Gas hydrate suspensions formation and transportation research

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Abstract. An experimental unit for studying the formation of gas hydrate suspensions and their transport properties is considered. The scheme of installation and the basic processes, which can be studied, are described. The results of studies of gas hydrates and a gas hydrate suspension formation in an adiabatic process in a stream of seawater are given. The adiabatic method of obtaining gas hydrates and forming gas hydrate suspensions is offered to use. Directions for further research are outlined.

1. Introduction

One of the main research areas of the Oil and Gas Engineering and Petrochemistry Department of the Engineering School of Far Eastern Federal University in the last three years is the study of the gas hydrates, gas hydrate suspensions formation processes and the possibility of their transportation.

The use of gas hydrates for the purpose of utilization of associated petroleum gases is a promising area. Earlier, the theoretical possibility of using this technology in oil fields for utilization of associated petroleum gases under certain gas factors was shown (V.D. Lapshin, A.N. Gulkov et al., 2015). Furthermore, a method of delivering natural gas to consumers in the form of a gas hydrate suspension was offered and patented (A.N.Gulkov. Patent RU MKI7S 07 C 5/02, Patent RU MKI7S 07 C 5/02, Patent RU MKI7 F17D1/02) [5, 6].

One of the starting points for the studies of transportation of gas hydrate suspensions is work on the Cold Flow technology of Norwegian colleagues from the Norwegian University of Science and Technology (NTNU) (E.Bokin et al., 2010). Also, in the early elaboration of the theoretical part of the guesses, materials on the kinetics of hydrate formation (D.Sloan, C.Koh et al., 2011) and studies of the factors affecting the clathrate structures fill rate were considered (R.Sun, Z. Duan, 2005).

It is proved that in order to successfully implement the method offered, it is necessary to investigate the main factors affecting the formation of gas hydrates, gas hydrate suspension and its stability in pipeline transport. To study these processes, an experimental unit was created consisting of a refrigerating machine, an evaporator reactor, a circulating loop, a gas measuring and feeding system, and an automation system supporting specified parameters [2, 3, 4, 7].
2. Materials and methods
In the Laboratory of Gas Hydrates, the experimental unit UOTG 1416.05-01 was created and put into operation (Figure 1). The unit allows studying the processes of formation, dissociation and transportation of gas hydrate suspension and changes in the rheological characteristics of the fluids.

The unit consists of a refrigerating machine, a reactor-generator of a refrigerated machine of a flooded type, a circulating hydraulic circuit, a system for measuring and feeding the gas of the hydrating agent, an automation system supporting the set parameters, and a system for recording the measured parameters.

Figure 1. Experimental unit UOTG 1416.05-01 for the study of formation and transportation of gas hydrate suspensions

A schematic diagram of the hydraulic circulation circuit of the unit used is shown in Fig. 2.

Figure 2. A schematic diagram of the laboratory scientific research unit UOTG 1416.05-01.
1 Homogenizer, 2 Reactor-generator (evaporator of the refrigerating machine of the flooded type), 3 Circulation pump, 4 Cylinder with hydrate-forming agent, 5 Measuring cylinder with hydrating agent, 6 - Inspection column, 7 Coil, 8 Pressure gauges, 9 Thermometers, 10 Isolation valves, 11 Atmospheric valve, 12 Safety valve, 13 Watt meter, 14 Thermometer, 15 Feeding tank with saltwater.
The hydraulic circuit is equipped with circulation pump 3, which allows moving both gas-saturated solutions and gas hydrate suspensions. In reactor-evaporator 2, the gas hydrate phase is formed due to the removal of the heat of hydrate formation by the refrigerating machine. Then the gas hydrate suspension is finally formed in the vessel of homogenizer 1. After that, isolation valve 10 is switched to the pumping mode through coil 7 simulating the field pipeline to investigate the transport properties of the resulting suspensions.

When setting up the installation systems, cyclic tests of the hydraulic circuit and the chiller were carried out. According to the test results, dependencies of the system chilling time on the flow rate in the hydraulic circuit were obtained (Fig. 3).

The unit under consideration makes it possible to carry out investigations in the pressure range from 0.1 to 5.0 MPa and temperatures from -10 to 25 °C. The initial plan provides the implementation of two fundamentally different methods for obtaining a gas hydrate suspension.

The first method: obtaining a suspension at the apparent interface between the liquid and gas phases, by gradually chilling the pumped medium and sharply raising the pressure in the pipeline to transfer the entire system to the coordinates of the imaging point of system condition $H_2O - CO_2$.

The second method: obtaining a suspension from the saturated solution of the hydrating agent by cooling it at a pressure sufficient to transfer the whole system to the coordinates of the imaging point of system condition $H_2O - CO_2$.

When obtaining a gas hydrate suspension, it is necessary to take into account the possibility of forming large aggregates of crystalline structures on the heat exchange surfaces and bends of pipelines. To prevent the hydrate crystals from adhesion, a homogenizer is provided in the preparation of the suspension by the first method, mechanically destroying the hydrate aggregates. In the second method, adhesion of hydrate crystals is prevented by grinding them in a reactor having a flat scraper that removes growing crystals from a cylindrical heat exchange surface. The experiments carried out showed the possibility of obtaining gas hydrate suspensions under certain system parameters [9, 10, 11].

3. Results and Discussion
Using the unit, studies of the gas-hydrate phase $CO_2$ adiabatic formation processes in high-mineralized water and in normally mineralized water (tap water) due to changes in pressure and temperature in the
system were held. As water of high mineralization, the seawater of the Peter the Great Bay and the Sea of Japan was used.

In the first experiment, the mineralized water circulating in the circuit was saturated with carbon dioxide and cooled by a refrigeration machine in a reactor-generator. Then, the pressure in the circulation system increased due to the supply of carbon dioxide, resulting in the formation of a gas hydrate in the form of a finely dispersed suspension that could be observed in the inspection windows (Fig. 4).

![Figure 4. A suspension based on carbon dioxide gas hydrate obtained in a reactor of a laboratory unit](image)

Let us consider the processes occurring on the P-T diagrams. At initial Point 2 (P = 2 MPa, t = +12 °C, P-T diagram, Figure 5), the water was saturated with carbon dioxide to a state of complete saturation (3.3 g CO₂/l 100 g  crab H₂O) (E. Perkins, 2003) and then cooled to a temperature of +4 °C (Point 2'). At Point 2, temperature reduction ceased despite the fact that the refrigeration unit continued to operate in the same mode with hydrate particles appearing in the sight glass installed in the plant's high-pressure circuit.

It should be noted that the termination of the decrease in the temperature of the H₂O → CO₂ system on the hydration line (Point 2') under the operating refrigeration system is explained by the fact that the formation of all gas hydrates, and CO₂ hydrate in particular, is accompanied by a powerful thermal effect. The formation of hydrate CO₂ at a pressure of 1 MPa is accompanied by the release of 430-450 kJ/kg of thermal energy (E.D. Sloan, C. Koh, 2008). Of special note is the fact that hydrate formation at Point 2' (Fig. 5) occurs inside the heat exchanger, from which the heat of hydration was removed by the refrigeration machine due to the boiling of coolant R22 [8].

As a result of gas hydrate phase formation, hydraulic resistance of circulation loop system H₂O → CO₂ in the annular gap of the reactor dramatically increased. It led to an increase in the electric power consumption on the circulation pump drive and the rotor of the reactor, which was recorded by means of wattmeter having a channel for outputting information to the computer. In general, such change in the rheological characteristics of a saturated hydrating solution converted to a gas hydrate suspension is expected and described in previous studies (V.D. Lapshin, A.N. Gulkov et al, 2015).

The second experiment, conducted as part of the adiabatic formation of the gas hydrate phase, was carried out at a pressure of 1 MPa (Process 1-6, Fig. 5). The water saturated with carbon dioxide was pumped by the circulation pump through the reactor-evaporator, as was mentioned above, under a pressure of 1 MPa.
Thus, through the operation of the refrigeration machine, the temperature of the homogeneous system $H_2O - CO_2$ was reduced from $12\,^\circ C$ to $2\,^\circ C$, with significantly less energy consumption than in the previously described case, when a suspension with a continuously increasing fraction of the dispersed phase was formed in the circulation loop.

After reaching a temperature of $2\,^\circ C$, the pressure of circulating water, saturated with carbon dioxide, in the hydraulic circuit increased sharply to $2\, MPa$ (Point 2'', Fig. 5), which led to the instant formation of the gas hydrate phase in the entire circuit simultaneously (Fig. 6).

Further, the experiments were carried out on isobars 3, 4 and 5 MPa, which led to an increase in the content of the gas hydrate phase in the circulating hydraulic circuit with the increase of pressure in it. In this case, each time the imaging point of system state $H_2O - CO_2$ returned to the equilibrium line (at Points 3', 4', 5'). It is characteristic that an increase in the content of the gas hydrate phase was observed with increasing pressure only up to a value corresponding to the coordinates of quadrupole point $Q_2$. It should be noted that above quadrupole point $Q_2$, carbon dioxide passes from the vapor state to the liquid...
state, which changes the character of the thermobaric conditions of hydrate formation on its basis (E.D. Sloan, C. Koh, 2008) [1].

4. Conclusions

The conducted experiments testify to the operability of the unit offered. The possibility of realizing two fundamentally different methods of gas hydrate suspensions' formation has been confirmed.

Studies confirm the validity of the assumption that there is no need for mechanical destruction of large hydrate crystals to prevent the formation of hydrate plugs in pipelines at certain phase and environment ratios in the dispersed system. The validity of the assumptions about the transport properties of gas hydrate suspensions has been experimentally demonstrated.

Further studies will be focused on studying the influence of various factors on the stable gas hydrate suspensions' formation and their transport properties.

References

[1] Sloan D, Koh C, Amadeu K Sum, Adam L Ballard, Creek J, Eaton M, Lachance J, McMullen, Palermo T, Shoup G, Talley L 2011 Natural Gas Hydrates In Flow Assurance (Elsevier) ISBN 978-1-85617-945-4

[2] Dandy Sloan E, Koh C 2008 Clathrate hydrates of natural gases. – 3rd ed. (CRC Press)

[3] Bokin E, Febrantini F, Khabibullin E 2010 Carlos Eduardo Sanches Perez. Flow Assurance And Sour Gas In Natural Gas Production (Thronheim)

[4] Ernie Perkins 2003 Fundamental Geochemical Processes Between CO2, Water and Minerals. (Edmonton, Alberta)

[5] Gulkov A N, Lapshin V D 2007 Device for preparation of natural gas for transportation. Patent MK17S 07 C 5/02

[6] Gulkov A N, Lapshin V D 2002 Device for transportation of natural gas. Patent MK17 F17D1/02

[7] Sun R, Duan Z 2005 Prediction of CH4 and CO2 hydrate phase equilibrium and cage occupancy from ab initio intermolecular potentials (Elsevier)

[8] Lapshin V D, Gulkov A N, Morozov A A, Nikitina A V 2015 Utilization Of Associated Petroleum Gas And Transport It As A Hydrate Dispersed System, Proceedings of the Scientific Conference Modern Technologies and the Development of Polytechnic Education (WIT Press)

[9] Podorozhnikov S, Shabarov A, Shirshova A, Berdyhev A 2016 Method for Diagnosing Formation of Gas Hydrates in Gas Pipelines MATEC Web of Conferences 73 DOI: 10.1051/matecconf/20167302025

[10] Kurushina V, Kurushina E, Shabarov A 2016 Technology Audit: Assessment of Innovative Portfolio MATEC Web of Conferences 73 DOI: 10.1051/matecconf/20167307028

[11] Nelyubov D, Shabarov A, Podorozhnikov S 2016 Complex-action reagent for oil-infield and oil-trunk pipelines Solid State Phenomena 871 185 DOI: 10.4028/www.scientific.net/MSF.871.185