

Nazar Pedchenko

DEVELOPMENT OF METHODS OF OPERATIVE DETERMINATION OF PARAMETERS OF REPEATED HYDRATE FORMATION IN LAYER SYSTEMS OF GAS HYDRATE DEPOSITS

The object of research is the methods of laboratory setting of the parameters of hydrate formation of well production and the design features of the equipment for its implementation. Methane hydrate is becoming a promising topic for a new energy resource. At the same time, hydrostatic formation is one of the most problematic areas in ensuring the transport of well products, and this primarily concerns the production of gas hydrate deposits. An analysis of the thermobaric parameters of the well production of gas hydrate deposits shows that when they are moved by technological lines, they are close to hydrate equilibrium, but due to the intensity of the process, the system does not have time to reach it. In addition, reservoir system water has a memory of hydrate structures, or a certain amount of gas hydrate solid phase is also present in the flow water. In this regard, a set of laboratory studies was carried out to assess the nature of the behavior of this type of systems during the re-crystallization of gas hydrate and its dissociation. Based on the results of the research, a method for the operational laboratory setting of the parameters of repeated hydrate formation in reservoir systems of gas hydrate deposits was developed. It provides for setting the parameters of mass crystallization of gas hydrate by visual fixation of the moment of appearance of the solid phase at the interfacial contact «liquid – gas». The design features of the laboratory facility for its implementation have also been developed and substantiated. The technique makes it possible to reduce the duration of the study of one sample by almost an order of magnitude (from several days to 8–10 hours). In addition to the information on the equilibrium parameters of hydrostatic formation, provided by traditional methods of laboratory research, an additional characteristic of the behavior of reservoir systems in non-equilibrium conditions has been obtained, which will help to quickly assess the risks of technogenic hydrate formation. The developed technique is important for systems that, at least, have a memory of hydrate structures. However, the preliminary transfer of a part of the water of the test sample through the gas hydrate form allows estimating the parameters of hydrate formation of any reservoir system.

Keywords: gas hydrates, gas hydrate dissociation, recrystallization, online control technique, optical system.

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1. Introduction

The unique ability of gases and water under certain thermobaric conditions to form gas hydrates, on the one hand, led to the formation of colossal deposits of methane in its composition [1], and on the other hand, created a significant problem for the oil and gas industry. Therefore, gas hydrates have been and remain a complex problem, the solution of which requires great efforts and resources [2].

However, natural gas hydrate is considered one of the new clean energy resources with a high potential to replace coal, oil and traditional natural gas in the 21st century [3]. It is characterized by high energy density. 1 m³ of hydrate can contain 150–180 m³ of methane under standard conditions.

According to estimates given in [4], the amount of methane gas in the composition of gas hydrate deposits is 2.1·10¹⁶ m³, which exceeds all reserves of carbon fuel. At the same time, less than 2 % of gas hydrates are probably concentrated in permafrost regions, and the rest are in marine sediments [5].

Gas hydrates, or clathrate hydrates, are nonstoichiometric crystalline compounds formed at low temperatures and high pressures [6]. Under these conditions, as a result of hydrogen bonding, water molecules (host) form a three-dimensional structure, which can be occupied by molecules from gas or liquid phases (guests), such as methane, ethane, propane, butane, carbon dioxide, etc.

Reliable and efficient hydrate management strategies have become an urgent need for safe and reliable oil and

gas production. An important component of these strategies is the development of methods for detecting early signs of hydrate formation in order to give operators sufficient time to take appropriate action to prevent hydrate formation.

Since the determination of equilibrium data for a wide range of pressure, temperature and concentration is a laborious and costly task, a reliable model [7] or software can be used. However, when the system contains gaseous mixtures or an aqueous solution of organic inhibitors, some methods are not perfect. Moreover, modeling may not provide for metastable states that occur under certain thermodynamic conditions, which may be common in hydrate reservoirs [8]. Therefore, experimental studies are still needed to obtain reliable parameters of hydrate formation [9].

First of all, this concerns the technological process of developing deposits of marine gas hydrates. In this case, the thermobaric parameters of the well production flow are within or approaching the conditions of hydrate equilibrium. But due to the intensity of the process, when moving by technological lines, the system does not have time to approach the equilibrium state. In addition, the presence of a certain amount of the solid phase of the gas hydrate is possible or guaranteed in the stream. At the same time, almost all water in the system, which is in a condensed state, has a memory of hydrate structures [10, 11].

Therefore, it is relevant to develop a methodology for establishing the parameters of hydrate formation, which, on the one hand, takes into account the properties of reservoir systems of gas hydrate deposits, and on the other hand, makes it possible to significantly reduce the duration of the research cycle. *The object of the study* is the methods of laboratory setting of the parameters of hydrate formation of well production and the design features of the equipment for its implementation. *The aim of the study* is to develop and evaluate a method for the operational laboratory setting of the parameters of repeated hydrate formation in reservoir systems of gas hydrate deposits and to improve the design of the laboratory installation for its implementation.

2. Research methodology

When developing offshore deposits of gas hydrates, the methods of dispersion, thermal action, chemical action, and replacement of methane with carbon dioxide, as well as a combination of several options, are used [12–14]. However, it should be noted that these methods create significant problems in the field of well safety, production management, environmental risks and other aspects [15]. Existing problems include primarily secondary hydrostatic formation, low production efficiency and engineering-geological complications such as underwater landslides and wellbore instability [16].

In this case, there is a need for constant and operational monitoring of the parameters of hydrate formation of reservoir systems.

In addition, the specific conditions of the marine environment determine the complexity and significant cost of maintenance operations for technological equipment. Also, when developing offshore fields, more stringent environmental requirements are imposed. Therefore, the operational monitoring of the parameters of hydrate formation at all stages of the technological chain is especially important.

The commonly used methods for measuring the phase equilibrium of gas hydrates are the isochoric pressure search method [17] and the isothermal pressure search method,

which have proven to be promising and reliable [18]. In this case, the conditions for hydrate formation depend on various factors (induction time, cooling rate, and memory effect), have a high degree of dispersion compared to the dissociation conditions, and are a fixed thermodynamic property; therefore, the hydrate equilibrium is determined at the dissociation stage [19]. The intersection point of the heating and cooling lines or a sharp change in the curve is considered the equilibrium point (shown in red) [20].

However, one common disadvantage of classical methods is the significant duration of the process of determining three-phase equilibrium curves for each gas hydrate system under study (the study lasts up to several days). Thus, this does not allow for prompt and effective monitoring of technological parameters by traditional methods in case of their frequent change. In addition, classical methods provide for fixing the equilibrium parameters of hydrate formation at the moment the system reaches equilibrium. However, in this case, it is necessary to evaluate the behavior of the system during a short period of time of its movement along the production line. At the same time, this system is guaranteed to be in a non-equilibrium state and will not be able to achieve it if the parameters change during the time it is in the production line.

Based on the analysis of the parameters of technological processes for the development of gas hydrate deposits, the bulk of the water in the composition of the well production formed as a result of the dissociation of gas hydrate is heated to a temperature not higher than 18–20 °C. That is, to a temperature that is significantly lower than the temperature of destruction of water hydrate memory structures (25–30 °C [10, 11]). In addition, together with water, the clay fraction of the rock is removed from the mine. (However, as is known, any impurities in water can act as centers of gas hydrate crystallization).

Thus, the induction period during repeated hydrate formation in such a system will be absent or its duration will be insignificant. Consequently, in the course of experimental studies, there is no need for long exposures before fixing the parameters of hydrate formation.

As shown in [19], a mixture of water and gas hydrate under conditions close to equilibrium is easily pumped by a technological line and does not create problems in the production process. However, after or after changing the process parameters, the crystals become coarser by their growth and/or coagulation. Therefore, the research methodology should provide for the fixation of thermobaric parameters at the moment of the beginning of the enlargement of gas hydrate crystals. The most effective and accessible way to fix this process is, of course, visual. In addition, given that the system may already have a solid gas hydrate phase. Therefore, changes in pressure and temperature during the study cannot be reliable signs of the beginning of the process.

Thus, the fundamental approach to the implementation of the method of operational laboratory control of the development of gas hydrate deposits is the task of establishing the parameters of repeated hydrate formation in the reservoir system (well production) under non-equilibrium conditions for a short period of time (within minutes).

3. Research results and discussion

3.1. Substantiation of design features of the laboratory unit. Currently, a wide variety of phenomena and processes

can be investigated using microscopy combined with imaging and imaging technologies. It is advisable to use information about the nature of the transformation of images of the studied sample recorded by the optical system as the main source of information on the methodology for studying the process of re-crystallization of gas hydrate in reservoir systems of offshore gas hydrate deposits.

Since the process of hydrate formation occurs predominantly on the gas-liquid interface, this requires the creation of an interfacial contact. As experience shows, the simplest and most effective method of mixing is bubbling gas through a layer of liquid. The essence of the process is that gas bubbles are pushed to the surface by a denser liquid. At the same time, moving through a layer of liquid, they mix it. At the exit from the liquid, the bubble overcomes the forces of surface tension and causes a short-term perturbation. In addition, the process of growth of an individual bubble at the opening of the bubbling device is actually a mixing process on the scale of the liquid surrounding the bubble (because it involves a gradual increase in the area of interfacial contact). Consequently, the process of bubble nucleation, increase in its size, detachment after reaching the critical size, movement through the liquid layer and perturbation at the moment of breakthrough to its surface is actually mixing of the local liquid volume in the reactor.

In addition, the composition of the gas phase in the reactor during the formation or dissociation of the hydrate will change. The paper [21] shows a monotonic increase in the methane fraction and a decrease in the ethane and propane fractions during each operation. Therefore, an additional positive effect of gas bubbling during the experiment is that each new bubble is a portion of gas whose composition has not undergone preliminary changes as a result of selective dissolution or hydrate formation.

Since, due to microbubbling in the zone of the capillary system, the saturation of the liquid with gas will be the highest, so crystallization will begin in this zone. Moreover, the first gas hydrate crystals can form both on the bubble and on the surface of the liquid. Therefore, the microscope of the optical system for fixing the signs of secondary hydrate formation must be adjusted to the area, which includes gas bubbles and the place of their breakthrough to the liquid surface. Moreover, for the convenience of adjusting the microscope and the quality of the resulting image, the object should be located directly behind the glass of the observation window. At the same time, it is advisable to orient the microscope relative to the viewing window of the reactor and the reactor in space in such a way that the horizontal line of contact «liquid – gas» divides the plane of the window in half. (So, a cylindrical reactor with a transparent window at its end must be oriented in a position close to horizontal).

Structurally, slow bubbling of gas and the possibility of visual control over the processes on the surface of the bubbles and the place of their exit can be realized using a capillary immersed in a liquid. Moreover, place it at an angle of 20–30° to the horizontal with the hole down (Fig. 1). This position of the capillary makes it easy to form and, if necessary, hold a gas bubble. In this case, the bubble is formed due to the balancing of the forces of surface tension, the pressure of the liquid column and the pressure of the gas in the capillary as a result of its minimum supply through the fine-tuning valve.

According to the results of previous studies, the intensity of bubbling of bubbles for organizing effective mass transfer and the possibility of qualitatively fixing the moment of formation of gas hydrate crystals on the bubbles and the surface of the liquid lies in the range of 1.5–3 bubbles per minute.



Fig. 1. Capillary gas supply system in the reactor

According to the methodology proposed above, a laboratory setup has been developed to establish the parameters of repeated hydrate formation in reservoir systems of gas hydrate deposits (Figs. 2, 3).

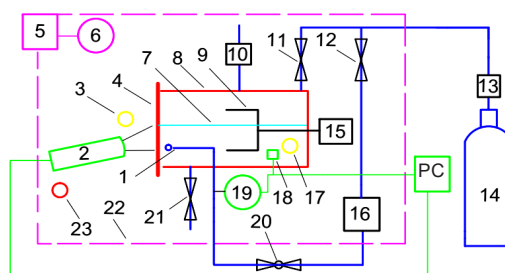


Fig. 2. Schematic diagram of a laboratory unit for setting the parameters of repeated hydrate formation in reservoir systems of gas hydrate deposits: 1 – capillary; 2 – microscope; 3 – external light source; 4 – observation window; 5 – refrigeration unit; 6 – thermostatic unit fan; 7 – liquid level in the reactor; 8 – reactor vessel; 9 – stirrer rotor; 10 – safety valve; 11, 12, 21 – valve; 13 – reducer; 14 – gas source; 15 – agitator drive; 16 – thermally insulated buffer tank; 17 – reactor lighting system; 18 – temperature sensor; 19 – pressure gauge (pressure sensor); 20 – valve for fine adjustment of gas supply; 22 – heat chamber; 23 – heating element; PC – computer

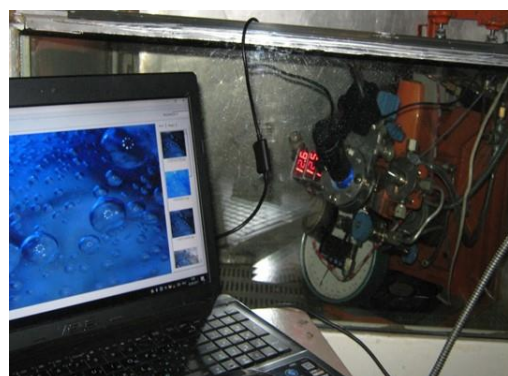


Fig. 3. Photo of the laboratory unit for setting the parameters of repeated hydrate formation

3.2. Previous experiments and method analysis. To develop the methodology and analyze the process of gas hydrate recrystallization in reservoir systems with a memory of hydrate

structures or containing part of the hydrate, a series of experimental studies was carried out. At the same time, the most favorable conditions for the start of its mass crystallization occur in the zone of bubble breakthrough to the liquid surface (Fig. 4, *a*), on the rims of the capillary opening (Fig. 4, *b*) and in the lower «pocket» of the capillary (Fig. 4, *c*). In the first case, the most active mixing occurs in this region, in the second and third cases, cyclic wetting of a certain surface of the capillary with a film of water, that is, the cyclic formation of a new surface of interfacial contact.

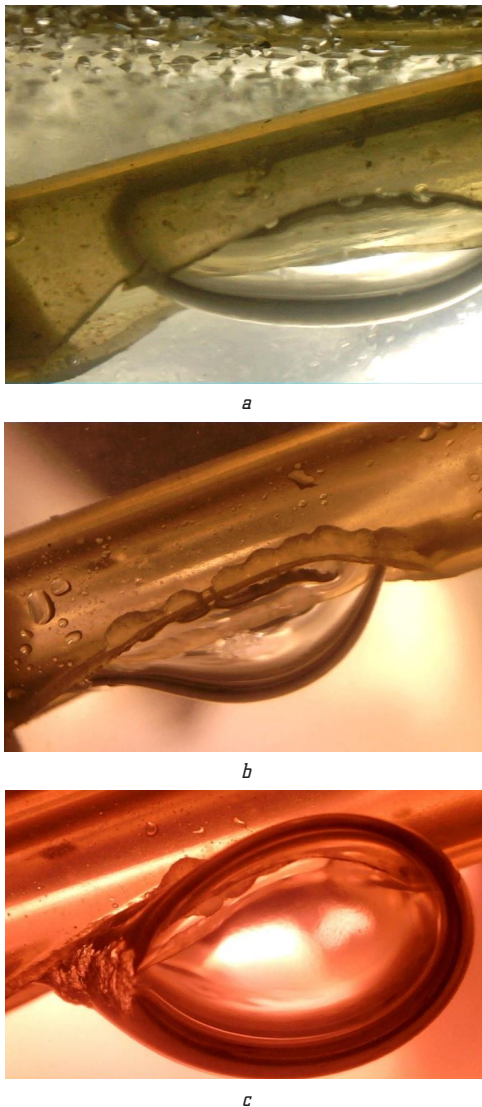


Fig. 4. Typical signs of the beginning of re-crystallization of gas hydrate: *a* – in the zone of bubble breakthrough to the liquid surface; *b* – on the crowns of the hole in the capillary; *c* – in the lower «pocket» of the capillary

Visually, the process of the beginning of mass crystallization is fixed by distorting the image (in comparison with the previous one) of the interfacial surface of a gas or liquid bubble in the reactor by the gas hydrate solid phase. Thus, according to the method of formation of a solid phase in the indicated places, it is identified as the beginning of mass crystallization of gas hydrate under given thermobaric conditions.

The method for experimental evaluation of the parameters of gas hydrate recrystallization in the reservoir

system model of a gas hydrate field after complete or partial dissociation involves the following operations:

1. At the preparation stage, a model of the well production of gas hydrate fields is created, which during the production process has undergone gas hydrate dissociation, but at least retained the memory of hydrate structures, or hydrate formation nuclei or part of the gas hydrate remained in its composition. This requires that at least 20 % of the water is included in the gas hydrate.

2. The gas hydrate dissociates, but under conditions that guarantee the preservation of the memory of hydrate structures, or part of it, or crystallization nuclei in water.

3. The prepared sample is subjected to gradual cooling. Gas is supplied at the same time. The feed rate assumes compensation for the pressure drop as a result of reactor cooling and only a slight increase by the end of the experiment (of the order of 0.2–0.5 MPa).

4. Gas is supplied through a capillary immersed in water. The supply of gas through the capillary makes it possible to maintain the composition of the gas in the study area, mix the volume of liquid adjacent to the capillary, and produce gas bubbles (objects for process control).

5. A marker of repeated hydrate formation is the formation of visually visible (with an increase in the range of 50–70 times) signs of the presence of solid phase crystals on the surface of the liquid in the reactor or gas bubbles. At the time of the appearance of obvious signs of repeated mass crystallization of gas hydrate, the corresponding thermobaric parameters are recorded.

As is known, the features of ethanol and methanol solutions are determined by their ability to shift the equilibrium parameters of hydrate formation. Therefore, in the case of the presence of these inhibitors in reservoir systems, the difference of the proposed method lies in the shift of the maximum mixture heating temperature in the process of dissociation to a lower one. However, the possibility of the simultaneous existence of ice crystals together with hydrate in this system under appropriate thermobaric conditions is not ruled out [22]. Therefore, at any inhibitor concentration in the solution, the maximum mixture heating temperature at the stage of gas hydrate dissociation should be above 0 °C. In addition, as shown by previous studies, these mixtures are characterized by a higher dispersion of the formed hydrate crystals and a lower tendency of microcrystals to coagulate. Therefore, with increasing concentration, the release of the hard phase somewhat slows down in the places determined by the method. This, in turn, somewhat complicates the possibility of fixing the hard phase and requires an increase in the number of experiments.

Fig. 5 shows the result of the operational setting of the parameters for the re-crystallization of the gas hydrate of the model of the reservoir system of typical composition according to the proposed method. As a result, objective information was obtained on the possible behavior of this system with an intensive change in parameters under non-equilibrium conditions. The given experimental data were obtained in less than 9 hours of the research cycle. The method showed insignificant, as for such a complex object, divergence of results (Fig. 5).

The developed technique is promising for systems that, at least, have a memory of hydrate structures. However, the preliminary transfer of a part of the water of the test sample through the gas hydrate form allows estimating the parameters of hydrate formation of any reservoir system. Therefore, under this condition, this technique can be used to quickly assess

the parameters of hydrate formation of any reservoir gas systems (including in gas hydrate form) and gas condensate fields (including those inhibited by thermodynamic reagents up to a concentration in methanol equivalent of 25–30 %). In addition, according to this method, it is possible to make a preliminary assessment of the effectiveness of inhibitors of hydrate formation of thermodynamic action at their concentration in the studied samples within similar limits.

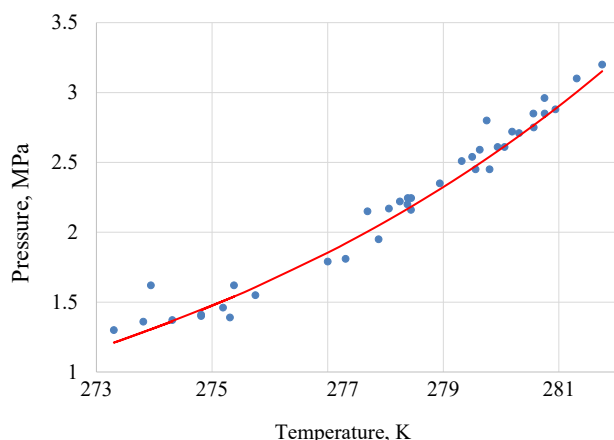


Fig. 5. An example of the result of setting the parameters of gas hydrate recrystallization of a reservoir system model of typical composition

Also, in the future, this technique is supposed to be adapted to study systems with a significant content of an inhibitor of hydrate formation (methanol, for example, more than 50 % vol.).

4. Conclusions

A technique has been developed for the operational laboratory setting of the parameters of repeated hydrate formation in reservoir systems of gas hydrate deposits (including in the presence of process inhibitors). The design features of the laboratory facility for its implementation have been developed and substantiated. The proposed method provides for setting the parameters of repeated hydrate formation by visual fixation of the moment of appearance of the solid phase at the liquid-gas interfacial contact in the reactor. The duration of the study of one sample is reduced by almost an order of magnitude (up to 8–10 hours).

Thus, in addition to information about the equilibrium parameters of hydrothermal formation, an additional characteristic of the behavior of reservoir systems of gas hydrate deposits in non-equilibrium conditions will help to quickly assess the risks of technogenic hydrate formation and effectively prevent it.

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Nazar Pedchenko, Postgraduate Student, Department of Oil and Gas Engineering and Technology, National University «Yuri Kondratyuk Poltava Polytechnic», Poltava, Ukraine, ORCID: <https://orcid.org/0000-0002-0018-4482>, e-mail: jashafenix@ukr.net