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## The effect of gas hydrates self-preservation in the process of their industrial development

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The negative influence of the gas hydrates (GH) self-preservation effect on the course of the technological process of their industrial development by the depressurization method is considered. The main parameters of the self-preservation manifestation: the porosity of the hydrate and its morphological characteristics are justified. An important practical conclusion was made that solving the problems of gas hydrates self-preservation should be facilitated by the selection of the optimal operation mode for the production well, which would harmonize the hydrate porosity and its morphological characteristics, and at the same time ensure the maximum possible production and control over the processes of gas hydrates dissociation.

**Keywords:** gas hydrates, development of gas hydrate deposits, self-preservation, ice crust, parameters of self-preservation manifestation during mining.

## Ефект самоконсервації газових гідратів в процесі їх промислової розробки

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Відзначено, що найперспективнішою на сьогодні технологією розробки родовищ газових гідратів (ГГ) є декомпресійний метод (метод розгерметизації), суть якого полягає в штучному зниженні тиску в пласті навколо свердловини або за рахунок скорочення тиску води на гідрат, або тиску вільного газу після їх часткового відкачування. Розглянуто негативний вплив ефекту самоконсервації газових гідратів на перебіг технологічного процесу їх промислової розробки методом розгерметизації. Обґрунтовано основні параметри прояву самоконсервації – пористість гідрату та його морфологічні характеристики. Розглянуто особливості призначення параметрів теплоти гідратоутворення чи ентальпії дисоціації при моделюванні процесів фазової рівноваги та процесів дисоціації газових гідратів. Подано наочний вигляд молекулярного складу гідрату метану, формулу сполуки та загальний вигляд його зразків. Описано методику і результати лабораторних експериментальних досліджень зі зразками штучно утвореного газового гідрату. Підтверджено розрахункову залежність пористості зразка від його початкової температури, як умови для прояву самочинної консервації газогідрату. Також встановлено, що при подальшому надходженні теплової енергії до зразка незалежно від його пористості відбувалось поступове плавлення утвореної льодяної кірки. Зафіксовано, що цей процес продовжується до тих пір, доки не вичерпувався «запас холоду» у зразкові, після чого дисоціація прискорювалась. Встановлено, що для гідрату пористістю понад 28% більша частина води проникала порами вглиб зразка. Зроблено важливий для практики висновок про те, що вирішенню проблем самоконсервації газових гідратів повинен сприяти підбір оптимального режиму експлуатації видобувної свердловини, який би узгоджував між собою пористість гідрату та його морфологічні характеристики та забезпечував при цьому максимально можливий видобуток і контроль за процесами дисоціації газових гідратів.

**Ключові слова:** газові гідрати, розробка газогідратних покладів, самоконсервація, льодяна кірка, параметри прояву самоконсервації при видобутку.



## Introduction

Gas hydrates (GH) were first obtained in laboratory conditions in the 1800s. In the following decades, laboratory experiments continued, but scientists did not expect that GHs could form in the natural environment.

Then, in the 1930s, man-made GH were discovered in gas pipelines, which blocked the transportation of natural gas. This triggered a new round of scientific research aimed at preventing the formation of GH in gas pipelines. Finally, in the 1960s, the development of the Messoyakh deposit in Western Siberia began, which confirmed the existence of natural methane hydrates [1].

In the 1970s, they were discovered in samples from a well on the North Slope of Alaska and at the bottom of the Black Sea. The results of research in the 1980s led to the fact that GH were considered as a new and potential source of methane [2]. And since the 1990s, targeted and large-scale programs for the detection and development of GH have been implemented around the world [3, 4].

## Review of the research sources and publications

The process of developing a GH deposit is carried out due to a phase transition - GH dissociation into water and gas, with subsequent extraction of the latter. At the same time, GH decomposition can be carried out in various ways, in particular: deviation of thermodynamic parameters from the equilibrium ones (that is, by increasing the temperature or decreasing the pressure in the reservoir); injection of inhibitors and other electromagnetic or acoustic influences [5].

Today, the most promising technology for the development of GH deposits is the decompression method (depressurization) [6]. Its essence is to artificially reduce the pressure in the reservoir around the well either by reducing the pressure on the GH of water or free gas after they are partially pumped out. When the pressure in the GH layer is lower than the phase equilibrium, it begins to break up into gas and water, absorbing heat energy from the environment.

Thus, the application of the decompression method is accompanied by the cooling of hydrate-bearing rocks and the manifestation of the self-preservation phenomenon of the hydrate itself. As a result, the gas hydrate surface is covered with an ice crust, which, on the one hand, increases its stability, and on the other hand, slows down or stops its dissociation, that is, the amount of production.

Such a problem was encountered in 2013 during the experimental and industrial development of gas hydrate deposits using the decompression method in the area of the Nankai trough near the coast of Japan [7]. In order to maintain the proper level of production due to pressure reduction in the process of liquid pumping, intensive removal of rock took place. Mining had to be stopped to solve this problem, which may be related to the phenomenon of GH self-preservation.

By the way, similar problems were noted in the course of other projects of experimental and industrial GH development [8–10].

## Definition of unsolved aspects of the problem

Analyzing the available practical results regarding the development of gas hydrate deposits by the depressurization method, it is possible to make a certain generalization that it was the self-preservation process that led to the premature termination of the experiment (significant removal of rock from the well and clogging of the separation equipment).

## Problem statement

Therefore, the study of the self-preservation effect for GH in the process of their development is an urgent task that requires careful study.

Currently, a number of studies on the self-preservation GH effect are known [11–17], but they do not take into account the porosity of the hydrate and its morphological characteristics. The actual article is devoted to the justification of the latter as the main parameters of the self-preservation manifestation.

## Basic material and results

Methane ( $\text{CH}_4$ ) forms hydrates or clathrates - crystalline structures in which it is surrounded by water molecules held together at low temperature and high pressure.

GHs are formed due to the inclusion of methane molecules (guest molecules or guest subsystem) in the cavity of an ice-like framework built by hydrogen-bonded water molecules (host framework or host subsystem) without the formation of a chemical bond between guest and host molecules.

Stabilization of aqueous clathrate frameworks, which are thermodynamically less stable than hexagonal ice (at  $T < 273 \text{ K}$ ) or water (at  $T > 273 \text{ K}$ ) is ensured by van der Waals host-guest interactions.

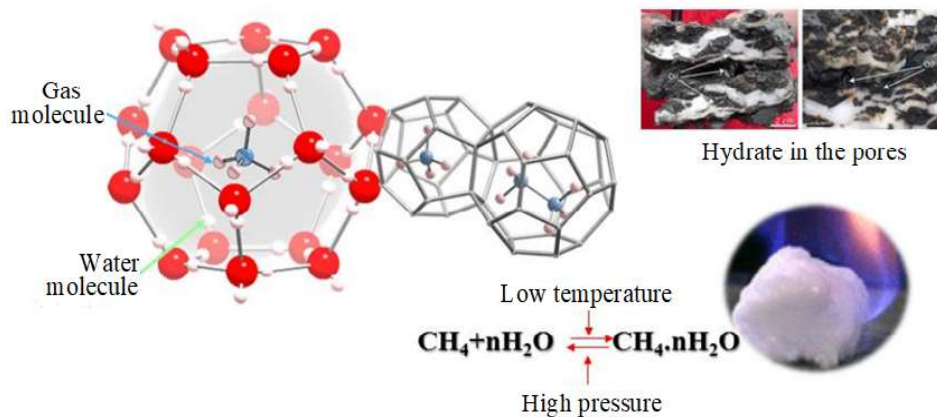
The general appearance of the methane hydrates composition is described by the formula  $\text{CH}_4 \times n\text{H}_2\text{O}$ , where  $n$  is a number showing the number of water molecules per one molecule of methane. The molecular composition of methane hydrate, the formula of the compound, and the general appearance of the samples are shown in Fig. 1.

One of the most important parameters in modeling phase equilibrium processes and GH dissociation processes is the heat of hydrate formation or enthalpy of dissociation [18].

The latter is equal to the amount of heat required to decompose the hydrate compound into water and gas at equilibrium temperatures and pressures and, in this case, is a function of temperature and pressure. Experimentally obtained values for the heat of the hydrates phase transition lie within 480–540 kJ/kg.

During hydrate formation, heat is released and the enthalpy is positive, while hydrate decomposition is negative.

Dissociation of hydrate inclusions occurs starting from their surface layer and then gradually moves deeper. The water layer formed on the surface of a hydrate particle as a result of the dissociation of its surface layer contacts the next hydrate layer.



**Figure 1 – The methane hydrate molecular composition, the formula of the compound and the general appearance of the samples**

At the same time, under certain conditions, the amount of energy spent on the dissociation of this layer may exceed the amount of energy required for crystallization (freezing) of this water layer. As a result, the formed ice crust will prevent further dissociation of the gas hydrate (from its slowing down to a complete stop). Therefore, the processes of hydrates dissociation in the pore space are characterized by a decrease in temperature, and as a result - a manifestation of the self-preservation effect.

In general, it consists of the following. If GH, obtained under normal equilibrium conditions, is cooled to a temperature below 0°C and the pressure is reduced to atmospheric, then after the initial surface decomposition, it self-isolates from the environment with a thin film of ice, which prevents further decomposition.

After that, GH can be stored for a long time at atmospheric pressure (depending on temperature, humidity and other parameters of the external environment). The discovery of this effect made a significant contribution to the study of natural GHs. In addition, the self-preservation effect opened up new opportunities for gas storage and transportation in a concentrated form without increased pressure [3, 4, 18, 19].

It has been experimentally proven that the clathrate framework of the host is metastable for hydrates [20; 21]. When the framework cavities are filled with "guest" molecules, its stabilization occurs. At a certain degree of filling, equilibrium occurs [22]. Gas hydrates are thermodynamically stable only when they almost completely (more than 95%) fill at least one of the types of cavities [18].

This especially applies to hydrates of the KS-2 structure, which include natural gas hydrates [18]. When the equilibrium conditions are disturbed, the hydrated lattice loses gas molecules and becomes metastable again.

Powdery and finely dispersed hydrates at atmospheric pressure dissociate almost immediately completely at temperatures below 273K and close to equilibrium. In large or monolithic samples, the dissociation process takes place in two stages: first, at temperatures below 273K, the surface of the hydrate decomposes into gas and ice, and then the ice begins to melt at a temperature

of about 273K. As a result, the surface of the sample is gradually covered with ice, which slows down its further dissociation [23].

As a result of self-preservation, hydrates at atmospheric pressure and temperatures below 273K exist in a metastable state for a long time without significant gas losses [24].

At the same time, there is also a partial dissociation effect, which is observed for samples of natural hydrates with initial temperatures of 273-278 K. Since dissociation is an endothermic process, the temperature of such a sample usually drops to 273 K. Decomposition of the hydrated clathrates surface leads to the formation of an ice crust, which actually stops their further destruction, while the temperature of the hydrate gradually increases to the initial one.

As the results of experimental studies prove, at temperatures from 272 K to 255 K, samples of gas hydrates with different morphology have different rates of dissociation [25].

During the study of the dissociation process for artificial gas hydrate samples, which contained up to 15% of trapped water, the destruction of the ice formed around the hydrate particles stopped already at a temperature of 258 K and atmospheric pressure, although the equilibrium temperature for such pressure is 195 K [16].

Ice and inclusions located in an ice-hydrate system with hydrate particles with a diameter of 15 mm (where the hydrate particles are encapsulated by an ice crust) with an ice layer thickness of 1 mm can withstand a pressure of about 0.5 MPa. At the same time, the strength limit of ice is more sensitive to the size of the crystals than to their temperature [15].

The metastability of natural gas hydrate is a consequence of an insufficient amount of heat, and if such storage is adiabatic, then the hydrate is stored for a long time [19]. The dissociation kinetics of the samples depends on the ratio of the surface area to the mass of the gas hydrate (monolithic or powdered). With its increase, both the rate of gas hydrate dissociation and the rate of temperature decrease increase.

In addition, in the process of melting, the sharp protrusions of the hydrate crystals are rounded. As a result, their surface area decreases [18].

In the geological environment, an important geochemical and technological problem is the prediction of thermobaric and morphological parameters of the self-preservation effect manifestation. Preliminary calculations made it possible to determine the thermobaric conditions of gas hydrate self-preservation depending on their porosity.

A cooled sample of gas hydrates under conditions of reduced pressure to atmospheric at a temperature above 273 K receives energy from the gas phase and heats up. At the same time, the amount of energy entering the gas hydrate sample is determined by the formula

$$dQ = \alpha (t_{GH} - t_{surf}) S d\tau, \quad (1)$$

where  $\alpha$  – heat transfer coefficient, W/m<sup>2</sup>·K;

$t_{GH}$ ,  $t_{surf}$  – temperature of the sample and air, respectively, K;

$S$  – the area through which heat flows, m<sup>2</sup>;

$\tau$  – sample heating time, s.

Integrating equation (1) over time  $\tau$  makes it possible to determine the amount of heat that will enter the sample from the external environment. Using dependence (1) and the value of the melting enthalpy of 1 mole of methane hydrate, it is possible to determine the duration of the dissociation process of a hydrate layer 1-2 mm thick.

Having determined the amount of water required to fill part of the pore space on the gas hydrate surface, it is possible to calculate the thickness of the continuous ice layer on its surface. As shown by previous experiments on the process of self-preservation of artificially formed natural gas hydrate samples for a typical composition and porosity ranging from 0.02 to 0.18, a layer of ice about 1-2 mm thick is sufficient for their high-quality preservation.

For samples with higher porosity, it is necessary to take into account the additional amount of water, which will fill the pores in the sample to a depth up to 1 mm. After receiving the appropriate amount of thermal energy, the surface layer of the gas hydrate sample will enter non-equilibrium conditions and begin to melt. The process of dissociation will be accompanied by the absorption of energy from the environment. The amount of energy required for the crystallization of this water amount is determined by the formula of O.V. Lykova

$$dQ_{cryst} = r_{cryst} \rho_{ice} \delta S d\tau \quad (2)$$

where  $r_{cryst}$  – specific heat of ice crystallization, J;

$\tau$  – freezing time, s;

$\delta$  – ice crust thickness, m;

$\rho_{ice}$  – ice density, kg/m<sup>3</sup>;

$S$  – the area through which the flow of cold flows, m<sup>2</sup>.

Since the thickness of the ice layer is relatively small compared to the size of the test sample, this object can be considered semi-infinite. The process of heat transfer to the sample during the crystallization of a certain water amount is assumed to correspond to the boundary

conditions of the first kind and is determined by the formula [26]

$$Q_{GH} = (t_{cryst} - t_{GH}) \sqrt{\frac{\lambda_{GH} \cdot c_{GH} \cdot \rho_{GH}}{\pi}} S \quad (3)$$

where  $t_{cryst}$ ,  $t_{GH}$  – respectively, the crystallization temperature and the initial temperature of the gas hydrate, K;

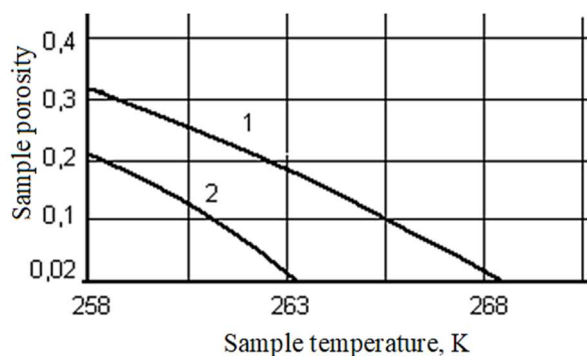
$\lambda_{GH}$  – thermal conductivity of hydrate, W/m·K;

$c_{GH}$  – specific heat capacity of hydrate, J/kg;

$\rho_{GH}$  – density of the gas hydrate sample, kg/m<sup>3</sup>.

Taking into account the duration of the energy required for the dissociation of the hydrate layer from the gas phase, using formula (3), we determine the amount of energy that will be used to freeze the ice layer in a given period of time.

Comparing the amount of energy required for the dissociation of the gas hydrate layer over a certain period of time and the energy required for crystallization of the volume of water released at the same time allows establishing the dependence of the porosity of the gas hydrate sample on its temperature for the manifestation of the self-preservation effect. The dependence obtained as a result is presented in fig. 2.



**Figure 2 – Dependence of the gas hydrate sample temperature on the porosity at atmospheric pressure for the manifestation of the self-preservation effect at an air temperature of 273 K (curve 1) and 278 K (curve 2)**

To verify the above calculations, experimental studies were conducted with samples of artificially formed GH. The gas hydrate was produced in a laboratory unit by mixing with a mechanical stirrer and subsequent separation of free water. However, part of the water remains trapped in the intergranular space, in drops covered with a hydrate crust and in the form of film water [26].

Therefore, to obtain samples, the formed gas hydrate was cooled to a temperature of 245 K, removed from the reactor, crushed, returned to the reactor and kept for three days at a temperature of 275 K and a gas pressure of 5.5 MPa. As a result, all the water turned into gas hydrate. After that, the gas hydrate was again cooled to 245 K, removed from the reactor, and compacted under a press.

The obtained hydrate samples had a porosity in the range of 0.34 to 0.02. In terms of structure and physical characteristics, they roughly corresponded to natural GH formed under geological conditions.

The samples were examined at temperatures of 273.3 K and 278 K. The beginning of the dissociation of the surface layer sample (by the release of gas microbubbles), the formation of a water film on its surface (according to the corresponding surface gloss) and the crystallization of the ice crust (clouding of the formed water film was observed) were investigated using an optical system with the possibility of photofixation.

The calculated dependence of the porosity for the sample on its initial temperature was confirmed, as a condition for the spontaneous conservation of gas hydrate.

With the further supply of thermal energy to the sample, regardless of its porosity, a gradual melting of the formed ice crust was observed. However, a sharp increase in the dissociation intensity of the sample surface was not observed.

This is explained by the fact that the protective ice crust, although melting, did not completely disappear. The melting of its surface was compensated by gradual freezing from the middle. As a result, a movement of the "water - ice - hydrate" boundary towards the center of the sample is observed. Under such conditions, the melting of the surface of the ice crust is accompanied by the draining of part of the formed water.

This process continues until the "cold reserve" in the sample is exhausted. After that, dissociation accelerated. For the hydrate with a porosity of more than 28%, most of the water penetrated through the pores deep into the sample. At the same time, the energy of the sample was not enough for its freezing, and therefore the process of intense dissociation was observed.

Therefore, for the development of gas hydrate deposits, knowledge of the above-mentioned properties for GH, the kinetics of their formation and dissociation processes is necessary. To date, there are a large number of kinetic models for hydrate processes [27].

At the same time, an important factor determining the extraction of natural gas from GH is the permeability and porosity of the host rocks. It was established that the volume of gas production depends linearly on the GH clusters area and the rate of its dissociation [28-31].

The gas hydrates processes of the transition from one phase state to another require a detailed study [32], as well as the study of the influence of water migration during gas production [33].

## Conclusions

Thus, the analysis of works devoted to the effect of GH self-preservation revealed significant technological complications in the process of methane production by the depressurization method. The solution to these problems should be facilitated by the selection of the optimal mode of operation for the production well [34], which would harmonize the factors listed above and at the same time ensure the maximum possible production and control over the GH dissociation processes. The improvement of industrial mining technologies requires a detailed study of the self-preservation phenomenon, which occurs as a result of a decrease in reservoir pressure during the volumetric cooling of a productive reservoir.

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