Influence of stirring working area on the synthesis of freon 134a hydrate by the method of explosive boiling of liquid hydrate-forming gas in volume of water during decompression

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Abstract. The presented work is part of a comprehensive experimental study aimed at finding the optimal operating parameters by the method of explosive boiling of liquefied hydrate-forming gas in a volume of water. The results obtained and published earlier showed the high efficiency and productivity of this method. This paper presents a study of the effect of the stirrer speed during the decompression of the working section on the gas hydrate synthesis.

1. Introduction
Gas hydrate is a clathrate type compound. It consists of host water molecules that form a framework with cavities occupied by guest hydrate-forming gas molecules, held by the Van der Waals interaction. This structure is stable under certain thermobaric conditions determined by hydrate-forming gas [1]. There are several types of gas hydrate structures: Cubic structure I (sI), Cubic structure II (sII) and Hexagonal structure (sH). However, no hexagonal structure is found in nature. The cubic structures consist of pentagonal dodecahedrons (5\text{12}, S-cage), as well as the tetradecahedron (5\text{12} \text{6}, M-cage) for sI and hexacaidecahedron (5\text{12} \text{6}, L-cage) for sII. The sI unit cell consists of 2 S-cages and 6 M-cages, and sII consists of 16 S-cages and 8 L-cages.

Gas hydrates are a promising source of hydrocarbons in the world for development. According to various estimates, more than 50% of all carbon is in a hydrated state, which are located as minerals in permafrost zones and on the bottom of the ocean shelf at a depth of 300 m. A lot of efforts are directed towards creating a technology for developing such deposits. Why is it especially important to know not only the features of dissociation and synthesis of natural gas hydrates [1-14], but also the thermodynamic and chemical properties [15-19]. However, the hydrated state itself has some properties that may be useful for various industries. Gas hydrates are a promising storage of gas, so up to 170 m$^3$ of gas itself can be contained in 1 m$^3$ of natural gas hydrate. At the same time, to keep the gas in a hydrated state, it is not necessary to have extremely low temperatures, since when using the self-preservation property, natural gas can be stored in a hydrated state at atmospheric pressure and a temperature of -20°C, while the traditional method of transportation and storage in a liquefied state requires maintaining the temperature of -162°C. Since each gas has individual thermodynamic conditions of hydrate formation, and with hydrate formation only pure water passes into the hydrate, the process of synthesis and dissociation of gas hydrates can be used as the basis for gas separation and water purification technologies, including desalination of sea water. Another unique property is
the large enthalpy of dissociation, which can be used for cooling and air conditioning. The maximum result is achieved when selecting a hydrate-forming gas so that it is stable at low pressure in the temperature range from 5 to 11°C, in which the use of hydrates has a higher efficiency than the use of ice [20-21]. Despite the many advantages, there are currently no economically feasible technologies based on the hydrate formation process in the world. This is due to the fact that the synthesis of gas hydrate is a difficult task. All existing and patented methods for producing gas hydrates have some disadvantages associated primarily with a low rate of hydrate formation and with a small generation of hydrate mass. This article presents a method that is devoid of the above disadvantages. It is based on the process of explosive boiling of the hydrate-forming gas in the volume of water during decompression. The results obtained and published earlier have shown the high efficiency and productivity of this method. This method was used to obtain gas hydrates of freon 134a, propane and carbon dioxide. Previously, the optimal parameters of the gas flow rate during decompression (100 l/min) and the initial water temperature (6°C) for the hydrate formation process were identified, and the synthesis process was visualized by the indicated method [22-26]. However, the studies carried out further showed that additional mixing during decompression significantly affects the hydrate synthesis, which means that this parameter is especially important for optimizing this method. This paper presents the effect of the stirrer rotation frequency on the synthesis of freon 134a hydrate.

2. Experimental setup
Experimental studies were performed on an autoclave-type installation, the working section of which is made of stainless steel in the form of a vessel with a diameter of 100 mm and a height of 300 mm, with a water jacket through which water is cooled by passing heat from a LOIP FT-316-40 cryostat (fig. 1). At this installation, experimental studies can be carried out with a working pressure of up to 25 MPa. Pressure relief during decompression was carried out through a flow regulator from 100 l/min. Stirring was carried out with a 40 mm diameter three-blade stirrer built into the working area, which was located at a height of 20 mm from the bottom. The maximum stirrer rotation speed was 1400 rpm. To control pressure and temperature, pressure and temperature sensors are introduced into the working section through the cover. The sensor is directly integrated into the vessel lid, and the temperature sensor is placed in a thermowell, where it measures the water temperature at the stirrer level.

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 [22].
3. Experimental method

The research methodology was as follows. Water weighing 200 g was placed on the working section and cooled. After reaching a temperature of 8°C, freon 134a with a mass of 200 g was introduced into the chamber. The gas pressure in the cylinder (from which the supply is carried out) significantly exceeded the pressure in the chamber, and its temperature was equal to room temperature. Entering the chamber, the gas was pressurized in it, cooled and condensed on the wall of the working section and, due to its higher density, flowed down with the formation of a layer of liquefied gas under the surface of water. It should be noted that the mass of hydrate-forming gas was selected so that the interface between the layer of liquefied freon 134a and the water layer was on the blades of the mixer. After reaching a water temperature of 6°C and a pressure of 0.4 MPa, the working section was decompressed by bleeding gas from the top of the unit with a constant flow rate of 100 l/min. Simultaneously with decompression, a stirrer, which mixed the hydrate-forming gas layer and the water layer, was launched. This led to explosive boiling of liquefied freon 134a in a volume of water. During boiling, additional mixing of the medium, which was mixed in this manner, occurred, and this led to the formation of a developed interfacial surface. Due to the phase transition, there was strong cooling of the water around the bubbles, which brought 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 simultaneous application of these factors leads to a rapid increase in the hydration mass throughout the volume of water in a short period of time. The duration of the process itself takes about 60 seconds. After reaching a pressure of 0.1 MPa, at which the medium is below the saturation line of freon 134a and above the stability line of gas hydrate, the pressure relief stops. Then, for 600 seconds, a pressure of 0.1 MPa is maintained in the system for a complete transition of liquefied gas residues to a gaseous state. After that the system is heated to 20°C. As a result, the conditions in the working section leave the thermobaric region of the existence of freon 134a gas hydrate, which leads to its dissociation into water and gas. As a result of gas evolution, additional pressure is created in the system, using which, through the equation of state, the amount of gas that has passed into a hydrated state is determined.

4. Experimental results

In this work, a series of experimental studies was carried out with varying the stirrer rotation frequency at the working section of 0, 350, 700, 1050 and 1400 rpm. In Fig. 2 shows A graph of the pressure change during the decompression process for the case without stirring and with stirring at a stirrer speed of 1400 rpm is shown in Fig. 2. As you can see from the graph, nothing happens in the first few seconds, then the working section is decompressed, as a result of which the pressure begins to drop down, starting the process of gas hydrate synthesis. After reaching a pressure of 0.1 MPa, the decompression of the working section stops. At this pressure, the system is in the thermobaric region of existence of the gas hydrate and below the saturation line of freon 134a. I would like to draw your attention to the fact that for the case without mixing (rhombuses), after the pressure was released to 0.1 MPa, the pressure in the system began to increase, which required additional pressure relief so that the system was always at a pressure of 0.1 MPa. I would like to note that this is not observed in the case of mixing (circles). This is due to the fact that when the working section is stirred, the hydrate-forming gas more intensively passes into a hydrated state (freon 134a practically does not dissolve in water), and in the absence of mixing during decompression process, the efficiency of the gas transition into hydrate is rather low, thereby, after the pressure is released, the gas continues to boil in the volume of synthesized hydration mass, creating additional pressure in the system.
Figure 2. The pressure change during the decompression process for the case without stirring (rhombuses) and the case with stirring at a mixer speed of 1400 rpm (circles).

The dependence of the amount of gas transferred to the gas hydrate state relative to the initial mass of the gas on the speed of the mixer is shown in fig. 3. As it can be seen from the graph, the coefficient of gas conversion to the gas-hydrate state is constantly growing depending on the increase in the speed of the mixer. This is due to the large mixing of the layers with each other and crushing of liquefied gas, which leads to intensification of heat transfer. The maximum effect is achieved at a stirrer speed of 1400 rpm, when 13.7% of freon 134a converts from the initial state to the gas-hydrate state.

Figure 3. The dependence of the amount of gas transferred to the gas-hydrate state relative to the initial mass of gas on the speed of the mixer.
Conclusions
The work presented 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 stirring speed of the mixer on the transition of the hydrate-forming gas to the hydrate state was estimated. It was shown that the maximum effect is achieved at a stirrer speed of 1400 rpm, when 13.7% of freon 134a from converts into a gas-hydrated state.

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