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THE INFLUENCE OF THE GAS HYDRATES MORPHOLOGY ON THE RATE OF DISSOCIATION AND THE MANIFESTATION OF SELF-PRESERVATION IN NON-EQUILIBRIUM CONDITIONS

The object for the research was samples of artificially formed gas hydrate of different morphology. Gas hydrates are clathrate compounds of water molecules and hydrate-forming gases. They create significant problems for the oil and gas industry. At the same time, they contain enormous natural gas resources. The study of gas hydrates requires the production of quality samples in laboratory conditions and the availability of appropriate laboratory equipment. However, it is customary to use averaged physical indicators when performing calculations and in works on modeling gas-hydrate processes. At the same time, their morphological differences are not taken into account. Therefore, there is a risk of obtaining distorted research results. Based on this, the paper presents an analysis of the morphological differences of artificially formed gas-hydrate structures depending on the method of their formation. An assessment of the influence of the method of gas hydrate formation and the morphology of artificially formed gas hydrate samples on its stability is also given. In addition, recommendations are provided for choosing a method of forming samples of gas-hydrate structures that simulate natural samples.

Gas hydrate samples for research were obtained at a laboratory facility by changing the method of mixing the contents of the reactor. The basis of the research methodology was the analysis of enlarged images of gas hydrate samples. The morphology of the gas hydrate samples was studied through the transparent viewing windows of the reactor. For obtain high-quality images, an optical system with a light source inside the reactor was used. The stability of the gas hydrate samples was investigated with gradual pressure release in the reactor. The difficulty of obtaining adequate samples of artificial gas hydrates for modeling the properties of natural analogues is shown. It is shown that morphological differences in the macro- or microstructure of artificially formed gas hydrate samples can affect the results of research. It was concluded that the results of experimental studies with samples of artificially obtained gas hydrate cannot be considered adequate for real conditions without appropriate corrections.

Keywords: *hydrate formation parameters, gas hydrate structures morphology, laboratory unit, hydrate-bearing rock, gas hydrate structures stability.*

1. Introduction

Gas hydrates are solid crystalline compounds of the $M \cdot nH_2O$ type, formed under certain thermobaric conditions from water (aqueous solution, ice, water vapor) and low-molecular gases, the size of molecules of which is within 3.8–9.2 Å (methane, ethane, propane, carbon dioxide, etc.). They look like snow or ice [1, 2].

The process of hydrate formation is a phase transition of the first kind, which includes two stages:
1) formation of crystallization critical nuclei;
2) crystal growth [3].

1 m^3 of gas hydrate can contain 160 m^3 of methane under normal conditions [4, 5]. In the water area of the Black Sea,

gas resources in the hydrate state are estimated at $25 \cdot 10^{12}$–$70 \cdot 10^{12}$ m^3 (in the economic zone of Ukraine – $7 \cdot 10^{12}$–$20 \cdot 10^{12}$ m^3, with an annual demand of about $70 \cdot 10^9$ m^3) [6, 7].

All work related to gas hydrates can be conditionally divided into the following directions:
– prevention and fight against hydrate formation;
– detection and control (identification);
– creation of technologies for exploration and development of gas hydrate deposits;
– creation of technologies based on the use of properties of gas hydrates (gas hydrate technologies).

To carry out any research, it is necessary to have the object of research or comprehensive information about it to create an appropriate model.

In the case of gas hydrates, natural or artificially formed samples are used as the object of research. The production of artificial (man-made) samples requires appropriate specialized laboratory equipment. At the same time, in most cases, samples of natural gas hydrate after their extraction from the geological environment and until the time of research are often exposed to the action of various factors (mostly changes in thermobaric parameters), which lead to irreversible, but not always noticeable, changes.

Therefore, when carrying out research using natural gas hydrate samples, and even more so with artificially formed ones, attention should be paid to the correspondence of their characteristics to real natural or man-made gas hydrates. First of all, it is important for research on improving technologies for the development of gas hydrate deposits. It is also important to adequately assess the gas hydrates characteristics when developing measures to prevent man-made hydrate formation in technological equipment.

Gas hydrate samples can have the following main differences: morphological, according to the type of crystal lattice, the composition of the hydrate-forming gas, the degree of filling of the crystal lattice. In addition, at a reduced temperature, the mechanical strength of the gas hydrate increases sharply. The gas composition determines the equilibrium thermobaric parameters of hydrate formation.

In work [8], the sizes of hydrate nuclei in a static system were studied. It was established that the critical size lies within 5–30 nm. The paper [9] determined the size distribution of hydrated cyclopropane particles (from 5.6 to 56.4 μm) and showed that the sizes of small particles increase rapidly due to growth and agglomeration. Thus, the maximum growth rate of ethane and propane hydrate crystals is 0.35 and 0.045 μm, respectively [9].

The effect of mixing on the particle size distribution of methane hydrate during hydrate formation was investigated in [10]. With an average diameter of crystals from 10 to 22 μm, it was observed that at a low mixing speed (250 rpm), the average diameter increases. At an average speed of 400 rpm, the size remains constant, and at 600 rpm – decreases. At a rotation speed of 500 rpm, the total number of crystals increases at a constant rate [10].

The morphological features of the formation of methane, propane, and ethane hydrates under static conditions and during mixing were studied in [1]. Three types of artificially formed crystals were found: massive, whisker and gel-like. At the same time, massive crystals began to form on the surface of the liquid at very low temperatures, and growth continued mostly in the gas phase. Whisker crystals can grow in both liquid and gas and appear at higher temperatures. Gel-like crystals are formed in the aqueous phase with gas dissolved in it. A very high porosity of gel-like hydrates was observed. Microparticles of such a hydrate are formed during mixing and contain a significant amount of free water between the solid phases of the hydrate [1].

In 1988, Canadian researchers Y. P. Handa [6] and D. V. Davidson were the first to observe and try to explain the high stability of gas hydrates at temperatures below zero. It was established that powdery and finely dispersed hydrates decompose completely at a temperature below 273 K and close to equilibrium almost immediately. In larger or monolithic samples, the dissociation process took place in two stages. At the first stage, at a temperature below 273 K, the surface of the hydrate dissociated into gas and water. At the same time, the surface

of the sample is gradually covered with a layer of ice, which stops further dissociation of the sample. The second stage occurs when the surface temperature reaches 273 K and the ice begins to melt. A similar property of self-preservation is characteristic of both natural and artificial natural gas hydrates.

The phenomenon of self-preservation means that hydrates exist in a metastable state during a long time. When the samples are stored at atmospheric pressure and temperature below the region of thermodynamic stability of the hydrate (below 273 K), it can exist for a long time without significant gas loss as a result of the formation of an ice crust. Moreover, this time depends on the morphology of the hydrate.

The existence of the partial dissociation effect was noted in [11]. It can be 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 decreases to 273 K. The surface is covered with an ice crust, dissociation stops and the temperature of the hydrate rises to the initial temperature. The influence of the environment on the stability of hydrates has also been established. The results of observations are presented in Table 1.

Table 1

The effect of insulation on the rate of dissociation of gas hydrates at 260 K [11]

Insulation	Time of existence, h	Notes
Open air	40	Ice sample control
Open air	36	There is no ice crust
Opened small box	80	0.1–0.2 mm ice crust
Closed polyethylene package	200	0.3–0.5 mm ice crust
Hermetic insulation	More 3600	Up to 30 % of the gas is lost

It was found that the stability of gas hydrates depends on humidity, the possibility of moisture sublimation from the surface of the hydrate ice crust, electromagnetic influence, the temperature of the surrounding environment, the formation of the crust, and mechanical actions. The main and determining factor in the dissociation of large samples of gas hydrates is the ratio of the surface area to the mass of the sample [11].

The stability of the gas hydrate also directly depends on its morphological structure. Therefore, the main difference that will determine different conditions of stability of hydrate samples is the morphological difference. Moreover, even with a slight difference in the structure of the samples, the speed of their dissociation under equal conditions will differ significantly. Table 2 presents the morphological characteristics of natural gas hydrates.

Thus, studying the kinetics of formation and dissociation of gas hydrates is important. First of all, this concerns the prevention of their formation during the extraction and transportation of natural gas, the development of gas hydrate deposits, the development of technologies based on the properties of gas hydrates. In turn, studies of the gas hydrates morphology contribute to a better study of the processes of their formation. However, both the morphology of crystal hydrates and the kinetics of hydrate formation remain insufficiently studied.

Table 2

Morphology of natural gas hydrates [11]

Physical description	Monolithic hydrate	Acicular and filamentous hydrates	Massive coarse-grained hydrate	Agglomerated ice hydrate
External form	The crust is on the inside	Needles, colonies, threads, thin crystals with branching and thickening at the top with a needle barrel diameter of 0.1–0.5 μm	Chaotic accumulation of regular geometric shape crystals	A monolithic complex structure, consisting of an outer ice shell 5–10 mm thick and an inner hydrate, which has a core of 20–30 mm
Color	Gray with a few white spots	Whitish thickened, gray at the top	White	The ice shell is colorless, the core is white
Transparency	Beautiful	Weak	Weak	Beautiful

Thus, *the object of research* is samples of artificially formed gas hydrate of different morphology. *The aim of this research* is to analyze the morphological differences of artificially formed gas hydrate structures depending on the method of their formation. In addition, the work evaluates the influence of the method of gas hydrate formation and the morphology of artificially formed gas hydrate samples on its stability. Recommendations are also given for choosing the method of gas-hydrate formation structures that simulate natural samples.

2. Research methodology

Gas hydrate samples for research were produced at a laboratory facility from distilled water and a mixture of hydrocarbon gases with the following composition: CH_4 – 78.2 %, C_2H_6 – 14.4 %, C_3H_8 – 7.4 %. The process was carried out at a pressure in the range of 5.8–6.2 MPa and a temperature of about 275–276 K. These parameters corresponded to significant subcooling of the system, but prevented ice crystallization.

The process of hydrate formation was stimulated by various mixing methods (mechanical stirrer, hydraulic stirrer, gas bubbling method; a combination of bubbling and mechanical stirring) and without stirring.

The time of gas hydrate formation in the version without mixing was about 48 hours, and in the others – within 35–40 minutes.

The morphology of the gas hydrate samples was studied through the transparent viewing windows of the reactor. To obtain high-quality images, an optical system with a light source inside the reactor was used.

Fig. 1 shows a photo of gas-hydrate structures formed without mixing, hydraulic mixing, mechanical mixing, and bubbling.

The morphological structure of the sample obtained by the combined method is practically similar to the structure presented in Fig. 1, *c*.

3. Research results and discussion

The stability of the gas hydrate samples was investigated with gradual pressure release in the reactor. At the same time, the rate of pressure drop and the temperature change of the reactor contents were recorded, and the process of dissociation of the hydrate mass was recorded visually and in a photo. The intensity of the release of gas bubbles during their passage through a layer of a water-gas-hydrate mixture was also recorded (for this purpose, free water was not removed from the reactor).In all variants except for the variant without mixing, rapid dissociation and a gradual decrease in the temperature of the mixture to 1 K were observed. The gas hydrate formed without mixing dissociated much more slowly, and the temperature of the mixture decreased to 272.4 K. In addition, in this variant, after the dissociation of the hydrate, a significant amount of «hydrate matrix» remained on the walls of the reactor and in the water – ice, which was formed as a result of the recrystallization of the gas hydrate into ice. At the same time, supercooled water was the intermediate phase. The formed solid phase was a large crystalline snow-like mass.

In other variants, when the pressure drops below 0.5 MPa, hydrate dissociation led to the active release of gas bubbles. This process resembled intense boiling. At the end of the process, the ice matrix gradually melted. This indicates that in these versions the hydrate concentration per unit volume was not enough to lower the temperature of the mixture below 273.15 K and manifest the self-preservation effect of the hydrate.

The gas hydrate formed without mixing (Fig. 1, *a*) was relatively stable for a long time (about 48 hours) at the «gas-water» interface from gas and water vapor on a solid surface (reactor walls and previously formed hydrate structures). Its structure is dominated by needle-like crystalline formations, which in all respects correspond to the structure of whisker crystal hydrates. The porosity of the sample was about 50–60 %.
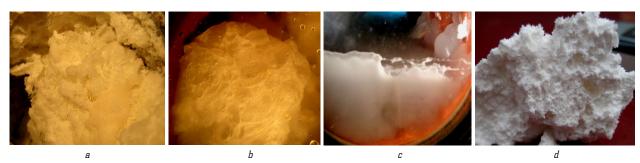

Fig. 1. Morphology of gas hydrate formed by different methods: *a* – without mixing; *b* – hydraulic mixing; *c* – mechanical mixing; *d* – bubbling

A comparison of morphological structures shows a significant difference between gas hydrates formed by different methods (Fig. 1). In contrast to the variant without mixing, where needle-shaped whisker crystal hydrates prevail, the structure of the other three variants samples consists of extremely porous (up to 60–80 %) amorphous formations with low mechanical strength. Whisker structures are not observed in these samples.

As it is known, the main problem in the production of artificial hydrates is their significant porosity and significant water content in the resulting mixture. This was confirmed on all samples. So, for example, in the variant with mechanical stirring, a continuous filling of the reactor contents with gas hydrate mass was visually observed, but calculations showed that its specific content does not exceed 32 %. For the options with hydraulic mixing and bubbling, this figure was 22 and 28 %, respectively, which is explained by the capture of a significant amount of gas as well.

As a result, foam-like structures are formed. The results of the analysis of differences in the morphological structure of artificial gas hydrates depending on the method of formation are shown in Table 3.

It has been established that effective separation of film water can be carried out only by converting it into a hydrate composition under appropriate thermobaric conditions. At the same time, whisker-type hydrate crystals are formed on the surface of hydrate particles. In the variant of water separation by pressing the sample, a significant part of it fills and remains in the intergranular space. After cooling the sample below 273 K, a monolithic ice-gas-hydrate structure with zero porosity is formed. Due to such forced conservation, the formed structure is quite resistant to dissociation.

In the sample without mixing, a significant part of the hydrate was formed above the water level in the reactor from the vapor phase, and therefore without its capture. Therefore, the stability of the hydrate and the manifestation of the self-preservation effect were studied on this sample. After that, the formed gas hydrate was cooled to 253 K, formed and compacted under a press. The resulting samples had a porosity of 0.34 to 0.02. At the same time, it is assumed that the physical and chemical characteristics of gas hydrate samples with minimal porosity will more closely simulate the natural gas hydrate that is part of the hydrate-bearing rock compared to more porous ones. The resulting samples then had an incoherent structure. The samples were sealed at atmospheric pressure in a transparent vessel with a drain. A capillary was connected to the lead. The end of the capillary was immersed in a glass of liquid. In this way, the intensity of dissociation was controlled.

At the same time, the nature of the change in the surface structure provided grounds for substantiating the essence of the process. Samples pre-cooled to 258–268 K were examined at an air temperature of 273–278 K. In the sample with a porosity of about 34 %, until the complete cessation of gas release, a gradual melting of the sample crystals with partial recrystallization and sedimentation was observed, but without visible signs of an ice crust formation on the crystal surface. This shows the absence of a layer of supercooled water and, therefore, the conditions for self-preservation of this sample with an ice crust. Therefore, the surface layer of the gas hydrate had insufficient density to absorb more energy than is required for the crystallization of the formed water layer. However, on a sample with a porosity of 10 % (and lower than 10 %), this effect was observed for a long time.

Fig. 2 shows the resulting dependence of the temperature of the gas hydrate samples on the porosity for the manifestation of the self-preservation effect at atmospheric pressure and air temperature of 273 K (curve 1) and 278 K (curve 2). The areas under the curves correspond to the formation of the ice crust. Self-preservation is impossible above the curves.
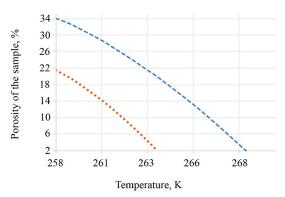

Fig. 2. Graphs of the dependence of gas hydrate temperature on porosity for the manifestation of the self-preservation effect at an air temperature: –––– – for temperature 273 K; ····· – for temperature 278 K

Thus, morphological differences in the macro- or microstructure, both among samples of natural gas hydrate and even more artificially formed, can affect the results of research. In many cases, they are not taken into account. Also, when making calculations and in works on modeling gas-hydrate processes, it is customary to use averaged physical indicators without taking into account possible morphological differences of the object.

In general, the results of experiments with samples of gas hydrate obtained artificially (with any of the mixing methods used) cannot be considered adequate for real conditions without appropriate corrections.

Table 3

The difference in the morphological structure of artificial gas hydrates depending on the method of formation

Method of formation	No mixing	Mechanical mixing and combined	Hydraulic mixing	Mixing by bubbling
Physical description	Needle-shaped and snow-shaped	Amorphous coarse-grained	Foamy large-pored	Amorphous porous
External form	Needles, colonies, threads, thin crystals with branching and thickening at the top	Amorphous granular with a grain diameter of up to 3.5 mm and significant water absorption	Foamy with significant water and gas absorption	Amorphous fine-grained (grain diameter up to 1.5 mm) and significant gas absorption
Color	White	White	White	White
Transparency	Weak	Weak	Weak	Weak

Taking into account the morphology of gas-hydrate structures when setting up experimental studies can significantly affect their results.

In the future, similar studies should be conducted on samples of natural gas hydrate extracted from hydrate-bearing rock of gas hydrate deposits.

4. Conclusions

During the research, the following was established:

1) the limit of the self-preservation effect is the same value of the energies of gas hydrate dissociation and crystallization of the formed water (on the condition that all water remains on the surface of the sample, for example, penetrates into the pores);

2) the effect of self-preservation in natural geological and artificial experimental conditions is the porosity of the hydrate mass in the range of 0.28–0.32;

3) dissociation of the surface of the gas hydrate sample due to heating is preceded by heating of the surface of the ice crust and the transition of the water crystalline phase into liquid. Moreover, this process proceeds more intensively, the higher the porosity of the gas hydrate.

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