Influence of intensively boiling liquefied gas on hydrate formation in self-organizing boiling-condensation process

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Abstract. In the framework of the method for producing gas hydrates based on the self-organizing cyclic boiling-condensation process of a hydrate-forming gas in a water volume, a study was conducted aimed at determining the effect of the boiling intensity of liquefied gas in the water volume on the hydrate formation process.

Introduction

Technological proposals for the storage and transportation of natural gas in a hydrated state appeared at the beginning of the 20th century. This method has attracted the attention of experts for a long time due to the properties of gas hydrates for concentrating large volumes of gas at relatively low pressures. Without a pipeline, a promising way of transporting gas is to convert it into a gas hydrate (solid) state and transport it at atmospheric pressure and low temperature (-10 ... -20 ° C) [1]. Properties of gas hydrates, basic conditions and features of their formation are described in [2-4] and some other works. The types of their crystallization, mechanisms of formation and decomposition of gas hydrates are given in [5-11].

In the present paper the method for producing gas hydrates was proposed, which is based on the self-organizing boiling-condensation process of hydrate-forming gas in a closed water volume. This method is characterized by high energy efficiency and the absence of any mechanical action on the gas-liquid medium. To start the method in the installation, thermobaric conditions are created in which the gas begins to condense and drop by the cooling walls to the bottom of the installation, where in turn, due to heating, boiling of liquefied gas takes place and the cooled bubble rises to the surface of the water, so much to compensate for the heat released during hydrate formation [12]. In the present work, the investigation of this method is continued and the influence of the boiling intensity of the liquefied gas layer under the water layer on the hydrate formation process is determined. The research team continues to search for effective ways to intensify the formation of hydrates by means of mechanical and thermal effects on gas-liquid media [13-16].

1. Experimental setup

The working area is a sealed vessel with a height of 740 mm and a section of 150X150 mm (fig.1). Two walls of the vessel are made of an optically transparent material and allow observing the processes taking place inside the working area. Maintenance of the required temperature inside the installation is carried out using the built-in cooling system (water jacket). The lower cover of the installation does not have thermal insulation and is heated from the external environment, or by supplying heat from a typical heating element. The temperature was measured by the DTS204-PT100
sensor, and the pressure was measured by the PD-100 sensor. The installation allows carrying out research within a wide range of temperatures (from -10 to 60 °C) and pressures (from 0.1 to 10MPa).

![Figure 1](image-url)

**Figure. 1** The schematic diagram of the experimental installation of the "autoclave" type:
1 — Blanking plug with gas inlet; 2 — Clamp; 3 — Top cover; 4 — Side walls with integrated cooling system; 5 — Pressure sensors; 6 — Temperature meter; 7 — Computer; 8 — Data collection system; 9 — Cryostat; 10 — Bottom cover; 11 — Liquefied Freon R-134A; 12 — Distilled water; 13 — Bubbles of Freon 134a; 14 — Freon hydrate.

2. Method and results

The essence of the experiment was as follows. The reaction vessel was filled with water to a level of 200 mm and cooled to a temperature of 4°C. Then a hydrate-forming gas (freon 134a) with a mass of 0.3 kg was introduced into the chamber, which condensed on the cold walls and descended through the water layer, concentrating on the bottom of the installation. The pressure in the chamber was set on the order of 0.45 MPa. Further, heating was carried out from the bottom of the installation with different intensity (≈50-900 W/m²), as a result of which the liquefied gas began to boil. During the passage through the water layer, gas hydrate film began to form on the surface of the bubbles. Having risen to the surface of the water, the bubbles were destroyed leaving flakes of gas hydrate behind them, and the released gas condensed on the cooled walls (with a temperature of the order of 2°C) and fell to the bottom of the installation, where they were again included in the boiling process. This process is cyclic and lasts until all the liquid Freon passes into the gas hydrate state. It should be noted that the formed gas hydrate "hat" does not interfere with the diffusive passage of the gas released from
the bubble emerging, and the liquefied gas descends the cold wall downwards, pushing the gas hydrate "hat".

This paper presents an experimental study of the effect of the boiling intensity of a liquefied hydrate-forming gas on the hydrate formation process. In Fig. 2, it can be seen that the heat supply and, consequently, the boiling point have a positive effect on the hydrate formation process, so, for a small heating $q_1 \approx 50 \, \text{W/m}^2$, the rate of increase in the gas hydrate "hat" is 0.66 mm/min, at $q_2 \approx 600 \, \text{W/m}^2$ the rate of increase is 1.82 mm/min, and at $q_3 \approx 900 \, \text{W/m}^2$ the growth rate of the gas hydrate "hat" is 2.37 mm/min, which is more than three times faster than growth rate in the first case.

**Figure 2.** Dependences of the growth rate of gas hydrate on the amount of heat supplied: Rhombuses: hydrate formation rate at 900 W/m$^2$. Triangles: hydrate formation rate at 600 W/m. Squares: hydrate formation rate at 50 W/m$^2$.

**Conclusion**

In this paper, the cyclic method for obtaining a modeling gas hydrate has been described. Experimental studies were carried out and a description of the processes taking place in the installation at the time of formation of the gas hydrate was compiled. Experimental studies have been carried out at different temperatures of the bottom of the installation. Dependences of the influence of the amount of heat supplied to the bottom of the installation on the growth rate of the gas hydrate were obtained.

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