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STUDY OF THE METHANE HYDRATES OBTAINING PROCESS IN STATIC CONDITIONS

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Abstract. *We have studied the process of artificial methane hydrates obtaining in static conditions from distilled and "secondary" water (prepared by the decomposition of methane hydrate), as well as the additional metal surface using inside of cameras. It was found dependence from the type of the liquid phase and the presence/absence of additional metal surface inside the camera; in the same initial conditions of temperature and pressure, it can be obtained samples with different degrees of transformation of the "water-gas" to hydrate and various crystalline morphology.*

Keywords: *methane hydrate, static conditions, synthesis, gas content, morphology of crystals*

Introduction

At present there are a number of methods of gas hydrates synthesis. Most methods of hydrates obtaining in the laboratory are based on an intensive mixing of the components inside the high pressure vessels of various configurations. This can be an intensive mixing of the liquid phase, with maintaining a constant pressure of the hydrate forming gas above it, bubbling gas through a solution or the injection of liquid phase into the compressed gas. Typically, these methods require significant energy and technically complex hardware design process of obtaining hydrates [1, 2, 3].

For obtaining of the artificial hydrate and their future research, we are searching the laboratory method of hydrates production, which does not require the use of sophisticated equipment and time-consuming experiments. It is well known that the speed of the heterogeneous reaction of gas hydrates production and to reach the maximum gas content of samples it is necessary to increase the contact area of the reactants, i.e. an area section of the liquid and gas phases. In this paper, by analogy with [4], we made an attempt to intensify the process of hydrate formation by using the additional metal surfaces within the reaction volume.

It is known from literature, that after the decomposition of hydrates, the released water ("secondary" water) preserves the cluster structure, which contributes to the formation of hydrate at lower super cooling system. The formation of "secondary" hydrate crystals were observed by the authors of [5]. The peculiarities of these crystals are their formation in the volume of water, not on the free surface of the gas-water contact. The process of hydrates accumulation is more intensive than the reaction with water, not

passed through the hydrate. The acceleration of the "secondary" hydrate during cyclic freezing-thawing of the pore water was watched by V.S. Yakushev. So, if the water in the rock has undergone phase transitions (ice, hydrate), then re-hydrate is much faster [6]. Dependence of the kinetic characteristics of the hydrate formation process on the history of water, from which the hydrate was obtained, studied in [7].

Based on the above data, we have tried to use for the hydrate formation the «secondary» water, in order to intensify the process of formation. Thus, this paper presents new data on the production of artificial methane hydrates in static conditions (in the absence of dynamic effects) from distilled and "secondary" water, as well as using inside the reaction chamber the additional metal surface.

The experimental part

Used in the experiments chambers are made of steel U8 (Fig. 1a). The inner height of the chamber is 17.5 cm, inside diameter is 9 cm, and the internal volume is 1.113 liters. The assembled chamber consists of a cylinder and a cover-flange, which are mounted gauge model (class 0.4) and the filling valve.

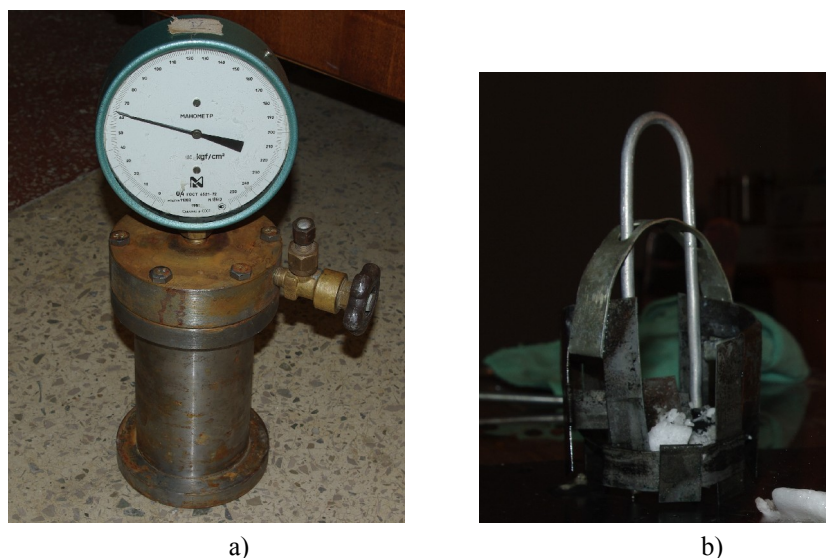


Fig. 1. Photos:
a – high-pressure chamber; b – metal construction

Homemade metal construction (MC) made of transformer steel plates with a total surface area of 215 cm² (Fig. 1b) was used as an additional surface. MC is made of 12 parts with this in mind that when MC half diving in the water 65 % of the total surface area of the MC will be under the water. In addition, aluminum handle designed for taking out the MC along with accrued hydrate is attached to the MC. MC height including handle is 13 cm, diameter is 7 cm.

The gas for hydrate formation is methane (99.99 % vol.), and a liquid phase – distilled water and "secondary" water, resulting from the decomposition of previously received hydrate, which was pre-filtered and defended for 24 hours at room temperature.

Course of the experiment is as follows:

– In the high-pressure chamber pour 200 ml of water (up to half of the MC). If the experiment is carried out with the MC, it was immersed so that it does not touch the walls. Next, create a vacuum in the chamber and fill with methane to a pressure of 50 atm at a temperature of 25 °C;

– Tucked chambers were placed in an incubator fridge MIR-254 (Fig. 2) where they are to stand for 2 hours at +20 °C, and the recorded change in pressure for leak testing chambers. During the next two days the temperature is gradually lowered to +6 °C (hydrate equilibrium temperature at a given pressure) to saturate gas hydrate environment;

– Then cooled camera with a gradient of 1 °C / day to -3 °C. In the experiment, every 3 hours, fixed pressure value. Further temperature for 24 hours was reduced to -7 °C to freeze not transformed into hydrate water;

– In one experiment refueled two chambers. In the first chamber hydrate prepared from water (distilled or "secondary") without using the MC, in the other chamber in the presence of MC. After hydrating chamber were opened to take photos and determine gas saturation of the samples;

– Opening chambers produced in a freezer at -10 °C. Dumped residual pressure in the chamber, then disconnect the cover-flange and take a few pictures obtained hydrates. Quickly selected ~ 50 g sample (pieces breaking off from the surface of the array, the selection of individual pieces or scraping the surface of the MC) was placed in an incubator at a temperature of +5 °C under a glass dome, which is connected to the gas meter GMR-400 and measured the volume of escaping gas. Since the purpose of this work is to develop a method of sample preparation laboratory hydrate the best possible quality, hereinafter gas content values are only describing the specimen, rather than the conversion to hydrate all loaded into the chamber of water.

Native morphology of the crystals of obtained gas hydrates was recorded with a digital camera Pentax K200D.

Gas saturation of the obtained hydrate (α) was calculated from measurements of the volume of gas released during the decomposition of a known quantity of hydrate sample, based on the fact that in theory in 1 liter of hydrate can contain 164 liters of gas [8, 9].



Fig. 2. Chambers in the refrigerator incubator SANYO MIR-254

Results and discussion

The studies found that the morphology of the static conditions of methane hydrates and the level of gas saturation of samples depend on the type of water, from which the hydrate is synthesized, and the presence/absence in the MC (Fig. 3, 4). Numerical data for all the experiments summarized in Table 1.

Table 1. Test data

Type of filling chamber	P, atm		T, °C		α , %	The synthesis of hydrates, day
	range of conditions hydrates formation*					
	beginning	ending	beginning	ending		
Distilled water + methane	44.5	41,84	+4	0	7	6
Distilled water + methane + MC	44.88	35,2	+5	-1	46	6
"Secondary" water + methane	44.4	30.8	+3	-1	71	4
"Secondary" water + methane + MC	45.4	26.8	+6	0	93	6

* A range of temperatures and pressures at which a rapid drop in pressure in the chambers associated with the formation of gas hydrates.

The sample obtained from distilled water without the MC can be seen at (Fig. 3a), which is at the surface of a mesh of thin "thread" in the form of frost, and white dots. Apparently, it is imbedded in the ice formed the methane hydrate. Gas saturation of the selected piece of solid surface sample was only 7 %.

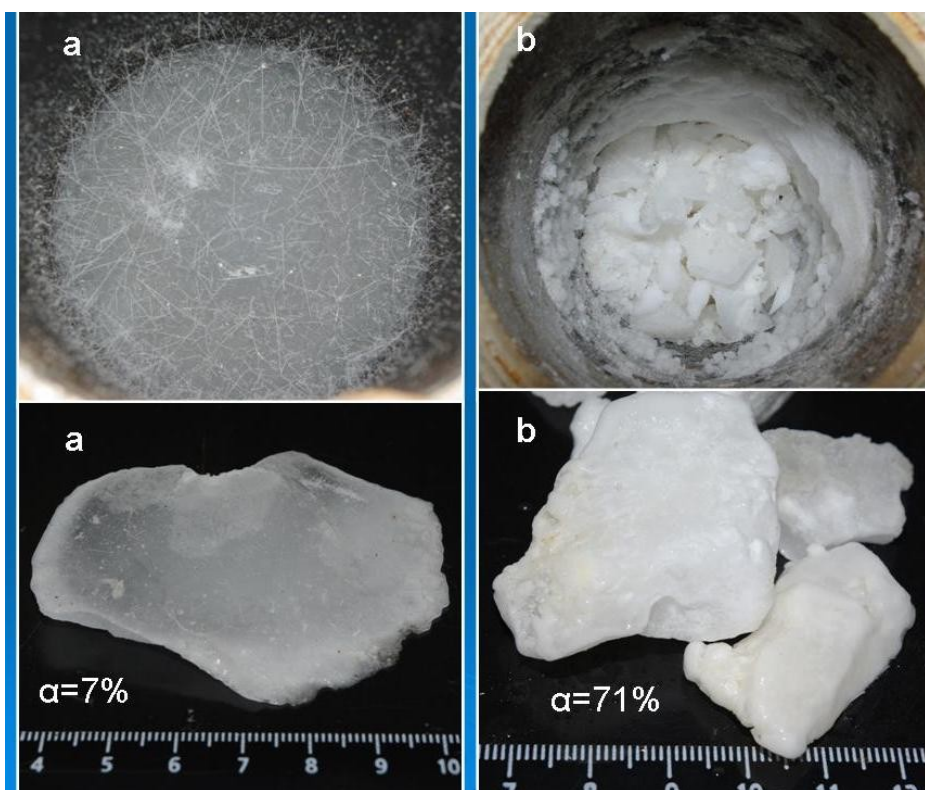


Fig. 3. Photos of synthetic methane hydrate obtained in static conditions of:
a – distilled water; b – "secondary" water

In Fig. 3b it is shown that methane hydrate from the "secondary" water (MC not used) abundantly formed in the chamber, and on its walls. Thus, methane hydrate obtained in static conditions from the "secondary" water presented morphological structures in the form of fairly large (2 to 5 cm), dense, opaque (white) of massive crystalline samples with gas saturation of 71 %. Perhaps these pieces were formed by the accumulation of hydrate on the wall of the chamber with capillary leak of water and when you reach a certain size broke off and fell down.

The studies show that the introduction of an additional reactor surface, leads to increasing of the surface contact "water-methane" in static conditions and can improve gas content of methane hydrate. Thus, the gas saturation of methane hydrate produced from distilled water, but in the presence of MC was 46 % (Fig. 4a, Table 1.), Which is 6 times higher than the gas saturation of methane hydrate in distilled water (Fig. 3a, Table 1.). It can be seen that the artificially produced from distilled water methane

hydrate obtained with usage of the additional metal surface consists of transparencies ice with numerous white inclusions on their surfaces (Fig. 4a).

Methane hydrate, derived from the "secondary" water in the presence of MC (Fig. 4b) with a morphological point of view is very different from previous samples. It occupies almost the entire volume of the chamber; the hydrate is presented as a colony of radially directed entangled needles. Gas content selected of the samples was 93 % (Fig. 4b, Table 1). It may be noted that the content of methane hydrate in the sample obtained from the "secondary" water in the presence of MC more than 13 times higher than that of methane hydrate obtained from distilled water without the use of MC.

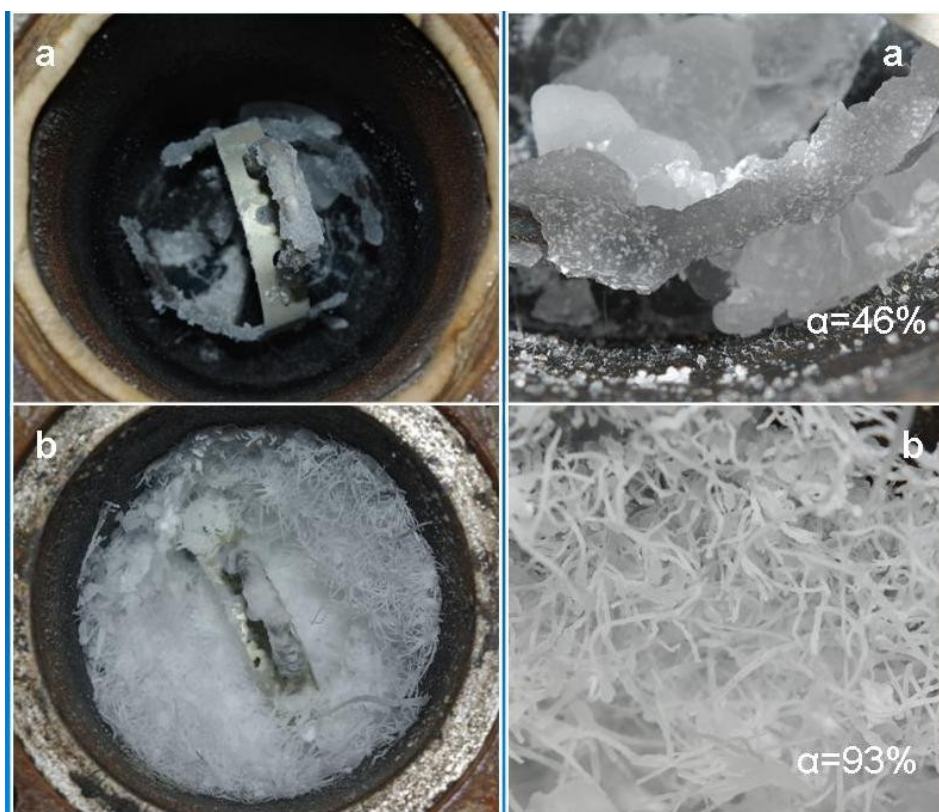


Figure 4. Photos of synthetic methane hydrate obtained in static conditions in the presence of MC:
a – distilled water; b – «secondary» water

Comparison of the effect of additional MC and type of water on the rate of formation of methane hydrate in static conditions is shown in Fig. 5. The dependence of the pressure in the chamber of the time but in this figure shows the total for all four experiments, the curve describing the change in temperature of the chamber with time. It is known that reducing the pressure inside the chamber is due to absorption of gas hydrate formation and due to thermal expansion (contraction) of gas. The latter process was the same for all experiments, the associated change in pressure is greatest in the first 40

hours (Fig. 5). We see that the value of the total pressure drop in the experiment correlates with the gas saturation of the samples (Fig. 5, Table 1).

The conversion of the "distilled water-methane" in the hydrate under static conditions is low (Fig. 5 – curve 1, Fig. 3a). The conversion of the "secondary water-methane" in the hydrate is about 10 times higher than that of distilled water (Table 1). It should be noted that the intense pressure change during the formation of hydrate from the "secondary" water is observed in the range of +3 °C to -1 °C for 4 days, with the change in pressure of 13,6 atm (Fig. 5 – curve 3).

From Fig. 5 (curve 2), the intensity of the change in pressure inside the chamber during the formation of hydrate of distilled water in the presence of MC comes from +5 to -1 °C for 6 days, then the process stops. The pressure change in this case was only 9.7 atm. In the formation of hydrate in the presence of a "secondary" water MC pressure change was 18,6 atm for 6 days (Fig. 5, curve 4). The time elapsed before the start of a rapid formation of hydrate in this case the smallest, and the conversion of the "water-methane" to hydrate – the greatest.

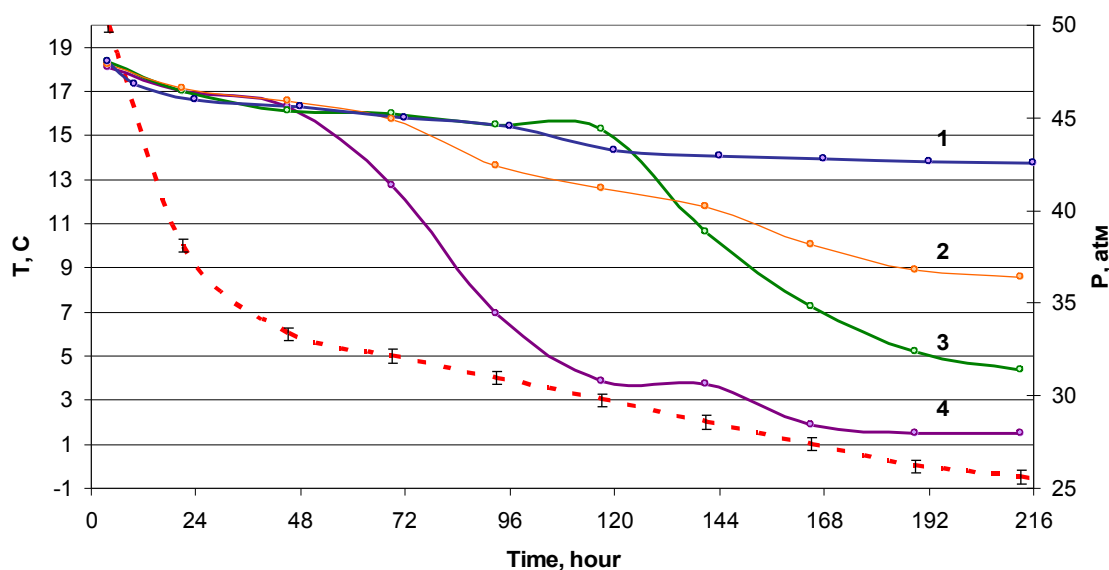


Figure 5. Graph of pressure versus time during the formation of methane hydrates:
 1 – distilled water; 2 – distilled water in the presence of MC; 3 – «secondary» water;
 4 – in the presence of a «secondary» water MC; the dashed red line – temperature cooling

Thus, in order to obtain in a laboratory methane hydrate with high gas saturation in static conditions one is preferably used as the liquid phase of the "secondary" water in combination with an additional metal surface inside the chamber of the synthesis.

During the experimental work, we noticed that there is an intensification of the process of corrosion of the chamber wall and the surface of the MC. For the first time this process has been described Makogon in [5, 10]. So in Fig. 6 shows that the inner surface of the chamber and the surface of the MC are covered with an oxide film, and it

is observed that the oxide layer on the coated surfaces of hydrate formation is much faster than before the oxide layer. The results of this study fall into the equipment covered by a layer of corrosion products. It can be assumed that the presence of this layer provides: 1) the presence of active sites that facilitate the formation of hydrate nucleation, 2) capillary transport of water to the zone of hydrate formation. The study of these phenomena is of undoubted scientific and practical interest, however, is beyond the scope of this paper and will be continued in the future.

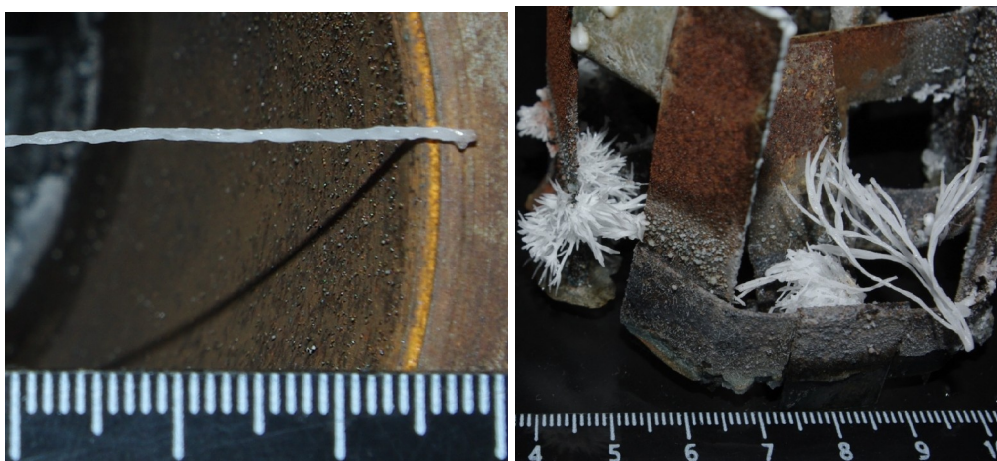


Fig. 6. Corrosion

The growth kinetics and morphology of the resulting gas hydrates – **related**, but complex and least studied problems. [10] Thus, the formation of hydrates with distilled water and water obtained after the hydrate decomposition, different. The difference, according to some authors, is determined by the structural state of water, which is stored in the volume of the water molecule clusters – part decomposed hydrate lattice [5]. However, according to Istomin, the key to explaining the results for "secondary hydrate formation" is not a hypothetical change in the structure of water (water memory block is not supported by modern physicochemical studies), but rather a super saturation of water with gas after the "primary hydrate" [5, remarks of scientific editor].

The obtained practical result in this research is a significant increase of the gas content of methane hydrates synthesized in static conditions from the "secondary" water can be explained on the base of the above hypotheses, and the influence of the quality/type of the inner surface of the chamber and the MC.

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