

Experimental study of the igbing properties of hydratic formation of sodium salt solutions

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Abstract. The paper presents some experimental studies of the process of the formation of methane gas hydrate in a cell containing in the initial state of methane and a solution of table salt. On the obtained dependencies of temperature and pressure in the cell, areas that correspond to the process of gas hydrate formation are allocated from time to time. Experimentally investigated the dependence of the start of hydratic formation on salt concentration. It is shown that with an increase in the concentration of salt in the solution, the start of hydratic formation increases according to the linear law.

1 Introduction

Gas hydrates are solid crystalline compounds of water and gas, the formation of which occurs with certain thermobaric parameters [1-5]. At the same time, gas hydraulic deposits contain quite large (about 10^{16} m³) gas volumes, mainly methane, the development of which will solve energy problems for several decades ahead [6]. Currently, experimental studies of processes associated with hydrate formation in saline solutions are relevant. This is due to the prospects for the development of gas condensate deposits of Eastern Siberia, which are characterized by high mineralization of reservoir and residual water. The mineralization of water in the manifold, as you know, leads to a change in thermobaric conditions in the intake zone of the layer, wells and fishing systems of gas. One of the first works, which experimentally examines the diffusion mechanism of hydrate formation in the reactor with a stirrer containing NaCl and KCl solutions [7]. In [8], a description of the kinetic curves of methane hydrate formation in distilled water and water containing inhibitors (salts concentration – up to 5 % mass). In accordance with the traditional ideas of formal kinetics, a process of passing the process was proposed, including the stages of gas dissolution, the formation of a metastabil hydrate cluster and the growth of a gas hydrate particle. The potential reversibility of each stage of the process was taken into account, and a general kinetic equation was proposed. The pressure of the gazahydratic former during the process was not maintained. The absorption rate of methane was calculated by the drop in pressure in the experimental cell. The effect of NaCl content on the strength of the kinetic inhibitor in the formation and decomposition of natural gas hydrates was investigated in [5]. The study was carried out using a linear change in temperature and isothermal method in swinging cells.

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It was established that inhibitors significantly reduce the temperature of the embryo formation of hydrates, and the presence of NaCl further enhances the inhibit force. The experimentally measured phase equilibrium of methane hydrate and the characteristics of inhibiting inhibitory liquids in the sea water of the Qatar is given in [10]. It is shown that a noticeable thermodynamic and kinetic effect of inhibiting hydrates is realized in the system of ionic liquids with sea water, while in the systems of ultra -low water it is absent. The presented work provides experimental studies of the formation of methane gas hydrate in a NaCl solution.

To study the kinetics of the formation of gas hydrates, the installation of RockingCellSystem RC5 (manufacturer PSL SystemTechnikgmbh, Germany, 2018) was used. It consists of 5 stainless steel cells (AISI 316L), which are attached to the frame that rocks the cells. The accuracy of temperature sensors is $\pm 0.01^\circ \text{K}$, and pressure sensors – 0.1%. Temperature and time pressure values were recorded during the experiment using specialized software. The hydrate chamber (reactor) is designed to study the synthesis and decomposition of gas hydrates at a pressure of up to 15 MPa in a wide temperature range. The coolant of the coolant in the camera shirt is carried out according to the standard refrigeration cycle "Evapacity - Capacitor". Process management in a hydrate chamber is carried out by a controller system and a specialized computer program. A methane was used as a gas, molar for which the mixture was 98.5%, Distilled water or sodium chloride of various concentrations was used as a liquid phase.

2 Formulation of the problem and basic equations

100 ml of distilled water (or a solution of electrolyte of a given concentration) is introduced into the hydrate chamber (cell), then the camera is placed in a cooling fluid, after which the gas is pumped to a certain pressure value. After the temperature and pressure values are stabilized, the software is launched for the development of the entire experimental protocol. Next, there was a cooling of the cell in a cooling fluid. At the same time, the camera was continuously swinging. For intensive mixing, a metal ball was placed in the working chamber, which, when swinging, could freely move along the entire length of the chamber.

The dependence of the temperature and pressure on the time in the cell containing a solution of sodium chloride (NaCl) with a concentration of 14 g/l and gas-methane are represented in Figure 1. The initial values of temperature and pressure are respectively equal to 22.4 °C and 56.4 bar. Vertical bar lines share the areas of pressure change. The gas temperature to the moment of 0.7 hours is reduced at a speed of 5 °C/h from the initial value of 22.4 °C to 10 °C. In the future, the temperature reduction rate is slightly reduced and until the moment of 7.1 hours is 2°C/h. A change in pressure in zones I and II obeys the law of temperature changes, in zone I the pressure decreases from 56.4 bar to 53 bar, a further decrease in temperature leads to a decrease in pressure to 52 bar. (Zone II). At the moment 5.5 hours at a temperature of 5.4 °C, the process of hydrate formation begins, this can be seen by the characteristic fracture for the dependence of the pressure on time (zone III), due to the transition of part of the gas to the hydrate and further cooling of the cell, the value of the pressure is reduced from 52 to 44 bar. Starting with 7 hours, a smooth increase in temperature occurs at a speed of 2°C/h this leads to dissociation of a previously formed hydrate and from the moment of 8.2 h the pressure in the cell begins to increase (zone IV). The dissociation of the hydrate stops at the time of 11 hours, in the future, the pressure in the cell rises due to an increase in temperature.

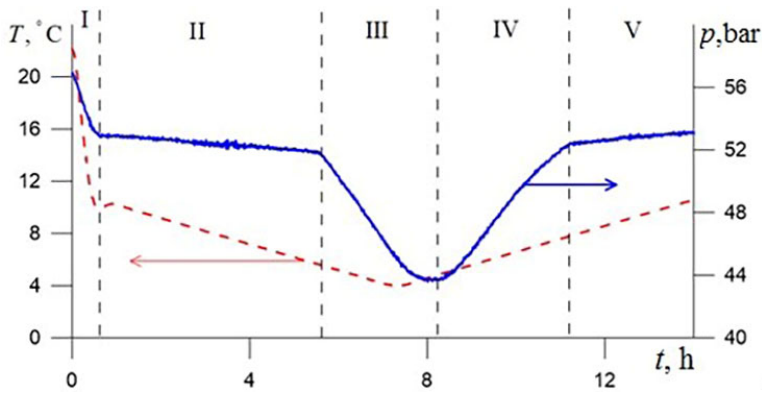


Fig. 1. The dependence of the temperature and pressure of the gas in the cell on time. The bar line corresponds to a temperature of °C, a continuous line - by pressure in a bar. Roman numerals indicate areas of pressure change.

The dependence of the pressure in a cell with a solution of sodium chloride with a concentration of 14 g/l (line 1) and with distilled water (line 2) is shown in Figure 2. It can be seen that the dependence of the temperature change in the cell from time to time has the same pattern as in Figure 1. The choice of sodium chloride as a liquid leads to a later time of the beginning of hydratic formation, for example, from Figure 3 It follows that the start time of hydratic formation for a salt solution is approximately 5.7 hours, and for distilled water, this time is 4.9 hours. The minimum value of the pressure, when the hydrate formation process for a solution of salt is stopped, is about 40 bar, and for distilled about 44 bar.

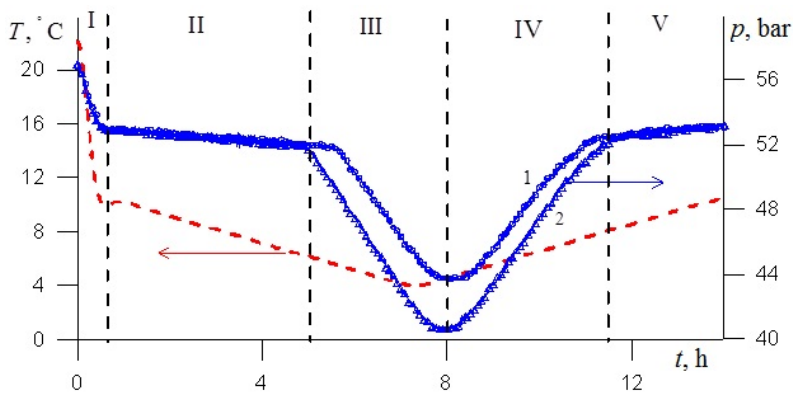


Fig. 2. The same as in Figure 1. Lines 1 and 2 correspond to a NaCl solution in water with a concentration of 14 g/l and distilled water.

The dependence of the start time of hydratic formation on the concentration of salt is shown in Figure 3. From Figure 3, it follows that with an increase in the concentration of salt in the solution, the start time of hydratic formation increases according to linear law. For example, with a concentration of a solution of sodium salt of 14 g/l, the beginning of hydratic formation is 4.5 hours, and with a concentration of 70 g/l - 5.8 hours.

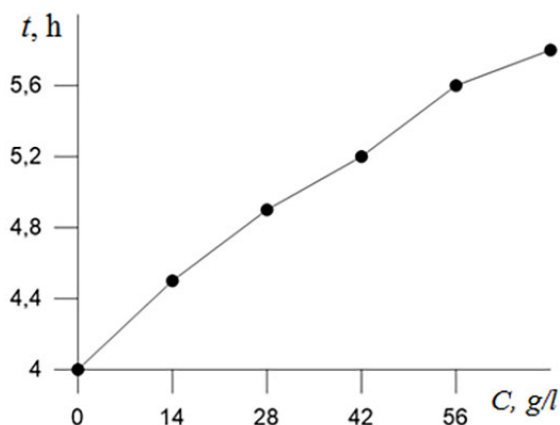


Fig. 3. The dependence of the start time of hydratic formation on the concentration of a solution of table salt.

3 Conclusion

Experimental studies of the process of formation of methane gas hydrate in a cell containing in the initial state of methane and a solution of table salt. On the obtained dependencies of temperature and pressure in the cell, areas that correspond to the process of gas hydrate formation are allocated from time to time. It is shown that the process of hydrate formation begins with a significant decrease in temperature, which leads to a decrease in pressure. Experimentally investigated the dependence of the start of hydratic formation on salt concentration. It is shown that with an increase in the concentration of salt in the solution, the start time of hydratic formation increases according to linear law.

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