Influence of initial water temperature on the synthesis of gas hydrate by the method of explosive boiling liquefied hydrogen-forming gas freon 134a in the volume of water

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Abstract. The paper presents an experimental study of the influence of the initial temperature of water on the amount of gas transferred to gas hydrate. The studies were carried out at constant operating parameters, with varying water temperatures before decompression. This work is a continuation of the study of a method of synthesis of gas hydrates developed by the team of authors, based on the explosive boiling of liquefied hydrate-forming gas (Freon 134a) in a volume of water.

1. Introduction
Gas hydrate is a lattice-type clathrate compound in which gas molecules (guests) are locked into an openwork framework formed by water molecules (hosts). Using the process of synthesis of gas hydrate as the basis of gas hydrate technologies has attracted specialists around the world for quite a long time. Such technologies will solve a lot of both global and local problems. All this becomes possible due to the property of gas hydrate to retain a large volume of gas (up to 300 volumes). This compound exists under certain thermobaric conditions, which are determined by a hydrate-forming gas, in violation of which it decomposes into gas and pure water. After the discovery of the effect of self-preservation of gas hydrate at negative temperatures, it became possible to maintain the gas hydrate in a stable state outside the stability zone of the gas hydrate [1-2]. The main promising direction is the transportation and storage of natural gas in the form of spherical gas hydrate granules coated with ice at atmospheric pressure and temperature of -15°C. We should note that in the volume of 1 m3 of methane gas hydrate, up to 170 m3 of methane gas can be contained. The solid aggregate state of the granules simplifies loading and unloading operations, while there is no need to maintain a negative temperature, such as during transportation in a liquefied state (-162°C). This can be useful in areas with a low average annual temperature, for example, for the Arctic region, where more time in the year there is no need to spend energy on maintaining the temperature necessary for hydrate stability. Gas hydrate technologies can also be useful in other areas of industry, for example, in gas separation, desalination of sea water, gas utilization, including greenhouse ones, accumulation of cold, etc. However, in spite of the whole visible prospect, there is currently no cost-effective gas hydrate technology. This is due to the fact that the synthesis of gas hydrate in itself is a very non-trivial and difficult task, and many scientific groups around the world are working on this problem [3-16]. Investigations of structural, thermophysical, and other properties are also important [17-21]. The article suggests the results of continuing research on a method developed by a team of the authors that is original and fast, it is based on the explosive boiling...
of liquefied hydrate-forming gas in a volume of water during decompression. This method can form the basis of cost-effective industrial hydrohydrate technologies.

2. Experimental Setup

Experimental studies were carried out on the installation of autoclave type with quick-release lid (Fig. 1). This installation is made of stainless steel with a wall thickness of 20 mm, capable of withstanding operating pressures of up to 25 MPa. The height of the working section of the installation is 300 mm, diameter is 100 mm. Mixing in the working area was carried out using the blades of a mixer with a magnetic coupling, the blades of which were at a height of 20 mm from the bottom. The installation is cooled by pumping the coolant from the LOIP 316-40 cryostat through a water jacket located along the entire height of the working section. Pressure and temperature sensors were located in the lid of the installation, gas was introduced through the valve built into it, and pressure was released. Pressure release was performed using the AALBORG flow controller. The temperature was measured using RTD PT100 with an accuracy of ±0.4°C.

![Figure 1. Scheme of experimental setup: 1 – vessel; 2 – Heating/cooling jacket; 3 – insulator; 4 – optical window; 5 – bottom valve; 6 – lid; 7 – cryostat; 8 – ADC&PC; 9 – tube with a thermocouple; 10 – mixer drive; 11 – pressure gauge; 12 – cooling coil [9].](image)

3. Experimental Method and Result

This paper presents an experimental study of the influence of the initial temperature at the work site on the synthesis of Freon 134a gas hydrate. An experimental study is performed as follows. Water weighing 200 g is placed on the working section to the level of the agitator blades, and then cooling is performed through a water jacket. After that, 200 g of freon is pumped into the working area, which, entering the chamber, condenses on the cold walls and, flowing down, forms a layer of liquefied gas under the surface of the water (due to its higher density as compared to water). Further, after reaching a certain temperature at the working section (2, 4, 6, 8°C), a pressure is released with a gas flow of 100 l/min. As a result, the liquefied layer of hydrate-forming gas begins to boil under a layer of water. Because of this, boiling liquefied gas cools the working area, transferring the medium to the stability region of the gas hydrate. Gas hydrate begins to form on the surface of the bubbles, and the heat released is absorbed by boiling the liquefied gas, while supercooling the medium minimizes the induction time of gas hydrate formation.
Due to the small height of the rise of bubbles on their surface, a significant hydration crust does not have time to grow and, due to the constant renewal of bubbles as a result of boiling, hydrate formation occurs at the surface stage, bypassing the diffusion stage. The imposition of these factors leads to a significant decrease in the rate of formation of a significant gas hydrate mass. The determination of the amount of gas transferred to the gas hydrate is carried out as follows. After reaching a pressure of 1 atm, at which there can be no liquefied gas, the working section is heated, as a result of which the gas hydrate decomposes systematically, and gas released in this case creates the additional pressure in the system. The mass of gas, which has passed into a gas-hydrate state, is determined by this additional pressure. In this paper, we studied the influence of the initial temperature at the work site on the hydrate formation process (Fig. 2). As it can be seen from the graph, at a small initial temperature, a large amount of parasitic ice is formed, while the amount of gas hydrate is very small. Further, as the temperature rises, more gas passes to the gas hydrate state. The optimum temperature of hydrate formation is about 6°C, at which 5.6% of the mass of gas relative to the initial amount of gas passed into the gas hydrate. With further increase in water temperature, the medium approaches closer to the boundary of the thermobaric stability of the gas hydrate, which negatively affects the synthesis of gas hydrate.

![Figure 2. Dependence of the part of gas transferred to gas hydrate K, % on the initial water temperature Ti, °C.](image)

**Conclusion**

In this paper presents the continuation of experimental work on the study of operational parameters by the method of synthesis of gas hydrate, based on the explosive boiling of a liquefied hydrate-forming gas (Freon 134a) in the volume of water. A study of the effect of water temperature before decompression on the synthesis of gas hydrate is presented. It is shown that the optimal initial temperature, with a gas flow rate of decompression of 100 l/min is about 6°C, at which 5.6% of the initial mass of gas passes to the gas hydrate state.
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