Study of the stability of methane hydrates in normal conditions

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Abstract
The problems of accumulation, transport and storage of gases and gas mixtures exist in many cases. Often the existent technologies appear to be ineffective for condensate or compressed gas transporting with pipelines. Therefore, the transportation and storage of gas in hydrate form can be an alternative to traditional technologies. Preservation of gas hydrate blocks can store them for some time at the non-equilibrium condition. The thermodynamic parameters of forcibly conservation of gas hydrate blocks theoretically are determined and experimentally verified.

Keywords: STORAGE OF GAS, GAS HYDRATES, HYDRATE BLOCK, THERMAL CONDUCTIVITY, FORCIBLY PRESERVATION, EQUILIBRIUM CONDITIONS

Nowadays gas transportation is performed with the help of pipelines or LNG-tankers. However, a significant amount of gas can be transported and stored for a long time in the composition of gas hydrates [1]. This technology is based on the ability of gas and water to form relative stable structures – gas hydrates. Metastable condition of gas hydrates can be supported not only due to the effect of self-preservation [2], but also forcibly preservation (layer of ice, more stable hydrate) [3,4].

However, the thermodynamic parameters of forcibly preservation of gas hydrates with layer of ice are studied insufficiently. The technology of gas hydrates transportation at the non-equilibrium conditions (the atmospheric pressure and temperature below zero) is the most attractive. Production of maximum stable of gas hydrate structures lies at its basis.

Hydrate blocks advisable to forcibly preserve with the layer of ice to prevent of gas losses and enhance their stability. However, thermodynamic and technological parameters of preservation of gas hydrate with the layer of ice are studied insufficiently for today.

Parameters of preventing of dissociation of gas hydrates when applied of water to the surface of the block and the time of its crystallization should be defined. Such preservation should be carried at a higher pressure behind the equilibrium of hydrate formation for temperature of gas hydrates. But such operation will complicate the technology under pressure significantly. Therefore, we can prevent significant losses of gas during forcible preservation under atmospheric pressure by decreasing of porosity to a minimum value of formed block. Moistened layer must have an ample supply of cold and corresponding porosity for the crystallization inflicted of water. So, we propose preservation of hydrates to carry out in its porous within 0.07 – 0.15 and initial temperature within 248 – 259 K and a pressure of 0.1 MPa.

Figure 1 Line 2 limits the area P-T parameters icy layer formation on the surface of hydrate of natural gas composition: CH_4 – 92.8%, C_2H_6 – 5.1 %, C_3H_8 – 2.1 %. To prevent dissociation of gas hydrates, according to Fig. 1, it is necessary to create conditions close to equilibrium.

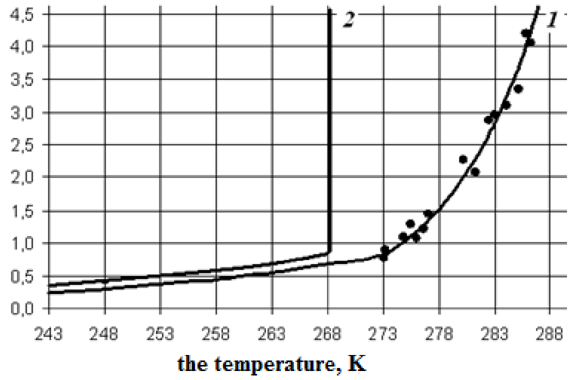

Figure 1. The equilibrium condition: 1 - the equilibrium curve of gas hydrate composition CH4 – 92.8 %, C2H6 – 5.1 %, C3H8 – 2.1 %; 2 – bounding area of P-T parameters

For example for the average composition of natural gas to maintain pressure not less than by 0.85 MPa. However, the process of crystallization of water at such temperatures occurs too slowly. Therefore, the initial temperature of the sample to hydrate the body should be lower. Optimal, in our opinion, is the temperature of 258 K. This dissociation of gas hydrates under the equilibrium curve (Fig. 1) will be advised at a pressure of 0.7 MPa.

However, these calculations do not take into account the possibility of manifestation of the effect of preserving the same samples when the equilibrium conditions after partial dissociation of gas hydrates, formed on its surface ice crust, which slows or stops the process.

Thus, if a small block of hydrate dissociation surface at the initial stage of the technological process will not prevent its implementation, in the future, taking into account the effect of the manifestation of the automatic preservation, forced conservation can be carried out without further dissociation under equilibrium conditions, for example at atmospheric pressure.

For the mathematical description of this process there formed the problem of non-stationary of heat conduction. The equation that describes the change in temperature of gas hydrate layer soaked with water, which can crystallize in cylindrical coordinates, has the following form

$$c_{\kappa}\rho_{\kappa}\frac{\partial T_{\kappa}}{\partial\tau}=\lambda_{\kappa}\left(\frac{\partial^2 T_{\kappa}}{\partial x^2}+\frac{1}{x}\frac{\partial T_{\kappa}}{\partial x}\right)+\rho_{\text{л}}L\frac{dV_{\text{в}}}{V_{\kappa}d\tau},$$

$$A\geq V_{\text{в}}\geq 0,\ 0<x<l,\ \tau>0, \qquad (1)$$

where $T_{\text{к}}$ – the temperature moistened gas hydrate layer, К; l – layer thickness, m; $V_{\text{в}}$, V_{κ}– volumes of water and ice formed on the surface, m^3; c_{κ} – specific heat capacity of gas hydrate layer saturated with water, J/kg.К; ρ_c, ρ_i – density crust and ice, kg/m^3; $\lambda_{\text{к}}$ – the thermal conductivity, W/(m·K); L – specific heat of crystallization water, J; A – certain amount of water on the surface, m^3.

Changing the temperature of dry block hydrate of time determined by the equation in cylindrical coordinates:

$$\frac{\partial T_{gh}}{\partial\tau}=a\left(\frac{\partial^2 T_{gh}}{\partial x^2}+\frac{1}{x}\frac{\partial T_{gh}}{\partial x}\right),\tau>0,l<x<R, \qquad (2)$$

whereT_{gh} – the temperature of dry hydrate block, К;a – thermal diffusion coefficient of dry gas hydrates, m^2/s; R – radius block, m.

The initial conditions

$$T_{\kappa}(x,0)=T_0,\ T_{gh}(x,0)=T_1$$

Boundary condition

$$T_{gh}(R-l,\tau)=f(x,\tau);T_{\kappa}(l,\tau=\varphi(x,\tau) \qquad (3)$$

When applied to the surface of the hydrate water block, it gradually saturates the surface layer and is crystallized in the pores. It stands a certain amount of heat. Incrementally this process of circuit is presented in Fig. 2.

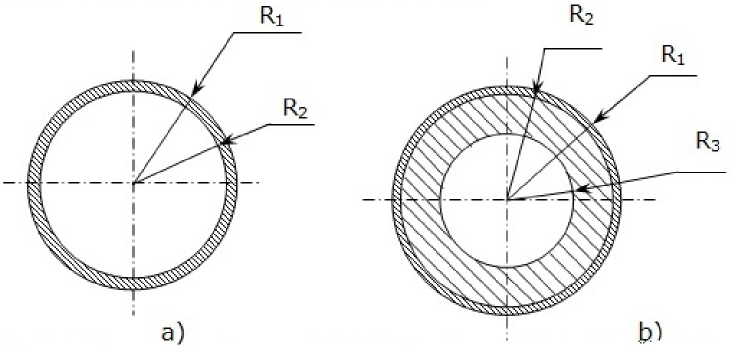

Figure 2. The formation of water film in the dissociation of gas hydrates a); b) – the pores water saturation and crystallization water: R_1 - radius of wet hydrate; R_2 - radius of dry hydrated block; R_3 - radius of water saturation hydrate.

At the interface of R_1 at a certain temperature of air T_{air} and heat transfer coefficient α, we write the extreme conditions of the third kind

$$\lambda_к \frac{\partial T_к}{\partial r}\bigg|_{r=R_1} = \alpha(T_{air} \quad T_1)\cdot \qquad (4)$$

Assuming that the contact at the interface R_2 is perfect, we may write as a boundary condition of the fourth kind

$$-\lambda_к \frac{\partial T_к}{\partial r}\bigg|_{r=R_3} = -\lambda_{gh} \frac{\partial T_{gh}}{\partial r}\bigg|_{r=R_3} \cdot \qquad (5)$$

where $\lambda_к$ and λ_{gh} – coefficient of thermal conductivity of water and ice, respectively, W/(m·K).

In the center of hydrate block there asked thermal symmetry condition

$$-\lambda_{gh} \frac{\partial T_{gh}}{\partial r}\bigg|_{r=0} = 0\cdot \qquad (6)$$

For bodies located in the flow we can write the equation for determining Nusselt number

$$Nu = 2\cdot\left(1+\beta\cdot \mathrm{Re}^{0.5}\cdot \mathrm{Pr}^{0.33}\right), \qquad (7)$$

where $\mathrm{Re}=\frac{wd}{\nu}$ – Reynolds number; $\mathrm{Pr}=\frac{\nu}{a}$ – Prandtl criterion; β – coefficient ($\beta = 0.34$).

For stationary environment ($\mathrm{Re}=0$) and for the number of $\mathrm{Re} << 1$ Nusselt number is $Nu = 2$.

The coefficient of heat transfer Nusselt number

$$\alpha = Nu\frac{\lambda_{воз}}{d}. \qquad (8)$$

where d - characteristic size (diameter).

From there, we get

$$\alpha = \frac{\lambda_{пов}}{R_1}. \qquad (9)$$

From equation there implied that the $\lambda_{пов} = const$, coefficient α is inversely proportional to the radius of block R_1, ie with increasing radius heat transfer coefficient decreases and vice versa. After water application saturation of the surface layer begins. The depth of penetration R_3 depends on the porosity and is determined experimentally basing on total porosity and water temperatures, block gas hydrate and air. Theoretically, one can argue that the heat balance has the following form

$$Q_п = Q_к + Q_{gh} + W\rho\cdot L, \qquad (10)$$

where Q_s - heat flux from the surface; $Q_к$ - heat flow in heating (cooling) saturated layer; Q_{gh} - heat flux on heating gas hydrates.

The heat flux from the surface is

$$Q_п = \frac{4\pi\lambda_в\left(T_1 - T_2\right)}{\frac{1}{R_1}-\frac{1}{R_2}} \qquad (11)$$

With the adopted boundary conditions, it follows that the temperature difference between the surface and saturated layer is zero, so the heat flow in heating layer $Q_к = 0$.

Warmth, perceived block hydrate, we define a heat conduction equation of the form:

$$q_V = \lambda_{gh}\left[\frac{d^2T_{gh}}{dr^2} + \frac{1}{r}\frac{dT_{gh}}{dr}\right], \qquad (12)$$

The relationship between Q_n and q_V in the form of:

$$q_V = \frac{Q_n}{V} = \frac{Q_n}{\pi d_3^2 H}, \qquad (13)$$

Integrating equation (4) with (3).

Integration constants is determined from the boundary conditions. In $r = 0$ (in the center of block) $\frac{dT_{gh}}{dr} = 0$. In $r = R_3$, the temperature $T_{gh}(r)$ is equal to the temperature of the boundary dry and moistened hydrate.

So finally we obtain

$$T_{gh}(r) = \frac{q_V}{\lambda_{gh}}\frac{r^2}{6} + T_3 - \frac{q_V}{\lambda_{gh}}\frac{R_3^2}{6}. \qquad (14)$$

Equation (14) to the center ($r = 0$) has the form

$$T_1 = T_3 - \frac{q_V}{\lambda_{gh}}\frac{R_3^2}{6}. \qquad (15)$$

$$Q_{gh} = 2\pi R_3 H \lambda_{gh}(T_3 - T_1). \qquad (16)$$

So finally we obtain

$$\frac{4\pi\lambda_\kappa (T_1 - T_2)}{\frac{1}{R_2} - \frac{1}{R_1}} = 2\pi R_3 H \lambda_{gh}(T_3 - T_1) + \rho W \cdot L^{\cdot} \qquad (17)$$

Heat balance equation (17) indicates the relationship of energy and geometric characteristics of the process of preserving hydrate unit. You can also find the energy justified calculated value of radius moistened layer and the velocity of the boundary.

Let us consider the boundary separation moistened hydrate - dry hydrate. The boundary conditions have the form provided

$$\lambda_1 \frac{\partial T_{gh}(t,\xi(t))}{\partial n} - \lambda_2 \frac{\partial T_{к}(t,\xi(t))}{\partial n} = L\frac{d\xi(t)}{dt}, \qquad (18)$$

where $\xi(t)$ – equation of the curve, which divides the phase, L – warmth aggregate transfer, [J/K] (empirically definable value to move water in ice $L \approx$ 335,2 kJ/kg), n – normal to the curve, $T_{gh}(t,r)$ –temperature solid phases, $T_K(t,r)$ – temperature phase irrigation, λ_1 – coefficient of thermal diffusivity of hydrate, λ_2 – thermal diffusivity of moistened hydrate.

Let us identify the type of curve $\xi(t)$. We are looking solutions for equation of heat conduction in the following self-similar form:

$$T(t,r) = f(z), \text{where } z = \frac{r}{\sqrt{t}}. \qquad (19)$$

Substituting (19) into (18) we obtain the following ordinary differential equation:

$$-\frac{1}{2}f'(z)\cdot z = \lambda\left(f''(z) + \frac{1}{z}f'(z)\right).$$

Where:

$$f(z) = C_1\int\frac{\exp\left(-\frac{z^2}{4\lambda}\right)}{z}dz + C_2,$$

where C_1 and C_2 – arbitrary constants of integration.

To find the shape of the curve $\xi(t)$bases (19) in the boundary condition (18).

Get: $\lambda_1 \frac{1}{\sqrt{t}} f_1'\left(\frac{\xi(t)}{\sqrt{t}}\right) - \lambda_2 \frac{1}{\sqrt{t}} f_2'\left(\frac{\xi(t)}{\sqrt{t}}\right) = L\frac{d\xi}{dt}$,

where

$$\frac{\xi(t)}{\sqrt{t}} = \overline{\alpha} = \text{const},$$

$$\lambda_1 f_1'(\overline{\alpha}) - \lambda_2 f_2'(\overline{\alpha}) = \frac{L}{2}\overline{\alpha}. \qquad (20)$$

As a result we receive

$$\xi(t) = \overline{\alpha}\sqrt{t}. \qquad (21)$$

where coefficient $\overline{\alpha}$ determined empirically, or as a solution to the transcendental equation (20) with known quantities L of heat aggregation transition of water in the crystalline state.

In known equation of the curve $\xi(t)$ that separates phases can be reduced to the solution of the initial problem solution equation of heat conduction with generalized (discontinuous) diffusivity coefficient:

$$\frac{\partial T}{\partial t} = \lambda(t,r)\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right), \qquad (22)$$

where

$$\lambda(t,r) = \begin{cases} \lambda_1, \text{if } 0 \le r < \theta R + \xi(t), \\ \lambda_2, \text{if } \theta R + \xi(t) \le r < R. \end{cases} \qquad (23)$$

The initial conditions:

$$T|_{t=0} = T_{\text{гг}} \text{ at } 0 \le r < \theta R + \xi(t). \qquad (24)$$

$$T|_{t=0} = T_K \text{ at } \theta R + \xi(t) \le r < R.. \qquad (25)$$

The outer boundary of the cylinder, ie. when $r = R$ considering boundary condition of the third kind:

$$\lambda_2 \left.\frac{\partial T}{\partial r}\right|_{r=R} = k(T - T_{\text{air}}), \qquad (26)$$

where T_{air} – ambient temperature, k – heat transfer coefficient.

The equation of motion of the boundary moistened hydrate and hydrate dry function is presented as:

$$\zeta(t) = \frac{1}{\xi(t)} \qquad (27)$$

that the graph of dimensionless variables is as follows: Figure 3. The physical dimension [m/s^{0,5}].

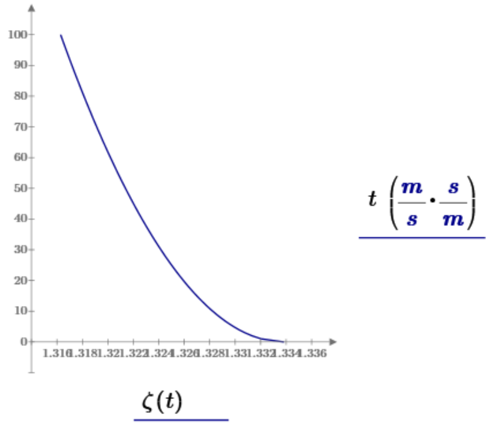

Figure 3. Curve motion of the boundary as a function of dimensionless time

The graph shows that the time limit stops moving. The final values depend on the external radius, temperature, thermal properties and porosity of hydrate. But under any conditions, limit will not be less than 0,8R – theoretical assumptions. For the technological conditions to adhere to higher ratios. Therefore, actual physical conditions in comparison with theoretical description, which is developed in this section will always be satisfied.

The distribution of temperatures in the hydration unit is determined by solving the equation of heat conduction, which is written above. For calculation there used finite differences of explicit numerical integration scheme. Thermophysical properties are determined from experimental data.

Generalized diffusivity coefficient is presented as follows:

$$\lambda(t,r) := \begin{cases} \lambda_1 & \text{if } 0 \le r < \xi(t) \\ \lambda_2 & \text{otherwise} \end{cases} \qquad (28)$$

Finite – difference scheme is shown in Figure 4.

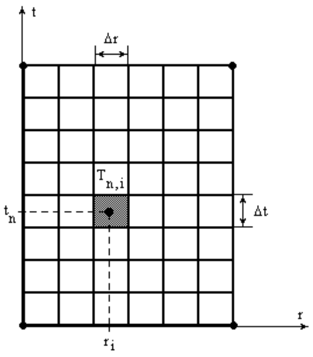

Figure 4. Analytical model

The temperature in an elementary cell calculation is determined by the equation

$$T_{n,i}(n) = T\left(t_n, r_i\right) \qquad (29)$$

Finite - difference approximation of the differential operator of the first derivative with respect to time:

$$\frac{d}{dt}T\left(t_n, r_i\right) = \frac{T_{n+1,i} - T_{n,i}}{\Delta t} \qquad (30)$$

Finite – difference approximation of the differential operator of the first derivative of the variable values:

$$\frac{d}{dr}T\left(t_n, r_i\right) = \frac{T_{n,i+1} - T_{n,i}}{\Delta r} \qquad (31)$$

Finite – difference approximation of the differential operator of the second derivative of the variable values:

$$\frac{d^2}{dr^2}T\left(t_n, r_i\right) = \frac{T_{i+1,j} - 2\cdot T_{i,j} + T_{i-1,j}}{\Delta_x^{\,2}} \qquad (32)$$

Finite – difference approximation of the Laplace operator in the cylindrical coordinate system based on symmetry:

$$\Delta T = \frac{T_{n,i+1} - 2\cdot T_{n,i+1} + T_{n,i}}{\Delta r^2} + \frac{1}{r_{i+1}}\frac{T_{n,i+1} - T_{n,i}}{\Delta r} \qquad (33)$$

Formation of the third kind boundary condition on the outer surface:

$$-\lambda_2\cdot\frac{T_{n,N_r} - T_{n,N_r-1}}{\Delta r} = k\cdot\left(T_{n,N_r} - T_{povitrya}\right) \qquad (34)$$

The results of calculations are presented in Fig. 5.

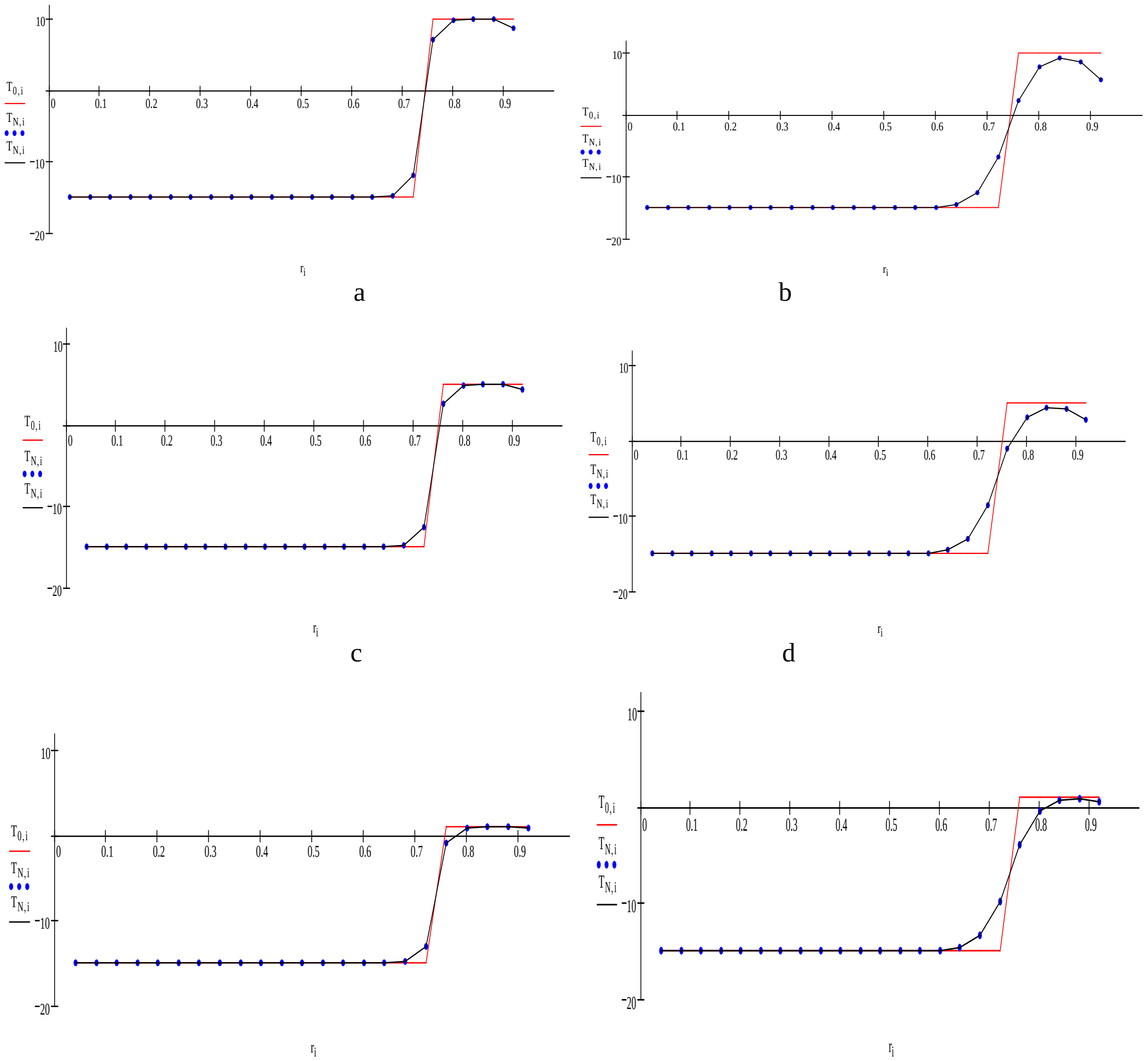

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Figure 5. Temperature distribution inside the hydrate block for dimensionless radius at T=-15oC; temperature of air T=-10oC and water temperature: a) Twater =10oC (observation time 5 minutes); b) Twater =10oC (observation time 8 minutes); c) Twater =5oC (observation time 5 minutes); d)Twater =5oC (observation time 8 minutes); e) Twater =1oC (observation time 5 minutes); f)Twater =1oC (observation time 8 minutes)

Calculated data shows that when placing dry hydrate block in an environment with temperatures 5 °C and 10 °C it is possible to achieve partial dissociation of surface gas hydrates for 4 hours. At the temperature of 1 °C crystallization takes about 8 minutes. Although the surface layer increases the temperature as a result of the phase transition of water in the pores, but the final temperature after 8 minutes is 0 °C. Inflicted water is completely crystallized and preserves the surface pore space.

Conclusions

To improve the stability and mechanical strength, we propose forcible preservation of the cooled (T <273K) gas hydrate blocks with the ice crust implement by double application of water of the temperature about 273 K.

Parameters for quality preservation of gas hydrates were defined: initial temperature of gas hydrate 248 – 259 K, porosity – 0.07 – 0.15.Quality of forcibly preservation of gas hydrates is defined by time of crystallization of deposited water, initial temperature of gas hydrates, and the temperature of the sample after crystallization of water, by thickness, equability and homogeneity of formed crust. Mathematical models of forcibly preservation of the hydrate block: cementation of the surface layer by freezing of water in the pores and freezing of the ice layer on its surface were proposed. Correlation analysis confirmed the adequacy of the proposed models. They will be applied in the industrial production of gas hydrate blocks.

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