Intensification of hydrate formation by means of explosive boiling incipience of rarefied gas in a bulk of water

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Abstract. The experiments on obtaining gas hydrate of refrigerant 134a were carried out by the method, based on explosive boiling-up of a layer of liquefied gas in a bulk of water at decompression. It is shown that this method combines several factors, leading to intensification of hydrate formation process, resulting in the fast gas hydrate growth. The effect of the decompression rate on the volume of produced hydrate was studied experimentally.

Introduction
As far back as in the beginning of the 20th century, the technological offers on the storage and transport of natural gas in the hydrate state appeared. This method attracts the experts’ attention for quite long time due to the property of gas hydrates to concentrate large volumes of gas at relatively low pressures. Without a pipeline a promising way of gas transportation is its conversion into the gas hydrate (solid) state and its transportation at the atmospheric pressure and low temperature ($-10 \ldots -20^\circ C$) [1]. In [2 - 5] and some other monographs, the properties of gas hydrates, basic conditions and features of their formation are described; the types of their crystallization, mechanisms of gas hydrate formation and decomposition are presented.

Previously, we have carried out the experiments on introduction of liquid nitrogen jet [6]. These studies were focused on a new method of gas hydrates production, based on the shock-wave method. The maximal pressure amplitude in experiments was 53 bar, and the rate of pressure rise was 567 bar/s. The advantage of the shock-wave method as compared to the conventional analogues is significant (by an order and more) intensification of the process of gas hydrate formation [7-9].

1. Experimental setup and methods
The studies were carried out using the setup in the form of a high-pressure reactor of up to 25 MPa. The working section was made as a stainless steel vessel (diameter of 100 mm, height of 300 mm) with a water jacket for thermal statting (Fig.1).
The experiment has been performed in the following manner. Water in the amount of 200 ml was
into the reaction vessel and cooled by the cryostat through the outer walls to the temperature of hydrate
formation. Further, 200 g of Freon 134a from the tank was fed into the water-filled vessel (with the
temperature of 2-8°C). The pressure in the tank is much higher than the pressure in the autoclave, and
the temperature of gas in the tank is higher than the water temperature. Entering the autoclave, gas
started pressurization. Gas was cooled to the temperature of water, causing it liquation and accumulation
in the form of a layer on the autoclave bottom. Then the pressure was decreased, liquefied gas under
the water layer started boiling over the entire volume, so that there was an increase in interfacial surface.
On the bubble walls, the growth of the gas hydrate layer started. Due to active boiling, the bubbles with
the hydrate film, formed on the interface, collided constantly and deformed, causing the hydrate film
peeling, and the rate of hydrate formation did not decreased. The heat released during hydrate formation
was compensated by heat absorption during boiling. Due to superposition of these processes, there was
a fast increase in the mass of gas hydrate.
Analysis of results
To perform the balance calculation, the following experiment was performed. Immediately after completion of refrigerant boiling, causing leveling the pressure in the working section with the atmospheric one, the system was brought to the state to be in the zone of hydrate stability. Further, the system was heated; to do this, the temperature in the thermostat was raised by \(1\)°C every 10 minutes. The pressure in the system remained almost unchanged until the hydrate equilibrium line was not passed, and gas hydrate decay into water and gaseous Freon started. Freon increases the pressure in the system (Fig. 2).

The mass of gas released at gas hydrate decay is determined using data obtained:

\[
\nu_g = \frac{\Delta P V - \nu_0 R \Delta T}{RT}
\]

\[
m_g = \nu_g M
\]

where \(\nu_g\) is the amount of released gas matter, \(\Delta P\) is the pressure jump in the system after gas hydrate decomposition, \(V\) is the volume of the gas layer in the autoclave, \(\nu_0\) is the amount of substance before gas hydrate decomposition, \(\Delta T\) is heating temperature, \(m_g\) is mass of gas, \(M\) is molecular mass of gas.

Taking this into account, we find the mass of produced gas hydrate:
where $\lambda_n$ is the coefficient of gas content in gas hydrate.

Since in experiments, all water converted into gas hydrate and ice, we find the mass of ice using the equation of mass balance $m_i$.

$$m_i + m_h = m_t + m_g$$

According to calculations, since the rate of pressure drop affects the mass of produced gas hydrate, at the rate of pressure drop of 10 l/min, the mass share of hydrate relative to ice is 15%, and for 70 l/min, it is 40.7%.

**Conclusion**

In this paper, the new method of gas hydrate production, based on liquefied gas boiling under the water surface due to pressure relief, was checked experimentally. The process of gas hydrates production was described, the advantages of this method over the other were determined. The diagrams in this paper show the presence of gas hydrate in the system due to an increase in pressure. The high rate of discharge increases the amount of produced hydrate.

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