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PROSPECTS FOR THE DEVELOPMENT OF HYDRATE STORAGE AND TRANSPORTATION TECHNOLOGY OF METHANE GAS

1. INTRODUCTION

In many cases, the traditional assembly technology, and use (consumption) much of the resources of hydrocarbon gases (associated petroleum, deposits, in-pit) are ineffective or economically unjustified. At the same time the recent years there has been rapid development of technology accumulation (storage), transportation and long term storage of hydrocarbon gases in hydrate form. However, widespread implementation of this technology due to insufficient testing of its elements, it has not yet acquired. The main problems that hinder the production of gas hydrates of natural gas, and hence the widespread introduction of gas hydrate technology is creating a closed cycle, withdrawal of gas hydrates formed, its maximum dehydration, maintaining the integrity of the formed hydrates. Plants for the production of semi hydrates, as applicable, and those that are under development, there are still quite underdeveloped in terms of energy consumption and optimizing industrial operations. The analysis of the structural features of known reactors showed that none of them, in our opinion, can fully meet the requirements of industrial applications.

The important issue for modern energy – a diversification of sources of natural gas supply. The alternative could become to Ukraine gas transportation by sea LNG-tankers. However effective this technology, based on considerable capital investments will be in the presence of considerable gas reserves and reliable contracts. Moreover, LNG-projects

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are economically feasible for realization of transportations to a distance not less than 5.5 km, while investments in LNG-projects are at a minimum 1.5–2.5 billion USD.

There are also problems of accumulation transportation, storage and rational use associated petroleum gas. This traditional technologies often find themselves ineffective. Therefore the world's 150–170 billion Nm^3 per year of associated gas flared. This cause the loss about 40 billion USD. Moreover to the atmosphere is flagged about 400 million tons of CO_2. Ukraine produces 17–20 billion Nm^3 natural gas, and in Russia the same quantity associated gas is burned. This cause the loss about 13 billion USD.

In this connection, in the world is constantly working on the improvement of gas production technology, and its transportation and storage.

But at the same time, hydrocarbon gases in contact with water under certain pressure-temperature conditions can form very stable compounds – gas hydrates. Therefore during the last years is observed rapid development of technologies associated with gas hydrates.

Direction analysis reflected in this paper is a meaning hydrate technology in the oil and gas industry. Namely, the development of production technology parameters of hydrocarbon gas hydrates to their rational use (accumulation, transport and long storage), and gas hydrate technology intensification production of natural gas in the final stages of field development. Thus in both cases based on technology is exothermic process of gas hydrate formation.

2. ANALYSIS OF RECENT RESEARCHES AND PUBLICATIONS IN WHICH THERE ARE EFFORTS OF PRESENTED PROBLEM SOLUTION

Equipment for the production of synthetic hydrates, gives possibility by different ways of creating contact between the liquid and gas. There are two popular ways:
– spray water into the gas phase (by spraying water into the gas fed through nozzles, conductors and sprayers),
– the introduction of gas into the liquid phase by bubbling or stirring method and combined input reagents.

During spraying water in gas at the stage of gas-water interconnection is hydrating. Its mechanism consists of the following steps [1]:
1) the embryo formed hydrates,
2) drop cover gas hydrate crust thickness 0.04 mm,
3) crust thickens to 0.24 mm.

The water in the hydrate capillaries rises to the gas phase. Since the fluid is compressed enough, the external gas pressure can break hydrated crust. Thus, hydrate enjoys the water.

During the bubbling gas to its liquid bubble covered hydration rind. As the gas is compressible, in this case appears [2]: crust under pressure breaks inside. Around formed crust particles formed hydrate. So, with this method of hydrate water is much less taken.

The process of hydrate formation is to create a contact interface for dissolving gas in water at appropriate pressure – temperature conditions, the formation and growth of hydrate

structures and allocate the appropriate amount of heat hydrate. Depending on how the contact phase in the gas hydrates can be a different, sometimes very large amount of water. And in the case of the captured water (water droplets covered with hydrate crust) it is difficult to remove or tie in gas hydrates. Capture by hydration structures of gas bubbles ultimately leads to improving the quality of the resulting product as bubbles covered hydrated crust, relatively easily broken, or there is a gradual diffusion of gas hydrate due to contact with free water and its binding. Therefore, for the production of gas hydrates with minimal water content appropriate to apply a way that provides for the introduction of gas in water volume. Bubbling gas into the bottom part of the reactor volume is being doing in such a way. However, the main problem of this method and the main direction of its improvement is to reduce the size of the bubbles to increase contact area phases, as well as extending the time of the bubbles in the liquid.

Depending on how the supply of energy to the working environment in order to create a contact phase contact apparatus for gas hydrate formation, similar to-the absorptive devices can be divided into units of energy supply gas phase, liquid phase, mechanical agitators and their combinations.

Characteristic feature of the apparatus of power supply liquid and gas phase is the presence or mechanical or hydrodynamic mixing device. The most widely used devices with mechanical mixers that are installed, usually over gas distribution device. The main disadvantage of apparatus with mechanical mixing devices are unreliable operation of these devices.

Main analysis

The study of the mechanism of free jet injection of gas involved many researchers [3]. Upon entering the free jet in the liquid volume (Fig. 1) injection of gas into a liquid and its dispersion to form tiny bubbles is in entry point, that is absorption of gas.
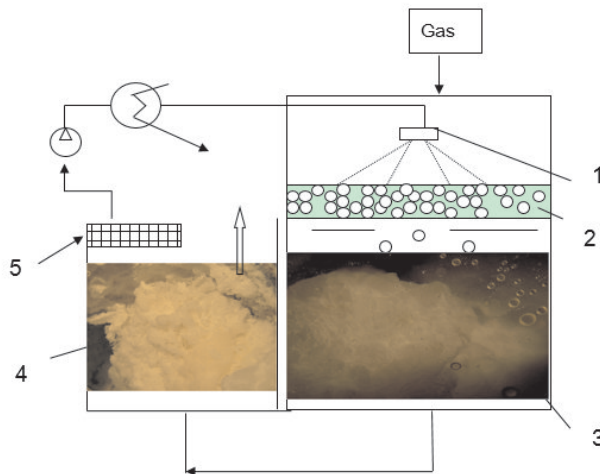

Fig. 1. Scheme of the mechanism of free jet injection gas: 1 – vortex apparatus 2 – layer, which forms a gas hydrate; 3 – gas hydrate in the form of gel; 4 – crystalline hydrate; 5 – filter

Bubbles of gas in the formation of hydrated crust around them will be subjected to variable deformation due to mechanical action liquid jet. Formed in such a way water--gas-hydrate mixture, in our opinion, will be the best quality, as containing the minimum number of enthusiastic hydrate water drops. This in turn will facilitate its further qualitative separation (Fig. 2).
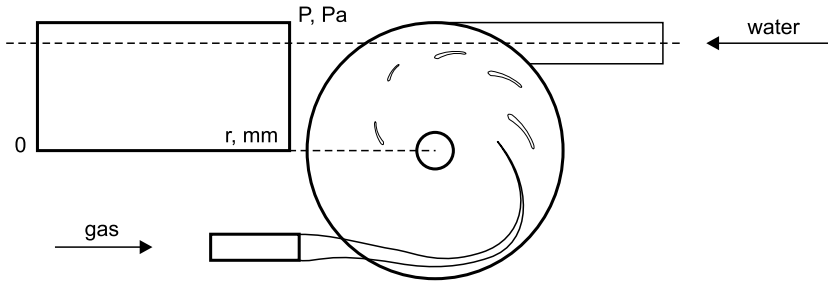

Fig. 2. Scheme vortex nozzle of claim I from Figure 1

Under certain conditions it is possible to hydrate formation from dissolved gas in water. Two-phase two-component system in accordance with the Gibbs phase rule is bivariant. For a complete describe the state of the system is necessary to specify any of the two independent variables, such as temperature and pressure. At constant pressure the temperature of gas hydrate formation from a solution in water is determined by the concentration of dissolved gas. Under the change of gas concentration in the water affects the change in temperature of hydrate formation. Thus, to determine the equilibrium conditions for the solution of gas hydrate formation in water required three-dimensional state diagrams P-T-x these systems and their projections on P-T, T-x or P-x plane of (x – molar share of gas in solution).

In Figure 3 is shown a fragment of high quality T-x state diagrams of water-gas at positive temperatures and pressures, which corresponds to the hydrate formation. Lines L-G and G-L related to the two-phase equilibrium liquid-gas determine the composition of the liquid phase (curve liquid L-G) in equilibrium with the gas composition and gas (vapor curve G-L) in equilibrium with the liquid at a given temperature. Lines L-H and G-H describing two-phase equilibrium liquid-hydrate and hydrate-gas, determining the composition of the liquid and gas phases, respectively, in equilibrium with the hydrate. Line L-H-G corresponds to the three- phase equilibrium water-hydrate-gas. The vertical line H determines the composition of the hydrate, which is in equilibrium with the gas or liquid phase.

Until recently it was thought that the two-phase equilibrium „liquid-hydrate" and „hydrate-gas" hydrate composition with temperature no changes. However, quantitative thermodynamic calculations and methods for determining the composition of hydrates spectroscopy showed that the lines of H, corresponding to the stoichiometric composition of hydrates in the diagram actually corresponds nonstoichiometric region (in Fig. 3 dashed line). So hydrates received from dissolved gas (left dashed curve branch, which limits the nonstoichiometric region on the diagram), containing less than gas hydrates formed when excess gas (the first branch of the curve).
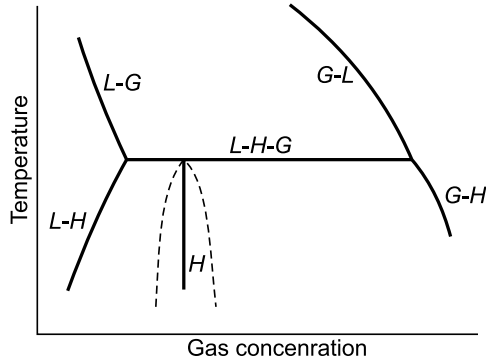
Fig. 3. Qualitative *T-x* diagram of the system water-gas
in the area hydrate formation

Gas hydrates under normal conditions are unstable compounds. A clear idea of possible changes in the system can be obtained from consideration of phase diagrams. In Figure 4 presents the scheme of *P-T* diagram for a two-component system „hydrate creator – H_2O" within the terms of the quadrupole Q_h which corresponds to the four phase equilibrium ice-water-hydrate-gas.
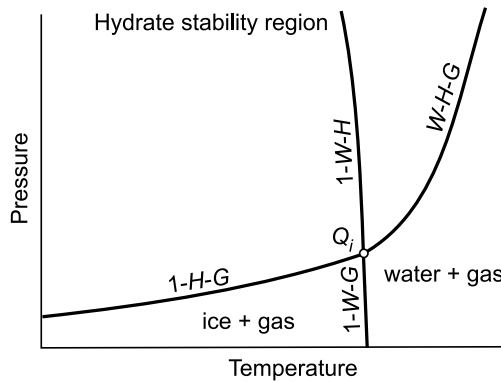

Fig. 4. The scheme phase diagram creator of hydrates – water within the terms
of the quadrupole Q_i

The point Q_i we obtain as a result of crossing lines of three-phase equilibrium ice-hydrate-gas (1-*H-G*), water-hydrate-gas (*W-H-G*), ice-water-gas (*IWG*) and ice-water-hydrate (*IWH*). Above the line 1-*H-G* and *W-H-G* is a region of stability of hydrates. Parts of the diagram is limited lines 1-*H-G* and *I-W-G*, complies with the conditions which are stable ice and gas. To the right of the line *W-H-G* located region two-phase equilibrium water-gas (*W-G*). Three-phase equilibrium conditions „methane-water-hydrate showing in Figure 5.
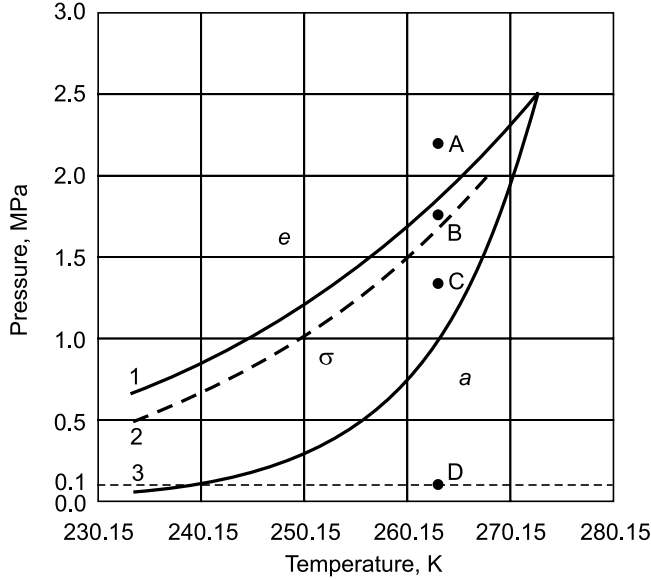
Fig. 5. Three-phase equilibrium conditions „methane-water-hydrate"

The proposed equipment using a vortex apparatus we create thermodynamic conditions (ratio of *P-T*), in which you can get methane hydrate corresponding to any point on the diagram (see Figs. 4, 5). Consider the mathematical model of the medium through which we define appropriate thermodynamic conditions and modes of operation apparatus.

Physical model proposed above boiling process in superheated liquid vortex devices can be represented by the following system of equations for the main area of the vortex:

$$\frac{dp}{dr} = K\rho M_x^2 \frac{W^2}{r};$$

$$PV\frac{d(rW)}{rdr} = \frac{1}{k}\frac{d}{dr}\left(\frac{1}{r}\frac{d(rW)}{dr}\right) + \gamma(r)W;$$

$$\frac{\rho}{r}\frac{d(rV)}{dr} = -\gamma(r);$$

$$\rho = const;$$

$$\gamma(r) = A_1 + A_2 r^{\alpha};$$

$$at \ r = 1, \ V = -1, \ W = 1; \ \rho = const;$$

$$at \ r \rightarrow 0, \ rW = 0$$

(1)

where:

P – pressure, Pa;
W – circumferential component of the velocity, m/s;
V – velocity phase, m/s;
T – temperature, K;
ρ – density, kg/m^3;
r – radius, m;
z – coordinate axis of the vortex chamber, m;
M_x – Max Number;
V – the radial velocity component, m;
$y(r)$ – mass removal rate (hydrate), presented as a series with coefficients Al, A2, and the exponent a;
U – axial component of velocity, m/s.

The solution of equation system (1) shown in Figure 6. Conditions for gas hydrate formation are at r-0-0,4.
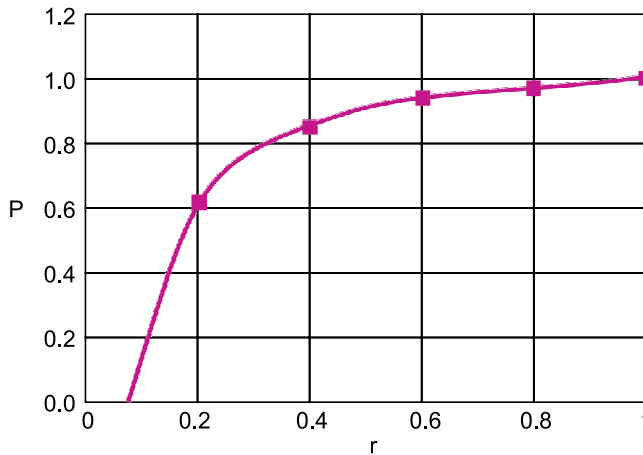

Fig. 6. Combined solution of flashing flows

Graph on Figure 6 shows dimensionless values of the radius and pressure. By specifying temperature of the liquid, we can define conditions for performing thermodynamic relation P-T mode of methane hydrate formation.

To extend (increase) in time of the bubbles in the water until complete dissolution and binding them to hydrate we suggested to provide additional mixing of the reactor contents with a relatively low speed (30–60 r/min). On this basis, and considering the process of gas hydrates as a whole and setting the target of its maximum and integrated optimization, we propose to make bubbling gas into a liquid and its mixing with one or more free jets of water at the appropriate places and at certain angles interact with the surface of the liquid.

When directing jets of water at an angle other than vertical, due to the transfer of kinetic energy to the contents of the reactor (a mixture of water and gas hydrates) will be moving it around the axis of the reactor and the relative movement of layers of a mixture of water and hydrates the height of the reactor. Thus, the proposed mixing free jet, except the extension time of the bubbles in the liquid, would reduce the thickness of the layer of liquid in the reactor, and hence its volume and evenly distribute heat hydrate. To improve the method of contacting gas and water in the continuous production of gas hydrates, the input of feed gas flow should carry through its bubbling in the bottom part of the reactor. At the top of the reactor should include the presence of a certain volume (eg 45–50% of the volume of the reactor) for the accumulation of gas. With this circuit and the technological solution circulation of gas takes place in the reactor volume without additional equipment, and the process of feeding raw gas will be binding on the relevant part of gas hydrates. The effectiveness of the method of contacting phases (mixing) free jet injection fluid determines its ability and coefficient of injection and gas.

To implement a continuous process of gas hydrates is mandatory to create conditions for continuous and uninterrupted his removal from the reactor, the reactor feed gas, and water and heat dissipation hydrate. The difficulty is that the parameters of the thermo baric property shown rapid enlargement of gas hydrate structures in a process of coagulation of micro particles and their subsequent agglomeration patterns in the critical size. However, accumulation of solid hydrate phase is undesirable, because it leads to complications related to the closing process lines and dead zones of the reactor, heat and mass transfer deterioration. Therefore, the production of gas hydrates, we offer to provide measures to prevent the consolidation of hydrate structures at the time of their arrival in the separation device.

Based on the proposed method of hydrate formation is proposed diversion of the basic process to make energy from the target stream (a mixture of water and gas hydrates) outside the reactor during its circulation through the heat exchanger. This method of heat removal will be simple and effective.

In order to confirm the fundamental possibility of continuous production of gas hydrates in the application of inkjet machine with free-falling stream as a device for contacting phases of a series of experiments were conducted on a laboratory gas hydrate installation diagram is shown in Figure 1. In addition, experiments established the rate of hydrate formation and verification capabilities of processes uninterrupted output produced mixture from the reactor prior to agglomeration of particles of hydrated mass circulation separated fluid to remove heat hydrate formation, agglomeration and accumulation of gas hydrate formed in the separator.

In experiments gas composition: CH_4 – 92.8%, C_2H_6 – 5.1%, C_3H_8 – 2.1%, with a density of 0.595 were used. Nozzle diameter was 2.05 mm. Circulation of fluid through the heat exchanger 18, the temperature in the reactor was maintained at 276 K. The gas pressure in the reactor was maintained at 4 MPa. In the process water fed to it under pressure 10 MPa.

During the experiment, the rate of formation of gas hydrates was measured amount of fuel gas per unit time. For this rate of pressure drop fixed in the gas tank. The experiment was continued until the pressure drop in the tank to 2.0 MPa, i.e. 0.5 MPa above the equilibrium hydrate formation conditions for the gas composition.

3.   CONCLUSIONS

1. Production of gas hydrates is proposed to make ejection of gas and mixing the contents of the reactor free liquid jet with the introduction of raw gas in the bottom of the reactor and the derivation water-gas-hydrate mixture until it is clear phase separation resulting in agglomeration of gas hydrates.
2. Ejection of gas and mixing the contents of the reactor using a free jet will greatly streamline and simplify the design of the reactor. This circulation of fluid in the direction of jet apparatus-reactor-separator-heat exchanger-jet unit will simultaneously perform the ejection of gas, improve the quality of contact phase flow reactor in the required amount of water recharge, heat dissipation and output hydrate formed hydrates.

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