in dissociation degree at 268 K. The ice-hydrate sample formed from ground ice (80–140 μm fraction) showed the lowest dissociation degree, yet decomposition continued even after 1300 minutes, indicating no preservation effect. For ice-hydrate samples prepared in ground frozen polyvinyl alcohol solutions, the dissociation degree increased with higher PVA concentrations: samples with 0.5 wt.% PVA reached about 40% dissociation after 400 minutes, while those with 3 wt.% PVA reached 60%. These experimental results demonstrate the absence of self-preservation effects in ice-hydrate samples prepared from ground frozen systems.

The dissociation of ice-hydrate samples prepared from “dry water” dispersed systems, stabilized with R202, concentrations ranging from 3 to 15 wt.% was investigated at sub-ice melting temperatures under isobaric conditions (Table 3). Figure 6 shows the temporal changes in dissociation degree at 268 K. Increasing the concentration of R202 silica nanoparticles from 3 to 5 wt.% resulted in approximately 40% dissociation of the ice-hydrate sample within 300 minutes, while concentrations above 5 wt.% led to a threefold increase in dissociation degree. This effect may be attributed to reduced water microdroplet size in “dry water” at silica stabilizer concentrations exceeding 5 wt.%, consequently decreasing the size of

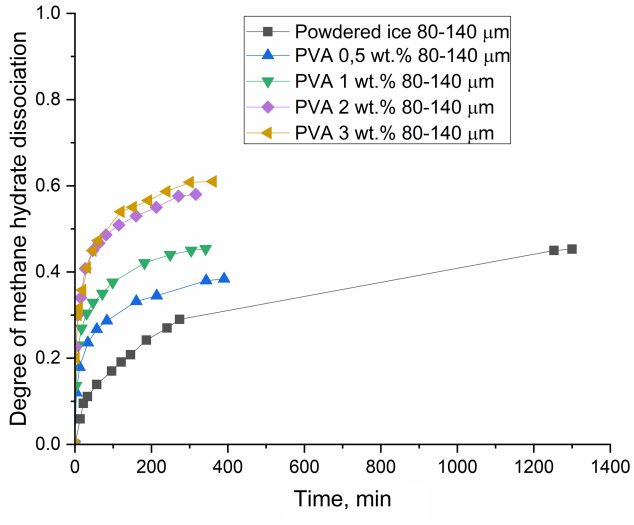


Figure 5. Degree of dissociation of ice-containing hydrate samples obtained in dispersed systems: powdered ice fraction of 80–140 μm; frozen powdered aqueous PVA solutions with concentrations of 0.5, 1, 2, and 3 wt.% (fraction 80–140 μm). Dissociation at a temperature of 268 K. Isobaric mode

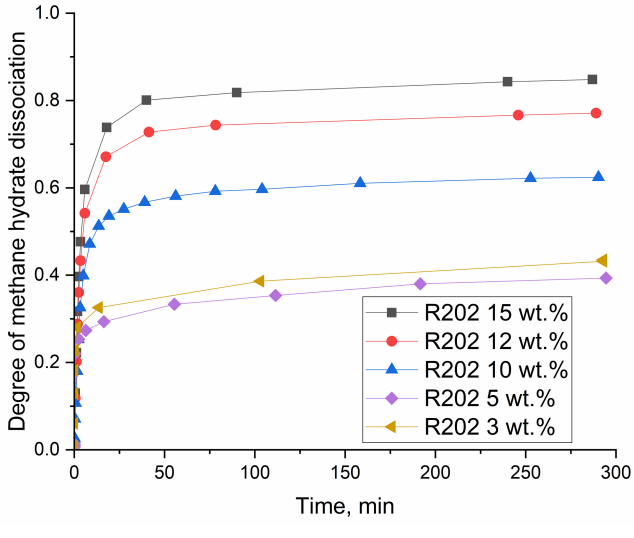


Figure 6. Degree of dissociation of ice-containing hydrate samples obtained in dispersed systems: “dry water” with the stabilizer R202 concentrations of 3, 5, 10, 12, and 15 wt.%. Dissociation at a temperature of 268 K. Isobaric mode. (Drachuk, 2018)

formed hydrate particles. Such small hydrate particles may undergo complete dissociation before ice crust formation. Thus, the reduction of water droplet size in the "dry water" system and the resulting decrease in methane hydrate particle size were responsible for diminished self-preservation efficiency (Drachuk, 2018; Melnikov et al., 2016).

Figure 7 shows the dissociation rates of ice-hydrate samples formed in the studied promoter systems, with rates determined at 5, 10, 50, 100, and 200-minute intervals after dissociation onset. The data reveals that ice-hydrate samples formed in "dry water" dispersed systems exhibited the highest dissociation rates both initially (5-minute interval) and over extended periods (200-minute interval). While samples from ground frozen solution-based promoter systems showed significant rate reduction at 100–200-minute intervals, their initial decomposition rates substantially exceeded those of liquid SDS/PVA solutions and ground ice systems. The sample from 0.05 wt.% SDS liquid solutions also demonstrated high dissociation rates, whereas liquid solutions combining 0.05 wt.% SDS with 0.3 wt.% polyvinyl alcohol additives displayed the lowest dissociation rates throughout the entire study period.

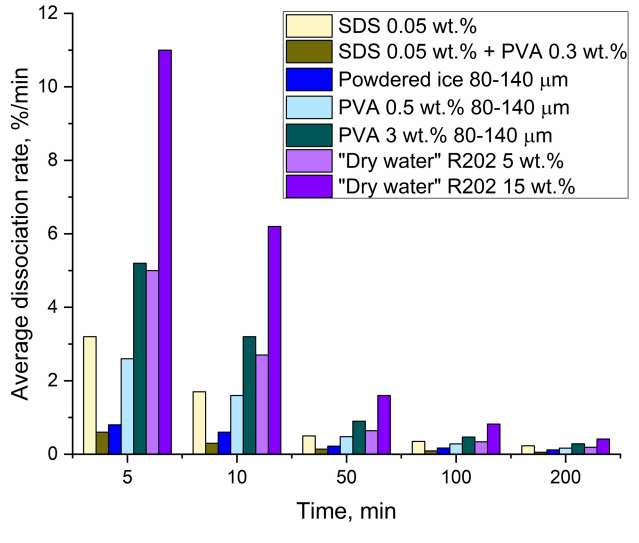


Figure 7. Dissociation rate diagram of ice-hydrate samples formed in various promoter systems (isobaric mode at 268 K)

## Conclusion

The study examined the effects of promoting additives and systems on methane hydrate dissociation rates. The results identified specific promoters among the tested candidates that warrant further investigation for methane hydrate self-preservation below 273 K and potential application in natural gas storage technologies using solid hydrates. Permafrost storage facilities with annual temperature fluctuations between 256–268 K were considered as potential venues for natural gas storage in hydrate form. The tested systems included soy lecithin solutions, sodium dodecyl sulfate (SDS), polyvinyl alcohol (PVA), ground frozen PVA solutions, and "dry water". Experimental data revealed that ice-hydrate samples formed from 0.5 wt.% soy lecithin solutions dissociated significantly slower at 263–265.5 K compared to 268 K. Furthermore, during dissociation of samples prepared from SDS (0.05–0.1 wt.%) and PVA (0.1–0.3 wt.%) solutions, the lowest dissociation rates were observed for the mixture containing 0.05 wt.% SDS and 0.3 wt.% PVA.

The study also revealed that among systems prepared from frozen powdered solutions, the ice-containing hydrate sample formed from finely dispersed ice without promoting additives demonstrated the lowest dissociation rate. The presence of PVA additive at concentrations of 0.1–3 wt.% in frozen powdered solutions increased the dissociation rate compared to samples formed from ground ice alone, with a clear concentration-dependent effect – higher PVA concentrations led to faster dissociation rates. Specifically, the addition of 3 wt.% PVA increased the dissociation rate by nearly fivefold during the initial dissociation phase compared to ground ice samples. For ice-hydrate samples prepared from the "dry water" dispersed microdroplet system, researchers established that increasing the concentration of hydrophobized nanosilica stabilizer proportionally increased the dissociation rate, demonstrating a direct correlation between stabilizer concentration and dissociation kinetics The obtained results are consistent with existing literature data indicating that hydrate particle size and porosity are determining factors for methane hydrate self-preservation. It should be noted that the available data are insufficient to assess the feasibility of gas storage in solid hydrate form through self-preservation effects at atmospheric pressure in cryogenic storage facilities constructed in permafrost regions. A series of studies on long-term storage of preserved methane hydrate under temperature conditions comparable to those of cryostorage facilities is required, along with an evaluation of how temperature fluctuations during storage affect the efficiency of methane hydrate self-preservation. Based on the results from such additional research, a conceptual technological scheme for gas hydrate storage could be developed.

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IN RUSSIAN

# Исследование диссоциации гидратов метана при отрицательных температурах

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Использование ресурсов криолитозоны в настоящее время – один из приоритетных вопросов в повестке научно-технологического и экономического развития Российской Федерации. Имеющиеся результаты изысканий подтверждают возможность использования криогенных процессов и явлений в инженерном деле, сельском хозяйстве, сохранении биологического разнообразия и в ряде других направлений, таких как, например, хранении газа в твердом гидратном состоянии. В данной работе приводятся результаты исследований диссоциации гидратов метана, полученных в системах с промотирующими добавками, с целью определения условий и эффективности хранения газа в твердом гидратном состоянии. Диссоциация гидратов, сформированных из жидких растворов или дисперсных систем, осуществлялась экспериментальными методами с использованием реактора высокого давления в диапазоне температур 263–268 К, то есть близких к температурам залегания многолетнемерзлых пород. Показано, что гидрат метана, сформированный из жидких растворов поверхностно-активных веществ – соевого лецитина и додецилсульфат натрия, обладает высокой пористостью, вследствие чего практически не способен к самоконсервации и не может применяться при реализации газогидратных технологий хранения газа. При этом добавка водорастворимого полимера поливинилового спирта в концентрации 0,3 мас.% приводит к росту более плотного гидрата метана, способного к самоконсервации при температуре 268 К. Данные, полученные в работе, могут быть использованы при разработке газогидратных технологий хранения природного газа в твердом гидратном состоянии.

**Ключевые слова:** газовые гидраты, диссоциация при T<273 К, эффект самоконсервации, кинетические промоторы, хранение природного газа в криолитозоне, мерзлотные хранилища

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