The influence of water level at working area on freon 134a hydrate synthesis by the method of explosive boiling of liquid hydrate-forming gas in water volume with simultaneous mixing

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Abstract. This work is part of a comprehensive study to search for the optimal operational parameters of the method based on the explosive boiling of liquefied hydrate-forming gas in a volume of water during decompression. Studies have shown the effectiveness of mixing the working area during decompression. Therefore, this paper presents an experimental study of the influence of the water level at the working site on the synthesis of gas hydrate by the studied method with stirring of the work area. Freon 134a was used as a hydrate forming gas.

1. Introduction
Gas hydrate is a lattice-type supramolecular clathrate compound formed by host (water) molecules with guest molecules (hydrate-forming gas) included in the cavity of the framework. The synthesis and dissociation of gas hydrate can be called a first-order phase transition. The transition is carried out not by a chemical reaction, but by the formation of an openwork framework by the water molecules with further inclusion and retention of hydrate-forming gas molecules by the van der Waals interaction. The resulting structure is formed under the conditions of transition to the thermobaric region of hydrate existence. Moreover, these conditions depend on the hydrate-forming gas.

According to various estimates, about 80% of all natural gas on our planet is in a hydrated state. However, hydrated deposits are located in remote places for mining: in permafrost zones and on the bottom of the oceanic shelf. There are many projects for forecasting, searching and creating technologies for the extraction of natural gas from hydrated deposits. Therefore, it is important to know the thermodynamic and chemical properties of the formation and decomposition of hydrates [1-6]. In the field of production and transportation of natural gas, gas hydrate is a parasitic phenomenon, it is formed in the bottom-hole zone of the formation, well tables and main pipelines, this problem is especially urgent in the northern regions. Therefore, many works have been devoted to the inhibition and dissociation of gas hydrates [7-14]. Significant amounts of gases can be concentrated in the gas-hydrated state, which opens up the possibility of transporting and storing gases in this state, and the self-preservation effect [15-16] allows the gas to be stored at atmospheric pressure and low negative temperatures. In addition to the oil and gas industry, synthesis and dissociation can be used to separate gases, purify water, utilize harmful gases, and also to accumulate cold. The latter is especially worth noting, since gas hydrate has a large enthalpy during dissociation, which can be used for cooling and air conditioning [17-18]. The 134a freon hydrate studied in this article is just suitable for these purposes.
because of the low formation pressures at positive temperatures, which makes this method much more energy-efficient than using ice. However, despite the promise of creating gas hydrate technologies, at present there is no universal economically feasible technology based on the processes of synthesis and dissociation of gas hydrates. This is directly related to the complexity of the preparation and decomposition of hydrates, which makes finding an effective method for these processes very important. Unfortunately, currently known methods have a lot of disadvantages associated with high energy costs and long hydrate synthesis times. Previously, hydrate synthesis methods have been proposed; they are based on the process of boiling liquefied gas in a volume of water, with which it is possible to synthesize large volumes of gas hydrate at low time costs [19-22]. The results obtained in this paper are part of a comprehensive study of the optimal operating parameters of the investigated method for gas, which in a liquefied state has a higher density than water. Freon 134a is used as such a gas. Within the framework of this method, studies were carried out on the synthesis of gas hydrate of carbon dioxide and freon 134a. For freon 134a, a method for the synthesis of gas hydrate was described, and the optimal operating parameters influencing the synthesis of hydrate, such as gas consumption during decompression of the working section (100 l / min) and the optimal initial water temperature before decompression of the working section (6°C) [23-25]. However, the subsequent studies demonstrated a significant contribution from the mixing of the working section during the decompression process to the synthesis of gas hydrate in the investigated method. Therefore, the article presents the next stage of the study of this method, namely, the study of the effect of the water level in the working area on the synthesis of gas hydrate by the explosive boiling method of the liquefied hydrate-forming gas during decompression with simultaneous mixing of the working area.

2. Experimental setup
The studies are performed on an experimental setup in the form of a cylinder with a diameter of 100 mm and a height of 300 mm (fig. 1). The unit is designed for high pressures and has a maximum working pressure of 25 MPa. Cooling is carried out by pumping the coolant through a water jacket with a LOIP FT-316-40 cryothermostat. Pressure relief during decompression is carried out through a flow regulator from 100 l/min. Mixing of the working section is carried out with a three-blade stirrer 40 mm in diameter with maximum rotation frequency of 1400 rpm. A pressure and temperature sensor is introduced through the top cover of the vessel to the working section, with the help of which the ongoing processes are monitored. In this case, the temperature sensor is located at the level of the mixer at a height of 20 mm from the bottom of the vessel. In this study, freon 134a is used as a hydrate-forming gas.

Figure 1. Scheme of experimental setup:
1 – pressure sensor;
2 – tube with a thermocouple;
3 – heating/cooling jacket;
4 – insulator;
5 – agitator blade;
6 – agitator drive;
7 – flow regulator [19].
3. Experimental method
The research methodology was as follows. Water was placed on the working section. Then it was cooled through a water jacket, after which gaseous freon 134a with a mass of 200 g was fed into the chamber. Gas pressure in the cylinder (from which supply) significantly exceeded the pressure in the chamber, and its temperature was equal to room temperature. Entering the chamber, the gas pressurized in it, cooled and condensed on the wall of the working section and, due to its higher density, flew down with the formation of a layer of liquefied gas below the surface of the water. It should be noted that the mass of hydrate-forming gas was selected for the interface between the layer of liquefied freon 134a and the water layer to be on the blades of the mixer. After reaching a water temperature of 6 °C, a stirrer was started with a rotation speed of 1400 rpm, which mixed the two layers with each other. At the same time, the working section was decompressed by gas bleeding from the upper part of the unit with a constant flow rate of 100 l/min. This led to explosive boiling of liquefied freon 134a in a volume of water. During boiling, additional mixing of the medium and strong cooling of water around the bubbles took place, bringing the medium into the phase region where hydrate formation is possible. The gas in the bubble had a minimum temperature close to the saturation temperature of freon 134a at the current pressure. In this case, the process absorbed heat generated during hydrate formation. The imposition of these factors led to the intensification of the hydrate formation process, while the time of the entire process was several tens of seconds. The amount of gas transferred to the hydrated state was determined by decomposition of the synthesized hydrate by heating the working section. During dissociation, the gas hydrate was separated into water with the release of gas, which created an increased pressure in the system. Then, using the equations of state, the mass of the gas that passed into the hydrate was determined.

4. Experimental results
This work presents a series of experimental studies with varying water masses of 50, 100, 200, 500, 1000 g, which corresponded to a water level of 6, 12, 23, 58, 116 mm. Fig. 2 shows a graph of the pressure change in the system during the depressurization process for a mass of water of 50 g and 500 g. As can be seen from the graph, nothing happens in the first seconds. Then the pressure is released, as a result of which the liquefied gas boils and the process of hydrate synthesis starts. After reaching the pressure in the system of 0.1 MPa, the discharge stops. At this pressure, the system is below the saturation line of freon 134a, while the system continues to be in the region of existence of a gas hydrate. With 50 g of water after reaching 0.1 MPa pressure begins to grow due to liquefied gas still present in the system, which can be located in the volume of the formed hydrate mass. The decompression process starts again and also stops at the pressure of 0.1 MPa. For 50 g of water it is required to do this manipulation two times. For 500 g, no additional pressure relief is required, since the system runs out of liquefied gas during the first decompression. Freon 134a is practically insoluble in water, therefore additional gas evolution is associated with a slight transition of the hydrate-forming gas to the hydration state, which is determined by the lack of water in the process of hydrate formation.
Figure 2. Pressure change in the system during the decompression process for a mass of water of 50 g. (crosses) and 500 g. (rhombuses).

Fig. 3 shows the dependence of the amount of gas transferred to the gas hydrate relative to the initial mass of gas on the mass of water in the working area. With a small mass of water with simultaneous stirring during depressurization, a significant heat sink occurs, turning all the water in the work area into ice, which prevents the effective synthesis of gas hydrate, which can be seen in the graph. The maximum effect is achieved with a water mass of 200 g, where 13.7% of freon 134a of the original gas is converted to a gas hydrate state, while a further increase in water mass only leads to a deterioration of the result, since a larger volume of water requires more significant heat removal, which can be achieved by increasing the mass of liquefied hydrate-forming gas. I would like to note that even though the difference between the gas transferred to the hydrate with a water mass of 200 g and 500 g is within the margin of error, however, for the effective application of the method under study it is necessary to minimize the amount of water used.

Figure 3. Dependence of the amount of gas transferred to the gas hydrate state relative to the initial mass of gas on the water level in the working area.
Conclusions
The article presents the research that is a part of a comprehensive study of the method of explosive boiling of liquefied hydrate-forming gas in a volume of water during decompression. The effect of the water level in the working section with stirring on the amount of the hydrate forming gas being transferred to the hydrated state has been assessed. The maximum effect is shown to be achieved with a water mass of 200 g, where 13.7% of freon 134a of the original gas is converted to a gas hydrate state. At the same time a further increase in the mass of water only deteriorates the result, since more water requires more significant heat dissipation, which can be achieved by increasing the mass of liquefied hydrate-forming gas.

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