METHODOLOGY FOR DETERMINING THE PARAMETERS OF THE START OF GAS HYDRATES MASS CRYSTALLIZATION

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Abstract

Man-made gas hydrates create serious problems for the oil and gas production industry. Prevention of hydrate formation requires significant costs. In addition, it is important to understand the physics and parameters of hydrate formation processes. Therefore, an urgent task is to establish the peculiarities of the kinetics and parameters of hydrate formation in technological processes. The object of the research was the parameters of the beginning of mass crystallization of gas hydrates in reservoir systems.

The process of hydrate formation at the phase boundary is manifested by the formation of a thin layer of hydrate in the form of a film. In the course of experimental studies, it was established that this process is visually fixed by clouding of the pre-specular phase boundary. The effect of distortion of the interphase boundary is explained by the formation, growth, and chaotic accumulation of gas hydrate microcrystals at this boundary. Based on the results of theoretical and experimental studies, the methodology of operative laboratory

determination of parameters of mass crystallization of gas hydrate is justified. The essence of the technique is to fix these parameters by the optical effect of distortion of the reflection of the light source on the mirror of the "liquid-gas" interphase surface.

The results of empirical studies are based on optical phenomena that were recorded on the interphase surface of the gas hydrate layer and gas. They were studied using microscopy, fixation and image processing methods. The main result of the experiments was the information recorded by the optical system and obtained after fixing the pressure and temperature.

The technique can be used to establish and operationally control the moment of mass crystallization of gas hydrates directly at the objects of the oil and gas industry (during the implementation of technological processes). This will make it possible to effectively prevent clogging of technological equipment with the solid phase of gas hydrate, as well as to prevent overuse of hydrate formation inhibitors. At the same time, the only limitation of the application of this technique may be the low light permeability of the aqueous solution as part of the formation system.

1. Introduction

Gas hydrates are formed from gases and water under certain thermobaric conditions [1]. Deposits of natural gas hydrates contain colossal volumes of methane in their composition, and man-made deposits create serious problems for the oil and gas production industry. For the formation of artificial natural gas hydrates, a necessary component is the presence of moisture in the condensed phase. In the wellbore and further along the collection and preparation system, the temperature of natural gas gradually decreases. As a result, moisture condensation occurs. The system composition and the gas mixture in it affects the conditions of thermodynamic the hydrate equilibrium [2].

Therefore, all processes of extraction, preparation, storage and transportation of oil, gas and condensate are accompanied by the possibility of the problem of the gas hydrate plugs appearance. Such processes are observed in the presence of appropriate thermobaric conditions and as a result of technological violations. As a result of reducing the internal pipelines cross-section, the operation of all technological equipment in the hydrate mode leads to a change in its operating modes, complete clogging of pipelines, fittings and equipment at oil and gas production facilities and the linear part and site facilities of mainline gas transport at UGS.

The analysis of the purpose of technological operations and equipment for extraction, preparation and transportation of natural

and petroleum (associated) gas shows that a significant part of them concerns the hydrate formation prevention. Therefore, the costs of preventing this spontaneous process make up a significant part of the hydrocarbon production cost.

For prevent or remove the formed hydrates in each specific case, it is necessary to understand the physics of pipeline operation processes for different operating modes, knowledge of the conditions of gas hydrate formation processes. The thermal and hydraulic regimes of gas pipelines, the optimal humidity of transported natural gas should be taken into account. Places of possible hydrate plugs formation   are determined by gas composition, thermobaric conditions, and its moisture content [3].

In the process of developing hydrocarbon deposits, a whole set of methods for preventing hydrate formation is used. The analysis of literary sources showed that all known prevention of the process methods are based on the elimination of at least one of the necessary factors: temperature, pressure or gas moisture. The classification of the most used methods of preventing the hydrates formation has the following form [4]: technological, physical and chemical methods.

The choice of methods is influenced by the existing thermobaric conditions, the possible place of hydrogenation in the technological system of gas production and transportation.

At the same time, in many cases, it is impossible to achieve the technological (hydrate-free) mode of their operation, only by maintaining the appropriate thermobaric conditions. In this case, there is a need to switch to chemical methods and the use of substances that are inhibitors of this process. Significant costs for preventing the formation of hydrates and mitigating their consequences are associated with the use of traditional thermodynamic hydrate inhibitors (TIG), such as methanol and monoethylene glycol (MEG) [5].

Therefore, management of hydrate formation processes has become necessary for safe and reliable oil and gas extraction [6]. Development of methods for detecting early signs of hydrate formation may be one such option. This will allow operators sufficient time to take appropriate measures to prevent hydrate formation.

There are various analytical methods that are used to identify the structures of gas hydrates that occur at the interface between the water and vapor phases. The study of the gas hydrates formation and dissociation is great importance for determining the conditions for safe passage of oil and gas through pipelines [7].

New methods for detecting early signs of hydrate formation have been proposed by the Center for Gas Hydrate Research at the University (Heriot-Watt). They will allow operators to have enough time to take appropriate measures [8]. The method based on the change in the gas phase composition the due to the hydrates formation is presented in [9]. This is one of these early warning methods of the gas-hydrate process.

During the formation of hydrates, the natural gas components are selectively captured in the hydrate cells, and as a result, the composition of the gas phase changes. [10]. Next, the speed of sound, thermal conductivity are determined and the equivalent concentration of the gas mixture components is established [9]. Based on this property, an experimental technique has been developed to detect early signs of hydrate crystal formation by determining the gas composition.

Yang [11] developed a reliable and fast method for detecting the composition of hydrocarbon fluid and establishing the stability zone of hydrates. The salts concentration, thermodynamic and kinetic inhibitors of hydrates is determined on the basis of the measurement of electrical conductivity and acoustic velocity data of the aqueous phase chemical composition and the stability hydrates zone is determined.

Tohidi [12] proposed a method for determining the reserve of stability of the hydrate zone based on the measurement of the water content in the gas phase. In the work [13], the authors propose monitoring systems for the prevention of hydrogenation based on dielectric properties and determination of the freezing point of the aqueous phase.

A large complex of gas hydrates properties, a diverse composition of reservoir systems, a wide range of thermobaric parameters and their fluctuations do not allow obtaining an acceptable and unambiguous result when applying most of the known methods. An important task remains the improvement of the method for operational hydrate formation forecasting in the systems of

collection and preparation of industrial products, as well as the principle scheme of the equipment for its implementation.

Therefore, the purpose of this study is the theoretical and experimental substantiation of the method for determination the parameters of the moment for mass gas hydrates crystallization. Establishing and controlling the moment of the beginning for mass gas hydrates crystallization in production at the objects of the oil and gas industry will allow to manage the process of hydrate formation and prevent the appearance of ice jams in gas pipelines and equipment, by timely introduction of the necessary volumes for hydrate formation inhibitors.

2. Theoretical substantiation

The hydrates formation is characterized by an induction period, which includes the appearance of crystal nuclei and their growth [14,15]. Further, in the stage of phase transition, when the hydrate plugs formation occurs, crystals agglomeration is observed [16,17].

The hydrate formation process occurs most intensively at the interface between the gas and water phases. Processes on the liquid mirror, drops and bubbles in the laboratory reactor, technological equipment are manifested by the formation of a thin layer of hydrate in the form of a film. Specifically, the study concerned the processes that occur on the bubble surface as a surface of separation of two phases - reactor water and hydrate-forming gas in the bubble.

Visually, this process is fixed by changing the mirror surface of the phase boundary to a matte one. It has defects in the reflection of light sources, their distorted reflections and complete impermeability of light. The dynamics of the process is shown in fig. 1,2 and 3.
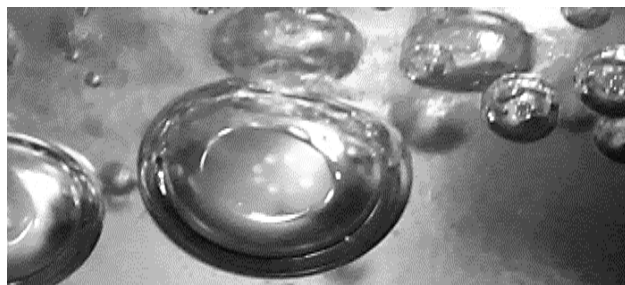
Fig. 1. Mirror interfacial surface of hydrate-forming gas bubbles in water (gas hydrate film is absent)

a   *b*

c   *d*
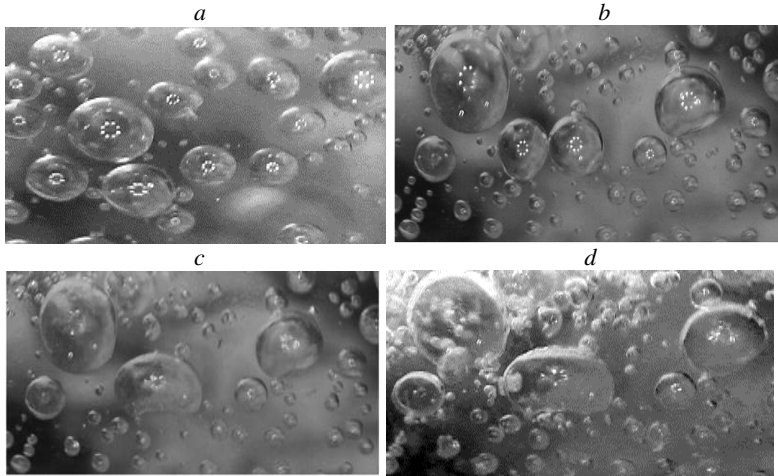
Fig. 2. Dynamics of distortion of reflections for point light sources on images of gas bubbles in water as a result of the formation of a gas hydrate film on the interfacial surface
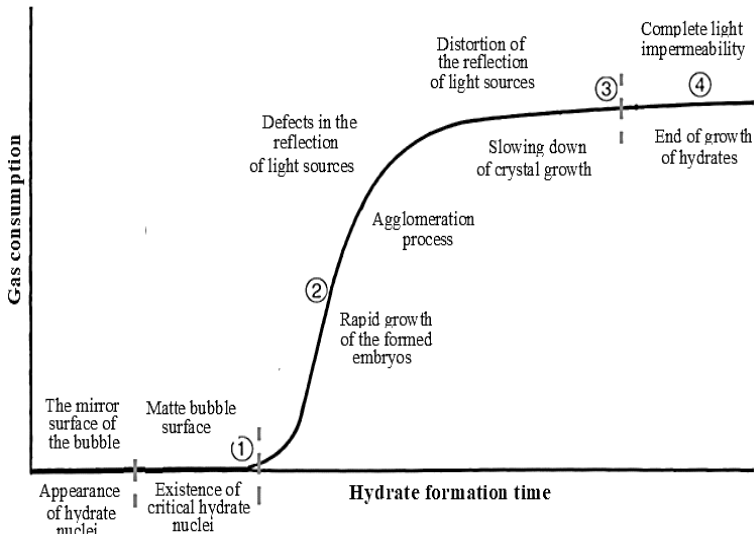
Fig. 3. The process of gas hydrates formation in water from a gas bubble

The effect of gradual the mirror distortion of the interphase boundary is explained by the formation and chaotic accumulation of gas hydrates on it. However, a significant deviation of thermobaric

parameters at the initial stage 1 (matte surface of the bubble) of the control system is practically not recorded.

Therefore, the initial period of hydrate formation 1 is characterized by the nucleation of hydrate nuclei (nuclei) due to the increase in Gibbs energy ΔG. At the beginning of the hydrate formation process, water, from the point of view of the classification of dispersed systems, can be considered as an ideal solution. One of the important properties characteristic of non-colored systems of a molecular degree of dispersion is the complete passage of light, transparency, and the absence of a scattering process. Therefore, the mirror surface of the bubble is visually observed.

Further growth and overcoming the energy barrier ΔG_{cr} will lead to their reaching the critical size r_{cr}, the value of which can be calculated using the formula

$$ r_{cr} = -\frac{2\sigma'_{ef}T_0}{\Delta H \Delta T} , \tag{1} $$

where ΔH - heat of crystallization of the hydrate former, kJ/mol; T_0 - equilibrium temperature of hydrate formation for the corresponding pressure, K; $\Delta T = T - T_0$ - relative cooling of the system; σ'_{ef} - effective specific surface energy of the seed, mJ/m ^{2}.

The value of the critical radius r_{cr} will decrease with the increase in the supercooling temperature ΔT for the «gas in the bubble - water in the reactor system».

As a result, a decrease in the induction time of hydrate formation will be observed. At the end of the induction period, water with formed critical nuclei of hydrates can conditionally be considered a colloidal system. It is known that the size of «true colloidal» particles lies within 1-100 nm [18].

The dispersed phase of the studied system is the nuclei of a critical size. For example, for natural gas hydrate with a density of approximately 900 kg/m³ at $T_0 = 278$ K and $\Delta T = 3$, the radius of the critical nucleus will be $r_{cr} \approx 15$ нм, and for the hydrate at $T_0 = 280$ K and $\Delta T = 1$, the radius of the critical nucleus will be $r_{cr} \approx 45$ нм.

Scattering or opalescence is inherent among the optical properties of all colloidal systems. Scattering (opalescence) is observed when the wavelength of light is greater than the linear dimensions of the

particles of the dispersed phase [19]. The light-scattering ability of dispersed systems depends on the size of the particles, the refractive index of the dispersed phase and the medium, and the wavelength of the light wave that is scattered.

Since the resolution for an optical microscope is about 10^{-7} m, colloidal particles (hydrate nuclei) cannot be seen with its help. However, it is precisely for colloidal systems that the maximum scattering of light corresponds. When the particle itself is not visible, but the scattering is quite well observed using an optical microscope under side illumination (focused light).

The sizes of the critical r_{cr} nuclei at the end of the induction time are much smaller than the wavelength of visible light ($400 < \lambda < 750$ nm). When light passes through a dispersed system, there is a slight scattering of light in lateral directions. As a result, a slightly matte surface of the bubble is visually observed.

The next period of rapid growth and agglomeration 2 is accompanied by further very rapid growth of the formed hydrate critical nuclei and depends on the method of heat removal of the hydrate formation process. For a reactor with a stirrer, the growth rate of hydrates is determined empirically

$$v = \alpha \Delta T^{\beta}, \tag{2}$$

where v - rate of gas absorption during hydrate formation; α i β - constants, the values of which depend on the energy for mixing the components of the system and are determined experimentally [10].

For the process of studying light scattering in a colloidal system, when the size of the particles of the dispersed phase does not exceed 0,1 wavelength of light - for particles with a size of 40-50 nm - the Rayleigh equation is used [19]

$$I_p = \frac{24\pi^3}{\lambda^4} \left(\frac{n_1^2 - n_0^2}{n_1^2 + n_0^2} \right)^2 \gamma V^2 I_0, \tag{3}$$

where γ - concentration of dispersed particles; V - volume of each particle; λ - wavelength of light; n_1, n_0 - refractive indices of the dispersed phase and dispersed medium; I_0, I_p - intensity of incident and scattered light.

The greater the difference between n_1 and n_0, the greater the turbidity and the stronger the scattering of light with other equivalent

parameters. The sizes of the formed hydrate particles have a significant effect on the intensity of scattering of light waves. The volume of each particle is determined as $V=(4/3)\,\pi r^3$, r is the radius of the hydrate particle. Then the scattering intensity I_{scat} according to the formula (3) is proportional to the volume of the formed hydrate particles V and the radius of these particles r^6. Therefore, even with a slight increase in the linear size of gas-hydrate particles, the scattering intensity or turbidity of the colloidal solution increases quite sharply. The dependence between the scattering intensity and the linear dimensions of the particles is shown in Fig. 4 [19].
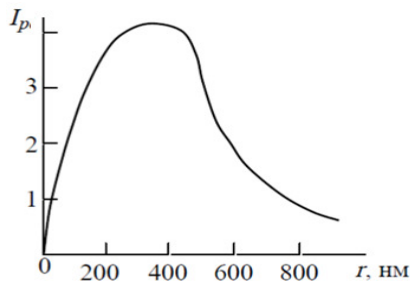
Fig. 4. Dependence of the scattering intensity on the linear dimensions of the particles

The growth of gas hydrate crystals as dispersed particles initially causes an increase in the effect of light scattering (opalescence) and increases the turbidity of the bubble surface. The uneven growth of dispersed particles leads to the beginning of the process of reflection of light waves (for the largest particles of gas hydrates, the size of which exceeds the light wavelength λ). As a result, light reflection defects on the bubbles are visually observed.

The next period 3 is the slowing down of the growth of hydrate particles. Volume diffusion growth of crystals will be observed on the free surface of the bubble and the already formed gas-hydrate crust. The rate of formation of gas hydrates will be determined by calculating the mass rate of water diffusion M_v through a flat hydrate film of thickness h and surface F [20]

$$M_w = D_w \cdot \frac{F \cdot \Delta f \cdot \rho w}{h}, \qquad h = \sqrt{\frac{2Dw \cdot \Delta f \cdot \tau}{n}}, \qquad (4)$$

where D_v - the diffusion coefficient of water through the hydrate film (for natural gas with a relative density of 0,6 $D_v=10^{-6}$ sm²/s); Δf – difference in volatility of water vapor over liquid and hydrate; ρ_v - density of water in the hydrated state $\rho_v=0,757-0,792$ g/sm³; h - hydrate film thickness during hydrate formation τ; n - mass ratio of water and gas in the hydrate.

For this kinetics period of gas hydrate formation, the linear dimensions of the particles of the dispersed phase will exceed the length of the light wave λ that passes through the dispersed system. Then they will observe its reflection, not scattering. Visually, this manifests itself in the distortion of the reflection of light sources.

The last period 4 is the end of the hydrate formation process. We have a thick, dense crust that covers a bubble of gas that is not part of the gas hydrate. At the end of the hydrate formation process, complete light opacity is visually observed. A dense crust does not let light through.

Thus, taking into account the information obtained in the process of the performed analysis, it is possible to record the earlier stages of the hydrate formation process and the moment of the beginning of mass crystallization.

Structurally, the task of low-dose gas introduction into the liquid volume in the reactor for its bubbling mixing with simultaneous control over the processes on the surface of the formed bubbles can be realized by mounting a gas introduction line through a capillary immersed in the liquid. However, this study is narrowly focused and concerns the processes of hydrate formation on the surface of a stationary bubble formed on a section of a vertical capillary in a liquid volume.

The periodicity of the formation of bubbles is appropriate for acceptable mixing of the sample in the study area and the possibility of capturing high-quality images at the level of 0,5-5,0 bubbles per minute. Therefore, it is advisable to place the gas supply capillary horizontally with an oval-shaped opening on the lower side (Fig. 5).

Consider the speed of movement of bubbles that will be formed in the case of horizontal placement of a capillary with a cut end at an angle of 45° for supplying gas to the reactor. This position and shape of the capillary opening makes it easy to organize and hold a certain volume of gas in the form of a displaced bubble. At the same time, a

bubble in the form of a hemisphere attached to the section of the capillary is formed as a result of the balancing of the forces of surface tension, gas pressure in the capillary and pushing out by a denser liquid.

To understand, let's take a closer look at the peculiarities of gas movement and the processes that will take place in the reactor. We will assume that the flow of gas entering the water from a horizontally placed capillary consists of individual spherical bubbles. Let us dwell on the process of formation and movement of one such bubble.

The time of a complete bubble cycle τ consists of:

- time τ_1 - from the moment of nucleation to separation from the capillary;

- time τ_2 - waiting time during renewal of the conditions (pressure difference in the capillary and above the reactor) necessary for the initiation of a new bubble on the capillary.

Then the bubble separation frequency f will be calculated as $1/\tau$.

Let the capillary in the reactor have a diameter d_{cap} and be placed at a depth h from the surface of the reactor liquid. The dimensions of the bubble when it is separated from the capillary section will be determined by its diameter d_{sep} (conditionally - the diameter of the separation), moreover, $d_{cap} < d_{sep}$. Such a gas-filled bubble will have some volume V.

During the entire time τ_1, the bubble will be acted upon by the force of gravity $F_{grav.}$, the force of surface tension $F_{sur.ten.}$ and the repulsive force of Archimedes $F_{Arch.}$ (Fig. 5).

In the process of bubble growth, the first two forces will prevail over Archimedes' force, but will balance out over time

$$\overrightarrow{F_{grav}} + \overrightarrow{F_{sur.ten.}} - \overrightarrow{F_{Arch}} = \vec{0} \qquad \overrightarrow{mg} + \overrightarrow{\sigma \pi d_c} = \overrightarrow{\rho_w g V_{bub.}}, \quad (5\text{-}6)$$

where m - mass of gas in the bubble; g - free fall acceleration; σ - surface tension of water; ρ_w, ρ_g - density of water and natural gas; $\pi = 3{,}14$; V_{bub} - the volume of the bubble.

After mathematical transformations, the equation for determining the diameter of the bubble at the time of separation can be written in the form

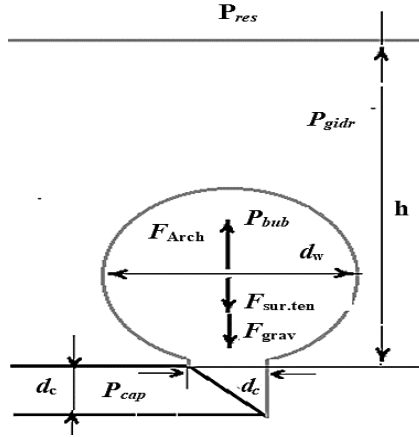$$d_w = \sqrt[3]{\frac{6 d_c \sigma}{g(\rho_w - \rho_g)}}$$

(7)

Fig. 5. Forces acting on the bubble

The gas density in the bubble is unknown, therefore, to determine ρ_g, consider the change in pressure in the «capillary - bubble» system. Gas pressure in a stationary bubble according to Bernoulli's law

$$P_{res} + P_{gidr} + P_{din} = P_{bub} = P_{cap} \qquad (8)$$

where P_{res} - pressure in the reservoir, MPa; $P_{gidr}=\rho_w g h$– hydrostatic pressure of the water column; $P_{din}=\rho_g w^2/2$ - dynamic pressure of the moving gas (for a stationary bubble $w=0$ m/s); P_{cap}– gas pressure in the capillary; $P_{bub=cap}$ - pressure in the bubble.

Based on the gas density ρ_g, we calculate the diameter of the separation of the gas bubble from the capillary d_w.

The speed of movement of the bubble when rising to the surface, taking into account the condition $\rho_w >> \rho_g$ [21] can be calculated by the equation

$$w = \sqrt{\frac{4 d_w g}{3C}} \qquad (9)$$

where C - coefficient of resistance of water in the reactor.

The C coefficient in the event that the conditions are met, namely for the Weber criterion $We>1$, the Reynolds number $Re>600$ and the Bond criterion $BO<13$, can be calculated by the Harmonti formula [17]

$$C = 0{,}568\sqrt{BO}, \qquad BO = \frac{g d_w^2 \left(\rho_w - \rho_g\right)}{\sigma} \qquad (10)$$

3. Experimental study

Even under such conditions, it is quite difficult to record the moment of «clouding» of the interphase surface as clearly and unambiguously as possible [22].

However, together with the process of clouding of the interphase surface, a gradual distortion of the reflections of light sources on it is observed. The beginning of their distortion was recorded much earlier than the visual signs of clouding of the mirror interfacial surface (bubbles in a liquid or drop in a gas atmosphere). The dynamics of this process is illustrated in fig. 2.

However, there are practically no other visual signs of the beginning of the hydrate formation process, except for the distortion of the reflection of light sources (Figs. 2*b* and 2*c*). This optical effect allows extremely sensitive (with high accuracy) to record the changes occurring at the micro level with the mirror interphase «gas-liquid» interface. It allows you to record the process of the beginning of the growth of critical nuclei and the transition to rapid mass crystallization.

Therefore, the moment of fixation of the optical effect of distortion of the reflection of the light source on the mirror of the «liquid-gas» interphase surface by microcrystals of gas hydrate can be used as the basis of the method of setting the parameters of the moment of mass crystallization of gas hydrates for complex reservoir systems under industrial production conditions.

4. Peculiarities of laboratory research

The simplest and most informative is the method of visual observations. This method is used in the study of gas hydrates. For example, in [23], the behavior of clathrate hydrates during crystal growth was studied using an optical cell under pressure. The method of quantitative measurement of film thickness using microscopy is described in [24]. Freer [25] used optical microscopy as a tool to determine the rate of growth of a methane hydrate film under the influence of temperature changes.

Therefore, in the process of research and verification of the methodology, the authors recorded and analyzed photo and video images of the processes of formation of gas hydrates in multicomponent gas mixtures (natural gas) when in contact with aqueous solutions. The research was carried out on the laboratory device shown in fig. 6.

Fig. 6. Laboratory installation: appearance and research process

In the course of research, the optimal level of image magnification was analyzed for maximum informativeness and technical implementation on laboratory equipment. The limitation concerns the magnification of the received image. During laboratory testing of the technique, it was established that increasing the image by more than 150-200 times will make it difficult to find the object under investigation behind the glass of the reactor viewing window, especially during bubbling, and to assess the overall picture of the process. Since the main investigated objects are mainly colorless and transparent, the illumination of the reactor contents by sources of different colors has become quite effective.

Thus, the proposed technique consists in setting the parameters of the moment of mass crystallization of gas hydrates based on the fixation of the optical effect of the distortion of the reflection of the light source on the mirror of the «liquid-gas» interphase surface.

5. The results of the experiment

Natural gas of the following composition was used for the analysis of the proposed express method, %: CH_4 - 87,17; C_2H_6 - 5,16; C_3H_8 - 2,48; i-C_4H_{10} - 0,67; n-C_4H_{10} - 0,90; i-C_5H_{12} - 0,12; n-C_5H_{12} - 0,17; C_6H_{14} - 0,17; C_7H_{16} - 0,28; CO_2 - 0,17; N_2 - 2,50; He- 0,21.

During preparatory operations, namely water preparation, it is necessary to saturate the water with hydrate-forming gas. Natural gases have the property of dissolving in liquid and thermobaric conditions have a significant effect. Water saturation in the reactor will be accompanied by a slight pressure drop. This was taken into account during experimental studies.

To evaluate the proposed express method of determining the beginning of mass crystallization of gas hydrates, it was necessary to perform a number of experiments.

The investigated parameters are the pressure in the reactor and the temperature at the moment of mass hydrate formation. According to the data obtained during the experiments, the curves of the beginning of mass hydrate formation for the indicated composition of natural gas were constructed (Fig. 7).
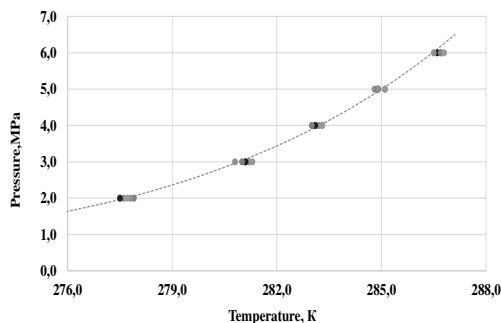
Fig. 7. Evaluation of the method of setting the parameters of the beginning of mass gas hydrate crystallization: – experimental data; ------ – is the equilibrium curve of hydrate formation, calculated according to the Barrer-Stewart equation

Conclusions

Therefore, the proposed technique consists in setting the parameters of the moment of mass crystallization (hydrate formation) based on the fixation of the optical effect of the distortion of the reflection of the light source on the mirror of the liquid-gas interphase surface.

The process of hydrate formation at the phase boundary is manifested by the formation of a thin layer of hydrate in the form of a film. Such a process is visually fixed by the transformation of the mirror surface of the phase boundary into a matte one. The effect of distortion of the interphase boundary is explained by the formation, growth, massive and chaotic accumulation, placement of hydrate microcrystals on this boundary. Simultaneously with the process of clouding of the interphase surface, a significant distortion of the reflection points of the light source occurs. The investigated optical effect allows to record with high accuracy the changes occurring at the micro level on the mirror interphase «gas – water» surface.

Thus, the proposed method consists in establishing the parameters of the moment of mass crystallization of gas hydrates based on the fixation of the optical effect of the distortion of the reflection of the

light source on the mirror of the «liquid – gas» interphase surface. It can be used to establish and control the moment of mass crystallization of gas hydrates in production at the facilities of the oil and gas industry, which will allow to manage the process of hydrate formation and prevent the appearance of ice jams in gas pipelines and equipment, by timely introduction of the necessary volumes of hydrate formation inhibitors.

The only limitation of the application of this technique will be the low light permeability of the aqueous solution as part of the formation system.

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