Investigating the effect of decompression rate on the synthesis of carbon dioxide gas hydrate by the method of explosive boiling of a liquefied hydrate gas

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Abstract. The article is part of a comprehensive study of the method by synthesis of gas hydrate based on the explosive boiling of liquefied hydrate-forming gas in a volume of water during decompression. Carbon dioxide is used as hydrate-forming gas. This article explores the effect of decompression rates on the amount of gas transferred to a gas hydrate at an initial gas temperature of 2 ° C.

1. Introduction

A gas hydrate is a supramolecular assembly, the structure of which is an openwork skeleton consisting of water molecules, in the cavities of which there are gas molecules. Depending on the specific gas, the compound is stable in a certain thermobaric region, on leaving it the gas hydrate decomposes into pure water and gas. A large amount of gas can be in a gas hydrate state, for example, in one cubic meter of methane gas hydrate it can contain up to 170 cubic meters of gas. A unique feature of gas hydrate is the effect of self-preservation, the ability of gas to desiccate outside the thermobaric stability area at negative temperatures due to the effect of self-preservation [1 - 2]. These features make gas hydrate technologies promising for various industries, for example, for the storage and transportation of natural gas, desalination, gas separation, etc.

Perspective is the capture and disposal of carbon dioxide in gas-hydrate state to solve actual environmental problems. However, at the moment there is no competitive gas hydrate technology due to the complex process of synthesis of gas hydrate, and scientific groups around the world are working to solve this problem [3-15]. An important condition for the development of effective gas hydrate technologies is the rate at the synthesized hydrate, as well as the possibility of scaling. Therefore, an important role is played by fundamental studies of the formation of hydrates, their structural and thermophysical properties [16–20]. This article presents a perspective and fast method for the synthesis of gas hydrate, based on the explosive boiling-up of a liquefied hydrate-forming gas in a volume of water, which in the future may be the basis of an efficient and competitive technology.
2. Experimental setup
Experimental studies were carried out on the setup, which is a high pressure vessel of the autoclave type with a height of 300 mm and a diameter of 100 mm with a thermostatted jacket. The maximum working pressure of this unit is 25 MPa (Fig. 1). Temperature control is carried out with LOIP FT-316-40 cryothermostat. Mixing in the working area is provided by the work of the agitator. On top of the unit there are five holes used for injecting gases, as well as for pressure and temperature sensors. Through the drop unit, which is located on a separate rack, the revolutions of the agitator are adjusted, and the processes are monitored.

![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.](image-url)

3. Experimental data and analysis
This experimental work is part of a comprehensive study of a method for synthesizing gas hydrate based on the explosive boiling of a liquefied hydrate-forming gas in a volume of water during decompression. The synthesis process by this method is described in detail in the article [9]. In the present work, we study the effect of the decompression rate on the amount of gas transferred to gas hydrate at an initial gas temperature before decompression of the working section of 2 °C. Carbon dioxide was used as a hydrate forming gas. The experimental study was performed as follows: 200 g of water were placed in the working area. Through the side walls the work area was cooled. Next, 500 g of carbon dioxide were pumped into the chamber, were cooled and began to condense on the side walls of the installation. Due to the lower density of liquefied carbon dioxide, it forms a layer above the water surface. The water level was chosen in such a way that the mixer blades were located at the interface of the water layer and the liquefied gas. After establishing a temperature of 2 °C and a
pressure of 4 MPa on the working section, pressure was released at various gas flow rates (50, 150, 250, 350 l/min). At the same time, the agitator was started at a constant speed of 1000 rpm. As a result, the liquefied gas boiled and mixed with water. Gas boiling was in the volume of water, resulting in medium mixing and a significant cooling of the liquid around the bubbles.

At the same time, the medium entered the region of existence of carbon dioxide hydrate, leading to the formation of gas hydrate shells on the surface of the bubbles. Due to regular collisions of bubbles, the gas hydrate shell exfoliates, without complicating the diffusion of gas into water, and forms a gas hydrate mass. The heat released during hydrate formation is absorbed by boiling the liquefied gas. Due to the combination of these factors, the growth rate of the gas hydrate mass is very high. Pressure relief stops when the pressure in the working section reaches 2.5 MPa. At this pressure, carbon dioxide exists only in the gaseous state, and the gas hydrate is in conditions of thermobaric equilibrium. After completion of the process, the mass of the gas transferred to the gas hydrate is assessed. For this, the working area is heated. As a result of heating, the medium leaves the thermobaric region of equilibrium of carbon dioxide gas hydrate, which leads to its decomposition into water and gas, which in turn creates additional pressure in the working zone (Fig. 2). Further, through the state equations, the mass of the gas that has passed into the gas hydrate relative to the initial mass of the gas is determined (Fig. 3). In the figure shows that with a small gas flow rate (50 l/min) cooling is not effective enough, as a result of which only a small part of the gas from the source gas goes into the gas-hydrate state. With an increase in the gas flow rate, the amount of synthesized hydrate increases, while the optimal value of the parameters of the current mode is achieved at a gas flow rate of 250 l/min, at which 15.4% of the hydrate-forming gas is converted into gas-hydrate. A further increase in gas flow during decompression leads to the formation of parasitic ice, which complicates the hydrate formation process.

![Figure 2](image.png)

**Figure 2.** Decomposition of carbon dioxide gas as a result of heating the working area.
Figure 3. The influence of decompression rate \( U_d, \text{ l/min} \) on the mass of carbon dioxide transferred to the gas hydrate state relative to the initial gas \( K, \% \).

4. Conclusions
The method of explosive boiling up of liquefied carbon dioxide in the volume of water during decompression has been studied. The effect of the decompression rate on the mass of carbon dioxide transferred to the gas hydrate state relative to the source gas has been estimated. It is shown that the optimal pressure rate is 250 l/min, at which 15.4% of the mass of carbon dioxide passed from the initial state into the gas hydrate state.

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