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Self-preservation Effect of Gas Hydrates

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Abstract: This work was performed to improve the storage and transportation technology of gas hydrates in nonequilibrium conditions. At atmospheric pressure and positive ambient temperature, they gradually dissociate into gas and water. Simulation of the gas hydrate dissociation will determine optimal conditions for their transportation and storage, as well as minimize gas loss. Thermodynamic parameters of adiabatic processes of forced preservation of pre-cooled gas hydrate blocks with ice layer were determined theoretically and experimentally. Physical and mathematical models of these processes were proposed. The scientific novelty is in establishing quantitative characteristics that describe the gas hydrates thermophysical parameters thermophysical characteristics influence on the heat transfer processes intensity on the interphase surface under conditions of gas hydrates dissociation. Based on the results of experimental studies, approximation dependences for determining the temperature in the depths of a dissociating gas hydrate array have been obtained. Gas hydrates dissociation mathematical model is presented.

Keywords: gas hydrates, self-preservation effect, experimental studies, mathematical modeling, dissociation

1. Introduction

It has now been established that the amount of natural, technically recoverable, gas-gas hydrate is ~ 3×10^{14} m^3 (Pavlenko 2020). Different, sometimes contradictory, data on gas hydrate content in the natural environment are specified in literary sources, but it is obvious that natural gas hydrate is a huge energy resource with global distribution in permafrost regions and oceans; its vast volume requires to be estimated as a potential energy source.

In addition to hydrate production technologies, one of the promising areas for the development of gas hydrate technologies is the transportation and storage of gases in the form of gas hydrates. (Boswell & Collett 2011, Zhao et al. 2015). The self-preservation ability at temperatures below 0 degrees Celsius is important for their storage and transportation (Brown et al. 2010, Chong et al. 2016). That is, if the pressure is decreased over the formed hydrate, it dissociates and forms a thin film of ice on its surface, preventing it from further dissociation. Considering the high gas capacity of the hydrate (up to 164 m^3 of gas per 1 m^3 of hydrate), it is possible to store and transport gas under atmospheric pressure in the form of solid pellets.

A characteristic feature of crystalline hydrates is that their formation temperature is much higher than water freezing point. However, as temperature rises to form a gas hydrate, it is necessary to increase the pressure.

Fig. 1 shows a methane-water system P-T phase diagram with stability areas of methane hydrates. As can be seen in Fig. 1a, the hydrate, formed at low pressure values, is stable if thermobaric conditions are located at the bottom right of the three-phase monovariant equilibrium line. Thus, under appropriate conditions, corresponding to the stability area, the hydrate will be formed sooner or later (with sufficient amount of gas and water). At very high pressures, since compression of fluid phases is higher than the solid hydrate, there comes a time when the hydrate phase volume and the phase of dissociation products are equalized and, therefore, hydrate dissociation curve (h_j) passes through a maximum (47.7°C at $5 \cdot 10^5$ kPa, Fig. 1b). Upon reaching point Q_h, a break in the hydrate dissociation curve is observed, resulting from formation of a new hydrate h_x, its composition and structure have not been studied yet. But since it is almost impossible to imagine any other than van der Waals interactions between methane and water, it can be assumed that this compound also has a clathrate origin.

Adding a gas molecule to the clathrate water lattice results in an increase in the packing coefficient compared to ice Ih ($k = 0.43$) to 0.47-0.52 for KS-II hydrates (with a stoichiometric composition 1: 17), for KS-I hydrates up to 0.53-0.58 and hydrates with completely filled voids up to 0.59-0.60. Hydrate properties under pressure varies from dissociation to different degrees of stabilization. The guest molecule complementarity and structural void is still not enough to form a denser structure with a factor close to 0.74. Therefore, at high pressures, the clathrate structure density becomes less than the gas phase density, resulting in the maxima in hydrate dissociation curves (just like in the case of methane hydrate, Fig. 1b).

It is worth mentioning the following feature: even under required thermodynamic conditions, the reaction of hydrate formation takes a while. Dissociation of hydrocarbon hydrates is usually an easier process than their formation; under metastable equilibrium conditions they can be stored for a long time as a result of their self-preservation effect (Kipyoung et al. 2014, Ke et al. 2019). It consists in the fact that, in the process of dissociation, gas hydrates are covered with ice crust, preventing their further dissociation.

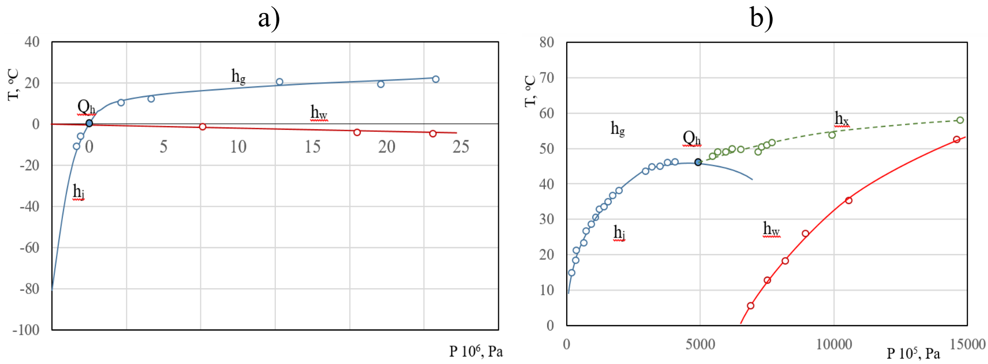

Fig. 1. P, T-phase diagram of a methane-water system; a – within the range from 0 to 250 · 10^5 Pa; b – within the range from 0 to 15 · 10^5 kPa

This property of hydrates allows significant volumes of gas to be transported and stored for a long time in gas hydrate stores (Archer 2007). Therefore, the metastable state of gas hydrate can be maintained due to its self-preservation effect (Vysniauskas & Bishnoi 1983). These issues were studied by (Koshlak & Pavlenko 2019, Pavlenko 2020, Pavlenko & Koshlak 2019, Pavlenko et al. 2014, Pavlenko et al. 2014a). However, thermodynamic parameters of forced preservation of gas hydrate with an ice layer are understudied.

Already in the 1990s, companies in Japan, Norway, England and others began to develop industrial technologies for production, preservation, storage, transportation and use of natural gas hydrates or NGH (Kim et al. 2015). Gas hydrate transportation under nonequilibrium conditions (with atmospheric pressure and temperature not less than 258 K) seems to be the most advantageous. It is based on production of gas hydrate structures, which under these conditions will be highest resistant to dissociation.

In (Veluswamy et al. 2017), a method for gas hydrate production in the form of granules covered with ice crust was proposed. However, given the considerable total surface area of granules, it will result in a significant increase in the ballast water (ice) in a hydrate.

Hence, thermodynamic and technological parameters of phase transitions during forced preservation of gas hydrate with an ice layer shall be determined.

2. Research results

Previous experiments have shown that forced self-preservation of hydrate blocks shall be performed at appropriate pressure and temperature at the boundary of thermodynamic saturation. In Fig. 2 curve 2 limits the area of P-T parameters of natural gas hydrate self-preservation (CH_4 – 92.8%; C_2H_6 – 5.1%; C_3H_8

– 2.1%). According to Fig. 2, the process shall be performed at a pressure higher than equilibrium values of hydrate formation.

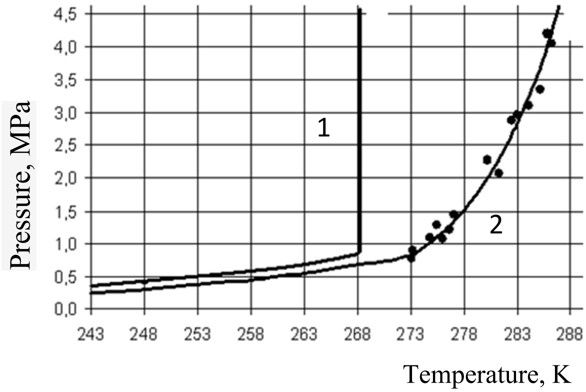

Fig. 2. Conditions of gas hydrate self-preservation: 1 is a gas hydrate equilibrium curve (CH_4 – 92.8%, C_2H_6 – 5.1%, C_3H_8 – 2.1%); 2 is a curve that limits the area of gas hydrate P-T surface parameters for self-preservation

For instance, for the average composition of natural gas, a pressure of not less than 0.85 MPa shall be maintained. However, water crystallization at this temperature will be too slow. Therefore, the initial temperature of a gas hydrate sample shall be lower. In our opinion, the optimal temperature shall be 258K. In this case, the gas hydrate dissociation, according to the equilibrium curve, will be prevented at 0.7 MPa. Therefore, the preservation process can be performed at a pressure higher than the equilibrium for the hydrate of this composition for the appropriate temperature.

However, this process under pressure will significantly complicate the technology.

Depending on heat transfer conditions on the hydrate surface, three main processes are distinguished. We present them in the order of intensification of heat supply to the surface: Self-preservation, ice crust melting and intensive hydrate dissociation. At self-preservation heat supply to the GH surface is relatively small. The gas hydrate surface temperature is one-two degrees below 0°C, and the ice crust does not melt.

To calculate hydrate storage, the dissociation process can be considered long enough to establish a stationary temperature distribution in the hydrate block. But the temperature range for hydrate self-preservation as the first process implementation, shall be determined to prevent its dissociation.

Let us consider a cylindrical gas hydrate block with height *h* and diameter *d*, cooled to a temperature below 273K.

Since a gas hydrate block has a negative temperature, water crystallizes on the block surface during time t_{kr}. The phase transition heat can be considered an internal source of energy of the wetted layer. Under adiabatic conditions, the released heat is dissipated into the middle of a sample to a colder dry gas hydrate. A physical model of the water crystallization process in the pores of the wetted surface layer a gas hydrate is schematically shown in Fig. 3.

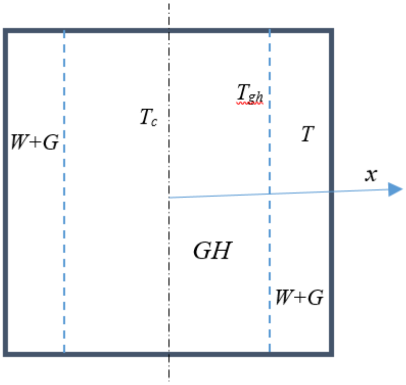

Fig. 3. Gas hydrate self-preservation: GH is gas hydrate; W + G – water and gas hydrate; T_c, T_{gh} is initial temperature of wet and dry gas hydrate, respectively; T_c is temperature in the sample center

For a one-dimensional temperature field, heat propagates in the direction of *OX* axis (Fig. 3). Thermal coefficients are assumed to be independent of coordinates and time.

In dry and wetted gas hydrate zones we will allocate elementary volumes of *dxdydz*. The difference between heat flows is the amount of energy, accumulated by the gas hydrate in this volume:

$$q_x dydz - q_{x+dx} dydz = c_{gg}\rho_{gg}\frac{\partial T_{gg}}{\partial \tau}dxdydz \tag{1}$$

The change in dry gas hydrate temperature over time in cylindrical coordinates is determined by the following equation:

$$\frac{\partial T_{gg}}{\partial \tau} = a_{gg}\left(\frac{\partial^2 T_{gg}}{\partial x^2} + \frac{1}{x}\frac{\partial T_{gg}}{\partial x}\right);\ \tau > 0, 0 < x < R;$$

where T_{gg} is dry gas hydrate temperature, K; a_{gg} is temperature conductivity coefficient of dry gas hydrate, m^2/s; R is a sample radius, m.

Let us consider characteristics of wetted gas hydrate heat transfer. The amount of heat, entering the elementary volume through a right face of *dydz* area per unit time will be $q_x dydz$, and the amount of heat, leaving it through the opposite face will be $q_{x+dx}dydz$. Water crystallization in gas hydrate is accompanied by heat release in an elementary volume:

$$\frac{dw}{d\tau}dxdydz = \rho L\frac{mdV}{Vd\tau}dxdydz.$$

The difference between heat flows of the wetted gas hydrate is the amount of energy, accumulated by the gas hydrate in this volume:

$$q_x dydz = \rho L\frac{mdV}{Vd\tau}dxdydz - q_{x+dx}dydz = c\rho\frac{\partial T}{\partial\tau}dxdydz$$

The equation, describing the change in temperature of the gas hydrate wetted layer during cementation, in cylindrical coordinates has the following form:
$c_k\rho_k\frac{\partial T_k}{\partial\tau} = \lambda\left(\frac{\partial^2 T_k}{\partial x^2} + \frac{1}{x}\frac{\partial T_k}{\partial x}\right) + \rho_w L\frac{dV_w}{V_k d\tau}; V_w = V_k m; A \geq V_w \geq 0; R < x < R + 1;\ \tau > 0;$
where: T_k is the wetted gas hydrate temperature, K; V_w, V_k are volumes of applied water and wetted layer, respectively, m^3; c_k - specific heat of water-wetted gas hydrate, J/(kg·K); ρ_k, ρ_w is density of wetted layer and ice, respectively, kg/m^3;
λ_k is thermal conductivity of the wetted layer, W/(m·K); L is specific heat of water crystallization, J; m is gas hydrate porosity; V is the amount of applied water per sample, m^3.
Initial conditions: $T_k(x,0) = T_0, R < x < R+1, T_{gg}(x,0) = T_1, 0 < x < R.$

Let us set thermal symmetry conditions in the center of a gas hydrate block, and a process of sample heat exchange with the environment is considered adiabatic. The contact is considered perfect at the dry and wet hydrate interface. Let us take up boundary conditions of the fourth kind. They will look as follows:

$$\tau > 0 - \lambda_{gg}\frac{\partial T_{gg}}{\partial x}\bigg|_{x=0} = 0;\ -\lambda_k\frac{\partial T_k}{\partial x}\bigg|_{x=R} = -\lambda_{gg}\frac{\partial T_{gg}}{\partial x}\bigg|_{x=R};\ \ q_k|_{x=R+1} = 0.$$

The problem was solved by the finite difference method (grid approach).

The behaviour the temperature field of a gas hydrate sample during self-preservation of its surface layer is shown in Fig. 4 (temperature distribution at the end of water crystallization in pores, depending on the formed layer thickness for blocks with a base radius of 0.08 and 0.6 m), Fig. 5 (temperature distribution in a hydrate block with a base radius of 0.08 m at the end of water crystallization in surface layer pores, depending on the gas hydrate initial temperature).

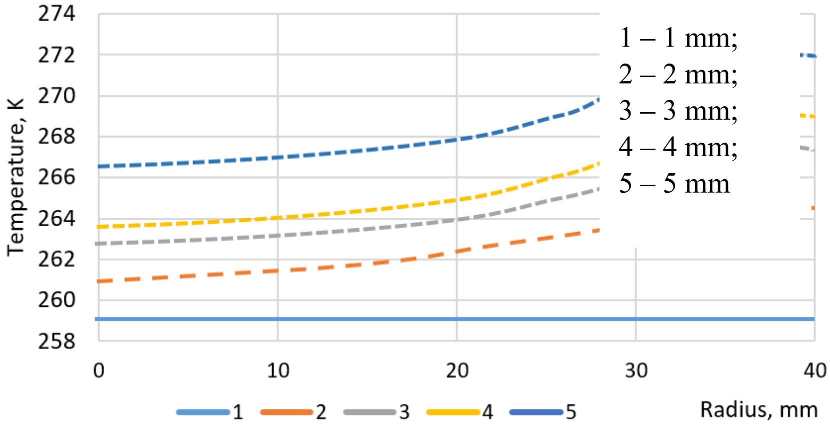

Fig. 4. Temperature distribution in a sample, 0.08 m in diameter, after water crystallization in the surface layer pores, depending on crust thickness (amount of applied water) and its crystallization time: initial temperature: a sample – 259K, water – 273.1K

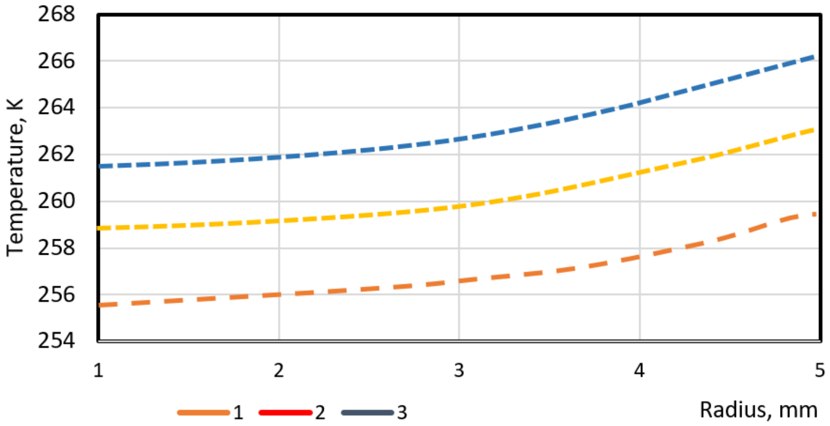

Fig. 5. Temperature distribution in a sample, 0.08 m in diameter, after water crystallization in surface layer pores, 2 mm thick, depending on the initial temperature (T_0) of a gas hydrate (water temperature is 273.1K):1 – T_0 = 259 K; 2 – T_0 = 256K; 3 – T_0 = 253K

Therefore, according to the calculation as a result of water phase transition in wetted layer pores, its temperature rises sharply (for a sample, 0.08 m in diameter to 272 and 268K, respectively, with a layer, 6 and 3 mm thick). However, at atmospheric pressure, the first option is unacceptable, as under these conditions, gas hydrate will intensely dissociate. At the same time, during layer preservation with a water film up to 2 mm thick, its dissociation will be minimal.

Water crystallization time in surface layer pores, 2 mm thick, at the initial temperature of a sample in the range of 253-259K is ≈ 100 s.

To verify the self-preservation process mathematical model, a series of experimental studies were performed. Formed and pre-cooled cylindrical gas hydrate samples, 0.08 m in diameter and 0.11 m high were studied. After formation, samples had an average porosity of 0.06, hydrate lattice filling is 83 mm. The effect of sample initial temperature on water crystallization time and formed protective layer thickness (initial temperature is 259 K) was evaluated. It was determined that in adiabatic conditions water, after partial dissociation at heat supply, completely crystallized in pores, no considerable dissociation is present.

The obtained experimental data on the self-preservation of gas hydrates are in good agreement with the calculated ones. Figures 6 and 7 illustrate this conclusion. The correlation coefficients are in the range of 0.99-0.97 and the coefficients of variation are 0.034-0.1. This testifies to the good accuracy of the proposed mathematical model.

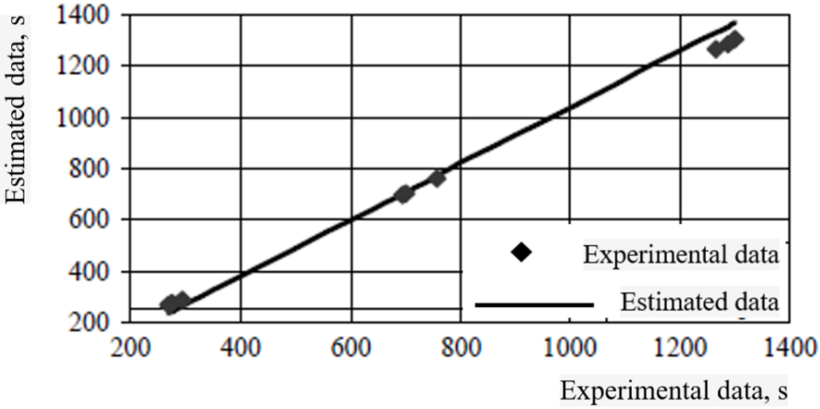

Fig. 6. Comparison of the calculated and experimental data on the crystallization time of water in the pores of the surface layer of gas hydrate, depending on its thickness

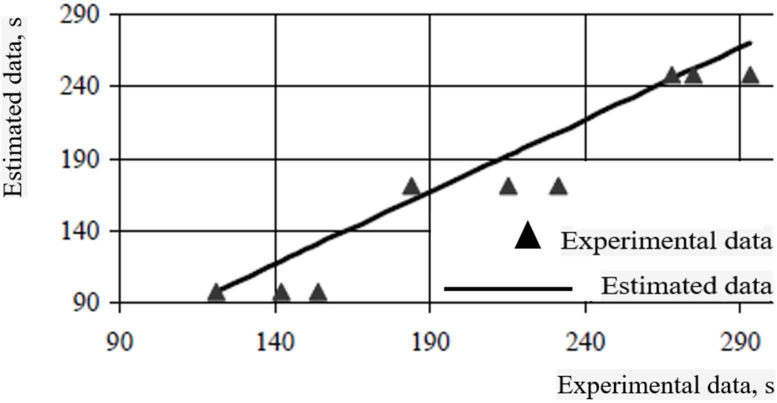

Fig. 7. Comparison of calculated and experimental data on the formation time of the ice crust for different initial temperatures of the gas hydrate block

3. Conclusions

The performed study results show that the main cause of a hydrate self-preservation effect is decrease of temperature in its deep layers as a result of partial dissociation. The ice crust formation on a dissociating GH surface is a consequence, not a cause of the self-preservation effect. Therefore, in the mathematical modelling of thermal processes that occur during hydrate block dissociation, it shall be considered that heat sink is a function of temperature and pressure at this point of the hydrate block.

The conditions under which self-preservation of hydrates of different gases can be achieved are determined. It is determined that the hydrate block size on a self-preservation effect depends on a temperature distribution inside the hydrate block. In a large block, a lower temperature is achieved in hydrate deep layers, contributing to its better storage.

GH concentration effect on distribution of temperatures and heat sink along a dissociating gas hydrate block "depth" is determined. The obtained dependence was confirmed by field experiment results.

References

Archer, D. (2007). Methane hydrate stability and anthropogenic climate change. *Biogeosciences*, *4*, 521-544.

Boswell, R.; Collett, T.S. (2011). Collett Current perspectives on gas hydrate resources. *Energy Environ. Sci.*, *4*, 1045-1528.

Brown, T.D.; Taylor, C.E.; Bernardo, M.P. (2010). Rapid Gas Hydrate Formation Processes: Will They Work? *Energies*, *3*, 1154-1175.

Chong, Z.R.; Yang, S.H.; Babu, P.; Linga, P.; Li, X.S. (2016). Review of natural gas hydrates as an energy resource: Prospects and challenges. *Appl. Energy*, *162*, 1633-1652.

Ke, W.; Svartaas, T.M.; Chen, D. (2019). A review of gas hydrate nucleation theories and growth models. *J. Nat.Gas Sci. Eng.*, *61*, 169-196.

Kim, K.; Kang, H.; Kim, Y. (2015). Risk Assessment for Natural Gas Hydrate Carriers: A Hazard Identification (HAZID) study. *Energies*, *8*, 3124-3164.

Kipyoung, K.; Youtaek, K.; Hokeun, K. (2014). Recent advances in natural gas hydrate carriers for gas transportation. *JKOSME*, *38*, 589-601, DOI: 10.5916/jkosme.2014.38.5.589.

Koshlak, H., Pavlenko, A. (2019). Method of formation of thermophysical properties of porous materials. *Rocznik Ochrona Srodowiska*, *21*(2), 1253-1262.

Pavlenko, A.M. (2020). Thermodynamic features of the intensive formation of hydrocarbon hydrates. *Energies*, *13*, 3396; DOI: 10.3390/en13133396

Pavlenko, A., Koshlak, H. (2019). Heat and mass transfer during phase transitions in liquid mixtures. *Rocznik Ochrona Srodowiska, 21*(1), 234-249.

Pavlenko, A., Szkarowski, A., Janta-Lipińska, S. (2014). Research on burning of water black oil emulsions. *Rocznik Ochrona Srodowiska*, *16*(1), 376-385.

Pavlenko, A., Usenko, B., Koshlak, A. (2014a). Analysis of thermal peculiarities of alloying with special properties. *Metallurgical and Mining Industry*, *6*(2), 15-19.

Veluswamy, H.P.; Kumar, A.; Kumar, R.; Linga, P. (2017). An innovative approach to enhance methane hydrate formation kinetics with leucine for energy storage application. *Appl. Energy*, *188*, 190-199.

Vysniauskas, A.; Bishnoi, P.R. (1983). A kinetic study of methane hydrate formation. *Chem. Eng. Sci.*, *38*, 1061-1072.

Zhao, J.; Zhu, Z.; Song, Y.; Liu, W.; Zhang, Y.; Wang, D. (2015). Analysing the process of gas production for natural gas hydrate using depressurization. *Appl. Energy*, *142*, 125-134, DOI: 10.1016/j.apenergy.2014.12.0714.