Anatoly Pavlenko*, Hanna V. Koshlak*, Oleg Vytyaz**

STUDY OF THE STABILITY OF METHANE HYDRATES IN NORMAL CONDITIONS

1. PROBLEM DEFINITION AND ITS RELATIONSHIP WITH IMPORTANT SCIENTIFIC AND PRACTICAL TASKS

To date gas transportation is performed with pipelines or LNG-tankers. However, a significant amount of gas can is 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 is supported due not only the effect self-preservation [2], and forcibly preservation (layer of ice, more stable hydrate) [3, 4].

However, the thermodynamic parameters of forcibly preservation of gas hydrates with layer of ice have been studied insufficiently. The technology of the transportation of gas hydrates at the no equilibrium conditions (the atmospheric pressure and a temperature the below zero) is the most attractive. Production of maximum stable of gas hydrate structures lies at its basis.

2. EXCRETION OF THE UNSOLVED EARLIER ASPECTS OF THE PROBLEM WHICH THE ARTICLE IS DEDICATED

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

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 out at a higher pressure behind the equilibrium of hydrate formation for the temperature of gas hydrates. But such an operation will complicate the technology under pressure significantly. Therefore, we can prevent of significant losses of gas during of forcibly preservation under atmospheric pressure by decreasing porosity to a minimum value a formed block. Moistened layer must have an ample supply of cold and corresponding

  * Poltava National Technical Yuri Kondratyuk University, Ukraine
** Ivano-Frankivsk National Technical University of Oil and Gas, Ukraine

porosity for the crystallization inflicted of water. So, we propose the 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 Figure 1, it is necessary to create conditions close to equilibrium
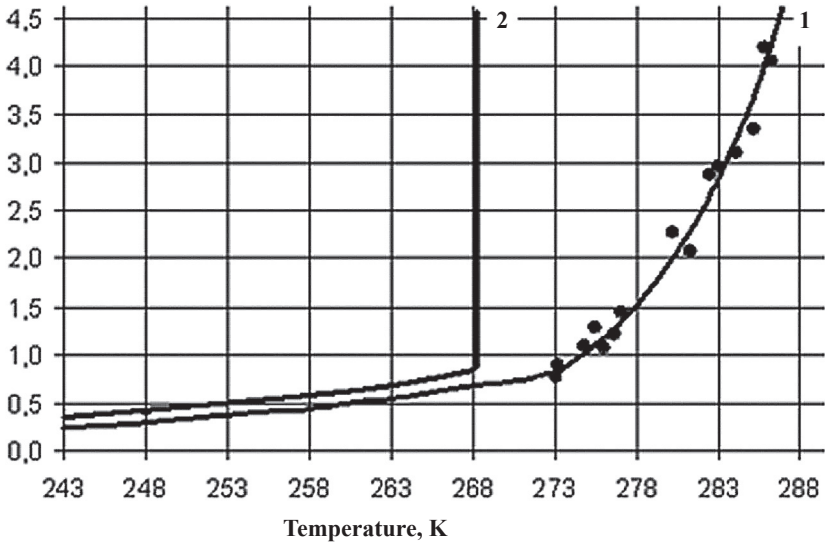

Fig. 1. The equilibrium condition: 1 – the equilibrium curve of gas hydrate composition CH_4 – 92,8%, C_2H_6 – 5,1%, C_3H_8 – 2,1%; 2 – bounding area of P-T parameters

For example for the average composition of natural gas to maintain pressure of not less than 0,85 MPa. However, the process of crystallization water at such temperatures occur 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) there 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.

3. ARTICLE PURPOSES FORMATION

The aim is to determine the technological parameters of the storage of gas hydrates, which would satisfy the requirements of their stability in industrial applications.

4. PRESENTATION OF THE MAIN MATERIAL

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

$$c_h \rho_c \frac{\partial T_m}{\partial \tau} = \lambda_c \left(\frac{\partial^2 T_m}{\partial x^2} + \frac{1}{x} \frac{\partial T_m}{\partial x} \right) + \rho_i L \frac{dV_w}{V_i \, d\tau}, \; A \geq V_w \geq 0, \; 0 < x < l, \; \tau > 0 \quad (1)$$

where:

T_m – the temperature moistened gas hydrate layer [K],
l – layer thickness [m],
V_w, V_i – volumes of water and ice formed on the surface [m^3],
c_h – specific heat capacity of gas hydrate layer saturated with water [J/kg. K],
ρ_c, ρ_i – density crust and ice [kg/m^3],
λ_c – the thermal conductivity [W/(m·K)],
L – specific heat of crystallization water [J/m^3],
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:

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

where:

T_{gh} – the temperature of dry hydrate block [K],
a – thermal diffusion coefficient of dry gas hydrates [m^2/s],
R – radius block [m].

The initial conditions:

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

Boundary conditions:

$$T_{gh}(R - l, \tau) = f(x, \tau); \; T_m(l, \tau) = \phi(x, \tau) \quad (3)$$

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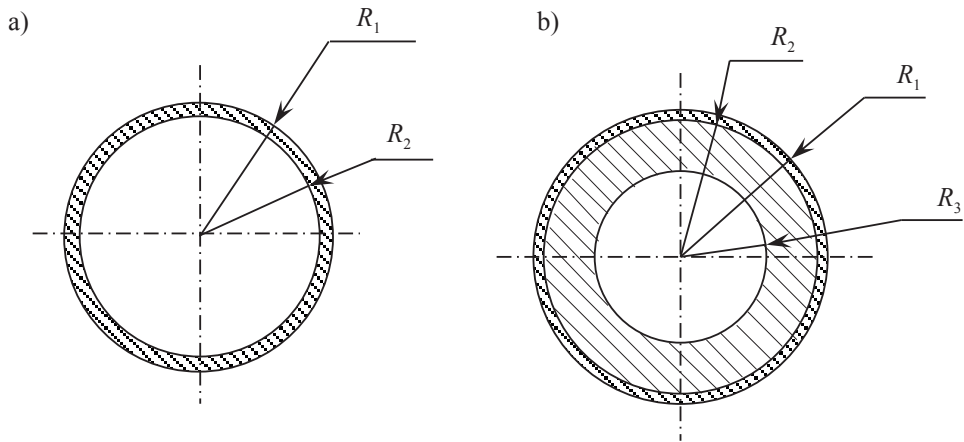
a)

b)

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

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:

$$\lambda_c \left. \frac{\partial T_m}{\partial r} \right|_{r=R_1} = \alpha(T_{air}, T_1) \tag{4}$$

Assuming that the contact at the interface R_2 is perfect, can be written as a boundary condition of the fourth kind:

$$\lambda_c \left. \frac{\partial T_m}{\partial r} \right|_{r=R_3} = \lambda_{gh} \left. \frac{\partial T_{gh}}{\partial r} \right|_{r=R_3} \tag{5}$$

where λ_c and λ_{gh} – coefficient of thermal conductivity of water and ice, respectively [W/(m·K)].

In the center of hydrate block ask thermal symmetry condition:

$$-\lambda_{gh} \left. \frac{\partial T_{gh}}{\partial r} \right|_{r=0} = 0 \tag{6}$$

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

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

where:

$\mathrm{Re} = \dfrac{wd}{\nu}$ – Reynolds number,

$\mathrm{Pr} = \dfrac{\nu}{a}$ – Prandtl criterion,

β – coefficient ($\beta = 0.34$).

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

The coefficient of heat transfer Nusselt number:

$$\alpha = \text{Nu}\,\frac{\lambda_c}{d} \tag{8}$$

where d – characteristic size (diameter).

From there, we get:

$$\alpha = \frac{\lambda_c}{R_1} \tag{9}$$

From equation implies that the λ_c = const coefficient α is inversely proportional to the radius block R_1, i.e. with increasing radius heat transfer coefficient decreases and *vice versa*.

After applying the water saturation of the surface layer begins. The depth of penetration R_3 depends on the porosity and is determined experimentally based on total porosity and water temperatures, the block gas hydrate and air.

Theoretically, one can argue that the heat balance has the following form:

$$Q_n = Q_k + Q_{gh} + Wp \cdot L \tag{10}$$

where:

Q_s – heat flux from the surface,
Q_k – heat flow in heating (cooling) saturated layer,
Wp – volume,
L – specific heat of crystalization water,
Q_{gh} – heat flux on heating gas hydrates.

The heat flux from the surface is:

$$Q_s = \frac{4\pi\lambda_c\left(T_1 - T_2\right)}{\dfrac{1}{R_1} - \dfrac{1}{R_2}} \tag{11}$$

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 $Q_c = 0$.

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

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

The relationship between Q_c and q_V has the form:

$$q_V = \frac{Q_c}{V} = \frac{Q_c}{\pi d_3^2 H} \tag{13}$$

Integrating equation (4) with (3).

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

So finally we obtain:

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

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

$$T_1 = T_3 - \frac{q_V}{\lambda_{gh}}\frac{R_3^2}{6} \tag{15}$$

$$Q_{gh} = 2\pi R_3 H \lambda_{gh}\left(T_3 - T_1\right) \tag{16}$$

So finally we obtain:

$$\frac{4\pi\lambda_K\left(T_1 - T_2\right)}{\dfrac{1}{R_2} - \dfrac{1}{R_1}} = 2\pi R_3 H \lambda_{gh}\left(T_3 - T_1\right) + \rho W \cdot L \tag{17}$$

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.

Consider the boundary separation moistened hydrate – dry hydrate. The boundary conditions have the form provided:

$$\lambda_1 \frac{\partial T_{gh}\left(t, \xi(t)\right)}{\partial n} - \lambda_2 \frac{\partial T_i\left(t, \xi(t)\right)}{\partial n} = L\frac{d\xi(t)}{dt} \tag{18}$$

where:

$\xi(t)$ – equation of the curve that 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,

$T_{gh}(t, r)$ – the temperature solid phases,

$T_i(t, r)$ – the temperature phase irrigation,

λ_1 – coefficient thermal diffusivity hydrate,

λ_2 – thermal diffusivity moistened hydrate.

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

$$T(t, r) = f(z) \tag{19}$$

where $z = \dfrac{r}{\sqrt{t}}$

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:

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

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:

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

$$\lambda_1 f_1'(\bar{\alpha}) - \lambda_2 f_2'(\bar{\alpha}) = \frac{L}{2}\bar{\alpha} \tag{20}$$

A result we receive:

$$\xi(t) = \bar{\alpha}\sqrt{t} \tag{21}$$

where coefficient $\bar{\alpha}$ 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:

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

where:

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

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The initial conditions:

$$T|_{t=0} = T_{gh} \text{ at } 0 \leq r < \theta R + \xi(t) \tag{24}$$

$$T|_{t=0} = T_i \text{ at } \theta R + \xi(t) \leq r < R \tag{25}$$

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

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

where:
T_{air} – ambient temperature,
k – heat transfer coefficient.
The equation of motion of the boundary moistened hydrate and hydrate dry function presented

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

that the graph of dimensionless variables is as follows Figure 3. The physical dimension $[m/s^{0.5}]$.
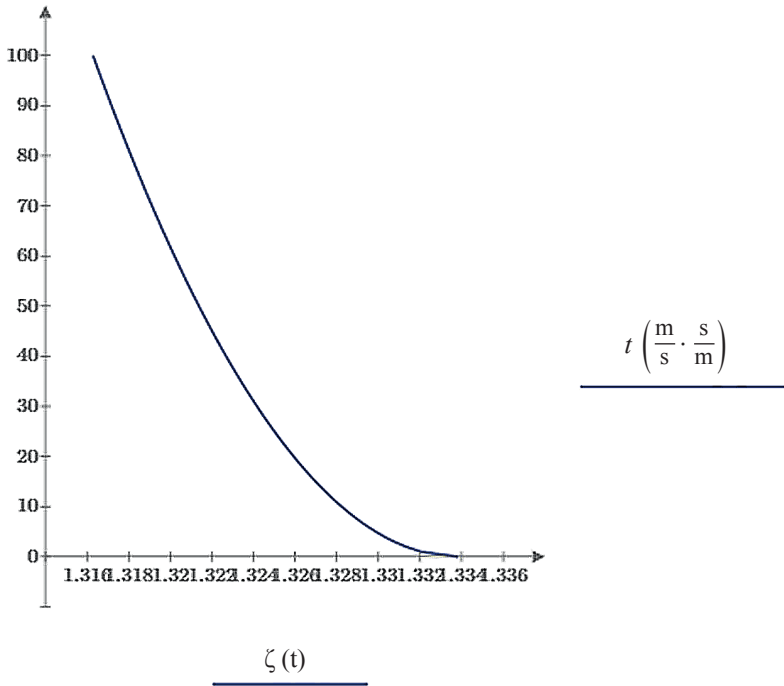

Fig. 3. Curve motion the boundary as a function of dimensionless time

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

The distribution of temperatures in the hydration unit determined by the solving equation of the heat conduction written above.

For calculation using finite differences explicit numerical integration scheme. Thermophysical properties determined from experimental data.

The generalized diffusivity coefficient present as follows:

$$\lambda(t, r) := \begin{cases} \lambda_1 & \text{if } 0 \leq r < \xi(t) \\ \lambda_2 & \text{otherwise} \end{cases} \tag{28}$$
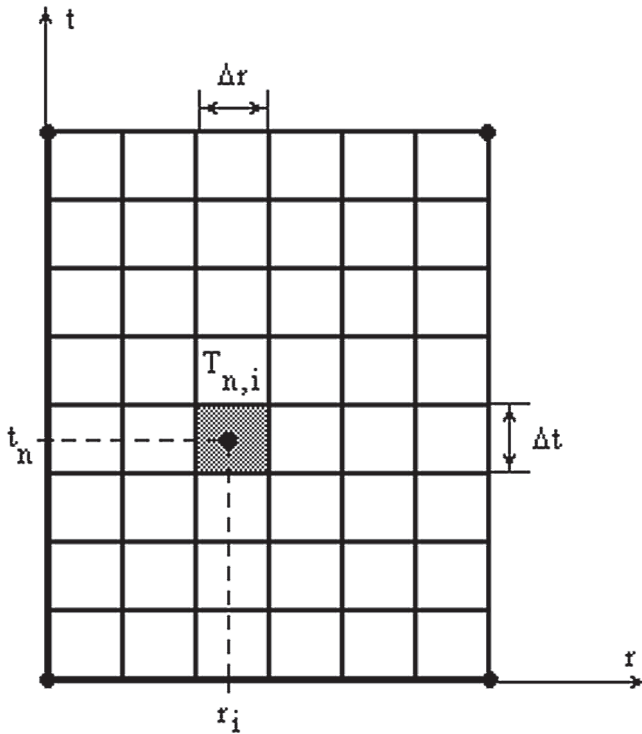
Finite – difference scheme is shown in Figure 4.

Fig. 4. Analytical model

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

$$T_{n,i}(n) = T(t_n, r_i) \tag{29}$$

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

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

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

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

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

$$\frac{d^2}{dr^2} T(t_n, r_i) = \frac{T_{i+1,j} - 2 \cdot T_{i,j} + T_{i-1,j}}{\Delta x^2} \tag{32}$$

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

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

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

$$-\lambda_2 \cdot \frac{T_{n,N_r} - T_{n,N_r-1}}{\Delta r} = k \cdot (T_{n,N_r} - T_{air}) \tag{34}$$
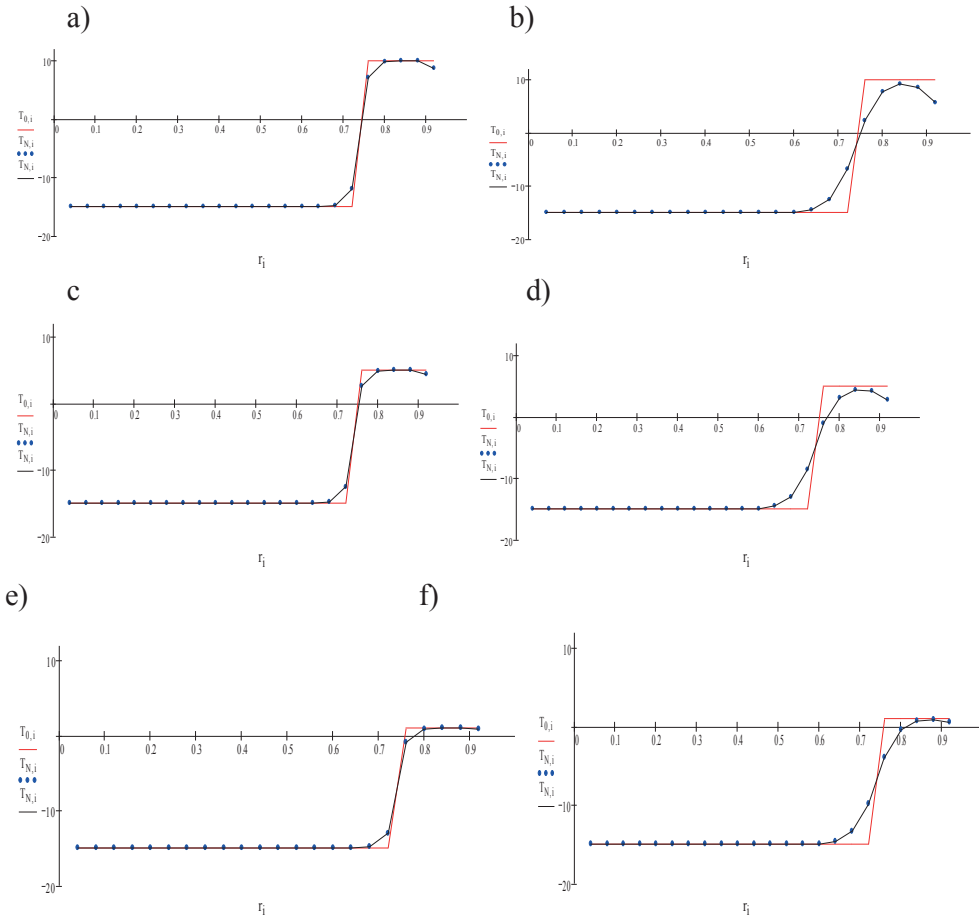
The results of calculations are presented in Figure 5.

Fig. 5. Temperature distribution inside the hydrate block for the dimensionless radius at $T = -15^{\circ}$C; temperature of air $T = -10^{\circ}$C and water temperature: a) $T_{water} = 10^{\circ}$C (observation time 5 minutes); b) $T_{water} = 10^{\circ}$C (observation time 8 minutes); c) $T_{water} = 5^{\circ}$C (observation time 5 minutes); d) $T_{water} = 5^{\circ}$C (observation time 8 minutes); e) $T_{water} = 1^{\circ}$C (observation time 5 minutes); f) $T_{water} = 1^{\circ}$C (observation time 8 minutes)

From the calculated data shows that when placing dry hydrate block in an environment with temperatures 5°C and 10°C possible partial dissociation of gas hydrates surface for 4 hours. At the same time duration of crystallization exceeds the time water running in the surface film. In a temperature of 1°C crystallization takes about 8 minutes. Although the surface layer the temperature increases 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.

5. CONCLUSIONS

To improve the stability and mechanical strength, we propose forcible preservation of the cooled ($T < 273$ K) gas hydrate blocks with the ice crust implemented by a double application of water of a temperature of 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 forcible preservation of gas hydrates is defined by time crystallization of deposited water, initial temperature of gas hydrates, the temperature of the sample after crystallization of water, by thickness, equability and homogeneity of formed crust. Mathematical models was proposed 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. 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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