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## MATHEMATICAL MODEL OF NATURAL GAS FLOW IN PIPELINES WITH ALLOWANCE FOR THE DISSOCIATION OF GAS HYDRATES

V. Sh. Shagapov,<sup>a</sup> N. G. Musakaev,<sup>b</sup> and R. R. Urazov<sup>a</sup>

On the basis of the methods and equations of mechanics of multiphase systems a system of ordinary differential equations describing the hydrodynamics and thermal physics of a flow in the gas main in the presence of deposits of gas hydrates on the duct walls has been obtained. Some methods for preventing and controlling the formation of hydrates in the process of natural gas transport in a pipeline have been considered.

**Introduction.** The processes of production of hydrocarbon raw materials are often accompanied by deposits of solid sediments in the form of gas hydrates building-up on the inner surface of underground and surface facilities. This problem is particularly topical for gas transport in lengthy gas mains, since hydrates may clog partially or completely the flow section of the pipe, which in many cases leads to serious operational complications and even to bad accidents.

To prevent the formation of sclerotic plaques or remove them, in each particular case one has to know the physicochemical processes proceeding under different operating conditions of the pipeline, in particular, it is necessary to determine the hydration conditions. If in the gas pipeline gas hydration conditions exist, then it is necessary to determine the build-up intensity of gas hydrate deposits on the pipe walls, which can be achieved by the joint solution of the equations of heat and mass transfer in the pipe and in the gas hydrate layer. Such an approach to the given problem was considered in [1-3] on the assumption that the rate of build-up of a hydrate layer is determined by both the heat transfer from the gas to the pipe wall and the surrounding ground and the supply of moisture to the reaction surface.

The proposed theoretical study differs from the works of other authors in that here an attempt has been made to generalize the hydraulic quasi-stationary model of the gas flow in pipes with allowance for the hydration to the case where this process is limited by the condensation rate of moisture from the moving gas. Moreover, the model has been complemented so that it is possible to study the influence of the introduction of liquid inhibitors into the gas flow on the hydrate dissociation dynamics.

**Basic Equations.** The necessary condition for the formulation of gas hydrates is the presence of water (or its vapors) and light hydrocarbon components, which, dissolving in the water under certain temperatures and pressures, form a solid phase [4]. In this connection and for a more complete account of the interphase mass transfer processes and the thermophysical phenomena connected with them, we assume that the natural gas flow in the pipeline consists of two components, namely: moisture, which is the main component in hydration, and the rest of the flow, which is essentially a hydrocarbon mixture. The first component in the flow can exist in the vaporous state and in the form of droplets.

Let us direct the z-axis in the direction of the gas flow, its origin coincides with the inlet cross-section of the pipe.

Neglecting the loss due to the formation of the solid phase and the terms connected with inertial effects, for the description of the gas flow in the pipeline we can write a system of equations in the quasi-stationary approximation [5] resulting from the fundamental mass, momentum, and energy conservation laws:

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<sup>&</sup>lt;sup>a</sup>Sterlitamak State Pedagogical Academy, 37 Lenin Ave., Sterlitamak, 453103, Bashkortostan, Russia; <sup>b</sup>Tyumen department of the Institute of Theoretical and Applied Mechanics, Siberian Branch of the RAS, 74 Taimyrskaya Str., Tyumen, 625000; email: UrazovR@yandex.ru. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 81, No. 2, pp. 271–279, March–April, 2008. Original article submitted May 23, 2006; revision submitted June 27, 2007.

$$m_{\rm g}\frac{dk_{\rm w}}{dz} = -J_{\rm w}\,,\tag{1}$$

$$m_{\rm g}\frac{dw_{\rm g}}{dz} = -S\frac{dp}{dz} - f\,,\tag{2}$$

$$m_{\rm g}c_{\rm g}\frac{dT_{\rm g}}{dz} = \frac{m_{\rm g}}{\rho_{\rm g}}\frac{dp}{dz} + m_{\rm g}l_{\rm w}\frac{d(k_{\rm liq}(1-k_{\rm m,liq}))}{dz} + m_{\rm g}l_{\rm m}\frac{d(k_{\rm liq}k_{\rm m,liq})}{dz} - Q_{\rm g\sigma},$$
(3)

where  $J_{\rm w} = 2\pi a j_{\rm w}$ ;  $f = 2\pi a \chi$ ;  $\chi = \lambda \frac{\rho_g w_g^2}{8}$ ;  $\lambda = (1.8 \log \text{Re} - 1.5)^{-0.5}$ ;  $\text{Re} = \frac{2a\rho_g w_g}{\eta_g}$ ;  $a = a_0 - \delta$ ;  $Q_{g\sigma} = 2a\pi q_{g\sigma}$ .

To close the above system of equations, we write the relation defining the current position of the gas flowgas hydrate boundary:

$$\frac{\partial \delta}{\partial \tau} = \frac{j_{\rm h}}{\rho_{\rm h}},\tag{4}$$

and assume the condition of "stoichiometry"

$$j_{\rm w} = (1 - k_{\rm g,h}) j_{\rm h} \tag{5}$$

and constancy of the mass flow of the gas

$$m_{\rm g} = \rho_{\rm g} w_{\rm g} S$$
,  $S = \pi a^2$ .

According to the physics of the process, deposit of gas hydrates begins in the cross-section  $z = z_s$ , where the condition  $T_{\sigma} \leq T_s(p)$  is fulfilled. For the dependence of the equilibrium hydration temperature  $T_s$  on the pressure p, the formula [1]

$$T_{\rm s} = T_{\rm h*} \ln\left(\frac{p}{p_{\rm s*}}\right) + T_{\rm s*} \tag{6}$$

is usually used. The intensity of solid phase deposit is determined from the heat equilibrium condition at the gas-hydrate interface

$$l_{\rm h}j_{\rm h} = q_{\rm \sigma G} - q_{\rm g\sigma} \tag{7}$$

with account for the dependence of the wall temperature  $T_{\sigma}$  in the form  $T_{\sigma} = T_{s}(p)$  and the relations defining the heat transfer intensity from the flow to the inner wall of the duct:

$$q_{g\sigma} = \frac{\lambda_{g} \text{Nu} (T_{g} - T_{\sigma})}{2a}, \quad \text{Nu} = 0.021 \text{Re}^{0.8} \text{Pr}^{0.43}, \quad \text{Pr} = \frac{v}{K}, \quad K = \frac{\lambda_{g}}{\rho_{g} c_{g}},$$
(8)

and the heat transfer intensity between the pipe wall and the ground

$$q_{\sigma G} = \alpha_{\sigma G} \left( T_{\sigma} - T_{G} \right), \tag{9}$$

$$\frac{1}{2a\alpha_{\sigma G}} = \frac{1}{2\lambda_{h}} \ln \frac{a_{0}}{a} + \frac{1}{2\lambda_{1}} \ln \frac{a_{1}}{a_{0}} + \frac{1}{2\lambda_{2}} \ln \frac{a_{2}}{a_{1}} + \frac{1}{\lambda_{G}} \ln \left(\frac{h}{a_{2}} \sqrt{\left(\frac{h}{a_{2}}\right)^{2} - 1}\right).$$

Formula (9) takes into account the heat resistance of the layer of gas hydrate deposits, the pipe, and the heat-insulating wrapping.

In the part of the pipeline  $z \ge z_s$ , a decrease in the moisture concentration  $k_w$  according to Eq. (1), i.e., depletion of the flow of moisture will occur. Therefore, in some section  $z = z_* > z_s$  the moisture transfer intensity against the background of the depletion of the flow of moisture will be equal to the value of the moisture consumption determined by formulas (5) and (7), which in turn implies the onset of the regime of gas hydrate deposit under the conditions of moisture deficiency. In this process, in the part of the pipeline  $z \ge z_*$  the current temperature of the inner surface of solid deposits  $T_{\sigma}$  will be determined from formula (7), and to calculate the intensity  $j_h$  (taking into account the "stoichiometric" condition (5)), we write the following expression:

$$j_{\rm w} = D\rho_{\rm g}k_{\rm w}{\rm Sh}$$
,  ${\rm Sh} = 0.021{\rm Re}^{0.8}{\rm Pr}^{0.43}$ ,  ${\rm Pr} = \frac{\nu}{D}$ ,  $\nu = \frac{\eta_{\rm g}}{\rho_{\rm g}}$ . (10)

This expression was derived on the basis of the known relations for the heat transfer, the analogy of the processes of heat transfer and diffusion in a turbulent flow was used for obtaining formula (10).

Analysis of the Conditions for the Formation of Gas Hydrates with Account for the Introduction of Methanol. The formation of gas hydrates can occur in those parts of the pipeline where the temperature near the duct wall is lower than the dew point of the moisture contained in the gas. Suppose that in the presence in the flow of water droplets the vapor-droplet mixture is in the phase equilibrium state and, therefore, the partial pressure of the vapor  $p_{w,v}$  is equal to the equilibrium pressure of water saturation  $p_{w,s}(T_g)$  for the current value of the gas temperature  $T_g$ . For the temperature dependence of the saturation pressure, the expression [6]

$$p_{\rm w,v} = p_{\rm w*} \exp\left(-\frac{T_{\rm w*}}{T_{\rm g}}\right) \tag{11}$$

is usually used.

On the other hand, for the partial vapor pressure in the flow we can write the Clapeyron-Mendeleev equation

$$p_{\mathbf{w},\mathbf{v}} = \rho_{\mathbf{w},\mathbf{v}} R_{\mathbf{w},\mathbf{v}} T_{\mathbf{g}} \,. \tag{12}$$

Moreover, this relation also takes place for the whole of the gas flow in general

$$p_{\rm g} = \rho_{\rm g} R_{\rm g} T_{\rm g} \,. \tag{13}$$

Then, on the basis of (11)–(13), taking into account that  $p_g \approx p(p_{w,v} \ll p_g)$ , it is easy to obtain the expression for the equilibrium concentration of water vapors

$$k_{\rm w,v} = \frac{p_{\rm w} R_{\rm g}}{p R_{\rm w,v}} \exp\left(-\frac{T_{\rm w}}{T_{\rm g}}\right). \tag{14}$$

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To prevent the formation of gas hydrates, one can, firstly, maintain in the pipe the optimal temperature conditions (the temperature of the inner wall of the duct  $T_{\sigma}$  should be higher than the equilibrium temperature of hydrate formation  $T_{s}(p)$  corresponding to the pressure in the flow) and, secondly, it suffices to provide at the pipe inlet a gas dryness satisfying the condition

$$k_{\rm w,v0} \le \frac{p_{\rm w*} R_{\rm g}}{p_0 R_{\rm w,v}} \exp\left(-\frac{T_{\rm w*}}{T_{\rm G}}\right).$$
 (15)

But if we fail to provide a dryness satisfying condition (15), then hydration can be excluded by creating certain conditions disturbing the inequality  $T_{\sigma} \leq T_{s}(p)$ . One of such ways of excluding hydration is decreasing the temperature  $T_{s}$ . This can be achieved by going to lower transfer pressures. In practice, however, this method is in most cases inapplicable because of the decrease in the conveyance of the pipe. Therefore, the most real method is decreasing the equilibrium temperature of hydration  $T_{s}$  by introducing into the gas flow inhibitors, in particular, methanol.

It is known [7] that the gas hydration temperature depends on the inhibitor concentration  $k_{m,liq}$  in water  $T_s = T_s(k_{m,liq})$ . Therefore, in introducing methanol into the pipe one has to select its flow rate so that the hydration temperature is not higher than the minimal temperature of the inner wall of the pipe and the ground temperature  $T_s \le T_G$ .

In the presence of methanol in the composition of water droplets spraying the pipe walls the gas hydrate surface temperature will decrease. In so doing, the value of this temperature is determined by the current concentration of methanol in the spraying dropping liquid. Selecting the flow rate of methanol and, consequently, its concentration as well, one can attain such operating conditions of the pipe under which the temperature of its inner surface  $T_{\sigma}$  will turn out to be lower than the corresponding temperatures  $T_{G}$  and  $T_{g}$ . Then the heat required to dissociate the gas hydrate may come from the side of both the gas flow and the ground. With such a method of removing gas hydrate plaques water will additionally enter the flow due to the dissociation of gas hydrates. Therefore, the concentration of methanol in the composition of water droplets will decrease, which in turn will lead to an increase in the surface temperature of the hydrate layer  $T_{\sigma}$  in the lower parts of the pipeline; this effect should be taken into account in the further calculations.

Let on some cross-section methanol with a mass flow  $m_{m0}$  be introduced into the pipe. Mixing with the moisture present in the flow, the methanol will form a binary vapor-droplet mixture. Based on the data of [7], assume that the value of the temperature decrease linearly depends on the concentration of methanol in the droplets. Then for the dissociation temperature of gas hydrates the expression

$$T_{\rm m,s} = T_{\rm s} - T_{\rm m,s*} k_{\rm m,liq} \tag{16}$$

 $(T_{\rm s}$  is the value of the dissociation temperature in the absence of methanol) holds.

Suppose that the temperature  $T_{\sigma}$  on the sprayed surface of the layer is equal to the value in accordance with expression (16), and the intensity of destruction of the gas hydrate layer will be determined from the thermal balance condition (7). In so doing, for finding the intensity of heat transfer from the flow to the inner surface of the pipe wall or to the surface of the gas hydrate when it is present on the surface of the pipe wall, relations (8) hold. For the heat transfer intensity  $q_{\sigma G}$  between the interior wall of the pipe and the surrounding ground, we will use expression (9). The rate of change in the thickness of the hydrate layer on the pipe walls and the mass intensity of destruction of this layer  $j_{\rm h}$  are related by relation (4).

The moisture formed by the dissociation of the gas hydrate gets into the flow and leads to a decrease in the concentration of methanol in the vapor-droplet mixture. In so doing, the exudation intensity of water  $j_w$  is related to the dissociation intensity of gas hydrates by relation (5).

As is known, methanol does not enter into chemical reactions. Therefore, its mass flow downstream of the place of its introduction will be constant, and the mass flow of water will increase due to the additional ingress because of the dissociation of gas hydrates. For the quantitative description of this process, we write the mass equations for the methanol and moisture

$$m_{\rm g} \left( k_{\rm liq} k_{\rm m, liq} + (1 - k_{\rm liq}) \, k_{\rm v} k_{\rm m, v} \right) = m_{\rm m0} \,, \quad m_{\rm g} \, \frac{d}{dz} \left( k_{\rm liq} \left( 1 - k_{\rm m, liq} \right) + (1 - k_{\rm liq}) \, k_{\rm v} \left( 1 - k_{\rm m, v} \right) \right) = 2\pi a j_{\rm w} \,. \tag{17}$$

Moreover, suppose that the mass concentrations  $k_{m,liq}$  and  $k_{m,v}$  are related by relations that can be obtained on the basis of the Raoult and Dalton laws:

$$R_{\rm m}k_{\rm v}k_{\rm m,v}p = R_{\rm g}p_{\rm m,s}\left(T\right)N_{\rm m,liq}, \quad R_{\rm w}k_{\rm v}\left(1 - k_{\rm m,v}\right)p = R_{\rm g}p_{\rm w,s}\left(T\right)\left(1 - N_{\rm m,liq}\right),$$

$$N_{\rm m,liq} = \frac{k_{\rm m,liq}}{\mu_{\rm m}} \left(\frac{k_{\rm m,liq}}{\mu_{\rm m}} + \frac{\left(1 - k_{\rm m,liq}\right)}{\mu_{\rm w}}\right)^{-1}, \quad (18)$$

where  $p_{m,s}(T_g)$  and  $p_{w,s}(T_g)$  are equilibrium pressures for the methanol and water corresponding to the temperature  $T_g$  and approximated by the following expressions:

$$p_{\rm m,s} = p_{\rm m*} \exp\left(-\frac{T_{\rm m*}}{T_{\rm g}}\right), \ p_{\rm w,s} = p_{\rm w*} \exp\left(-\frac{T_{\rm w*}}{T_{\rm g}}\right).$$

In calculating the dissociation intensity of gas hydrates on the interior walls of the pipe, one has to know in each section the value of the mass content of methanol in the droplets  $k_{m,liq}$  determining, according to (16), the change in the equilibrium hydration temperature. Equations (17) and (18) represent a system consisting of four equations with four unknowns. Therefore, the given system can be solved uniquely for  $k_{m,liq}$ . Omitting awkward manipulations, we write the expression obtained for finding  $k_{m,liq}$ 

$$A_1 k_{m,liq}^3 + B_1 k_{m,liq}^2 + C_1 k_{m,liq} + E_1 = 0, \qquad (19)$$

where

$$A_{1} = BC^{2}D - BCD - BC + B - R(C - 1)^{2}; \quad B_{1} = A - 2AC + AC^{2} - B + 2BC - 2BC^{2}D + BCD - AB$$
$$+ ABCD + ABC - ABC^{2}D + 2RC^{2} + RB - (2 + B)RC; \quad C_{1} = 2AC - 2AC^{2} - BC + BC^{2}D - AB + ABC^{2}D$$
$$- C^{2}R + RBC; \quad E_{1} = AC^{2} + ABCD; \quad A = \frac{m_{m0}}{m_{g}}; \quad B = \frac{R_{g}p_{m,s}}{R_{m}p}; \quad C = \frac{\mu_{m}}{\mu_{w}}; \quad D = \frac{p_{w,s}R_{m}}{p_{m,s}R_{w}}; \quad R = k_{w}.$$

Expression (19) represents a cubic equation with real coefficients, which can have several roots (including complex ones). But we will be interested in those roots that lie in the interval (0; 1), since the values of  $k_{m,liq}$  lying outside this interval have no physical meaning.

Using expressions (17) and (18), we can obtain the value of the required flow rate of methanol for preventing hydrate deposits. In the absence of hydration the flow rate of moisture  $m_W$  will be preserved along the full length of the pipeline. Then in accordance with Eq. (17) at  $j_W = 0$  we can write

$$m_g \left[ k_{\rm liq} \left( 1 - k_{\rm m, liq} \right) + \left( 1 - k_{\rm liq} \right) k_{\rm v} \left( 1 - k_{\rm m, v} \right) \right] = m_{\rm w0} \,. \tag{20}$$

Let the concentration of methanol providing a decrease in the hydration temperature to the required value  $T'_{m,s} = T_G$  (to the minimum value of the temperature of the interior wall of the pipe, which is close to the temperature



Fig. 1. Pressure (a) and temperature (b) distribution along the pipeline at the initial instant of time when the gas hydrate layer is absent. The hydration conditions are fulfilled at  $z \ge z_s$ . p, MPa;  $t_g$ ,  $t_s$ ,  $t_G$ , <sup>o</sup>C; z, km.

of the surrounding ground) be equal to  $k'_{m,liq}$ . Then on the basis of Eqs. (18) we can write the expressions for the mass concentration of vapor in the gas flow and the mass concentration of methanol in the vapor-methanol mixture

$$k'_{\rm v} = \frac{p_{\rm m,s} (T_{\rm G}) N'_{\rm m,liq} R_{\rm g}}{pk'_{\rm m,v} R_{\rm m}}, \quad k'_{\rm m,v} = \frac{1}{1 + \frac{p_{\rm w,s} (T_{\rm G}) (1 - N'_{\rm m,liq}) R_{\rm m}}{p_{\rm m,s} (T_{\rm G}) N'_{\rm m,liq} R_{\rm w}}}.$$
(21)
  
asis of (20) we can obtain

On the other hand, on the basis of (20), we can obtain

$$k'_{\rm liq} = \frac{\frac{m_{\rm w0}}{m_{\rm g}} - k'_{\rm v} \left(1 - k'_{\rm m,v}\right)}{\left(1 - k'_{\rm m,liq}\right) - k'_{\rm v} \left(1 - k_{\rm m,v}\right)}.$$
(22)

Substituting (21) and (22) into the first equation of (17), we obtain a formula for calculating the minimum rate of flow of methanol at which gas hydrate deposits are not formed on the interior wall of the pipe

$$m'_{m0} = m_{g} \left( k'_{liq} \, k'_{m,liq} + (1 - k'_{liq}) \, k'_{v} \, k'_{m,v} \right) \,. \tag{23}$$

**Results of the Calculations.** In the numerical calculations, we used the following data: L = 10 km,  $a_0 = 0.11 \text{ m}$ ,  $T_G = 279 \text{ K}$ ,  $c_g = 2911 \text{ J/(kg·K)}$ ,  $R_g = 450 \text{ J/(kg·K)}$ ,  $\lambda_g = 0.03 \text{ J/(m·sec·K)}$ ,  $\eta_g = 11 \cdot 10^{-6} \text{ kg/(sec·m)}$ ,  $\lambda_h = 2.2 \text{ J/(m·sec·K)}$ ,  $\lambda_1 = 58.24 \text{ J/(m·sec·K)}$ ,  $\lambda_G = 2 \text{ J/(m·sec·K)}$ ,  $p_{w*} = 3.94 \cdot 10^9 \text{ Pa}$ ,  $T_{w*} = 4228 \text{ K}$ ,  $R_v = 461 \text{ J/(kg·K)}$ ,  $l_w = 1.7 \cdot 10^6 \text{ J/kg}$ ,  $p_0 = 3.2 \text{ MPa}$ ,  $T_{g0} = 323.15 \text{ K}$ ,  $m_g = 0.683 \text{ kg/sec}$ ,  $V_g = 0.89 \text{ m}^3/\text{sec}$ ,  $k_{w0} = 3 \cdot 10^{-3}$ ,  $p_{s*} = 3.2 \text{ MPa}$ ,  $T_{s*} = 282.65 \text{ K}$ ,  $T_{h*} = 8.28 \text{ K}$ ,  $\rho_h = 917 \text{ kg/m}^3$ ,  $k_{g,h} = 0.1$ ,  $l_h = 2.3 \cdot 10^6 \text{ J/kg}$ .

Figure 1 shows the distributions of the gas pressure and temperature (the temperature of the pipe wall practically coincides with the gas temperature) over the length of the pipeline at the "zero" instant of time when gas hydrates on the duct walls are absent. For the given composition of the gas in the pipeline, the value of the equilibrium hydration temperature is  $T_s(p) = 282$  K (9°C). Figure 1b shows the line corresponding to this temperature. It is attained in the cross-section with the coordinate  $z_s \approx 2$  km.

Figure 2 presents the results of the calculation of the process of destruction of the hydrate layer, as well as the corresponding distributions of the mass content of methanol in droplets  $k_{m,liq}$  over the length of the pipeline. Numbers by the solid curves correspond to the time (in days) from the beginning of feeding the inhibitor with a mass flow  $m_{m0} = 30$  kg/day. The dashed curve shows the profile of the gas hydrate layer at the initial instant of time (the layer was formed in 60 days). It is seen from the graphs that upon the dissociation of the gas hydrate layer two characteristic features are observed. The first feature is the fact that in the front part the gas hydrate layer is destroyed and, as a consequence of this, the left edge of the sclerotic plaque is displaced to the right boundary of the pipe. This de-



Fig. 2. Change with time in the hydrate layer thickness (a) and methanol content in droplets (b) upon the injection of methanol into the pipe ( $m_{\rm m0} = 30 \, \text{kg/day}$ ).  $\delta$ , cm; z, km.



Fig. 3. Distribution of the temperature of the gas, the inner surface of the pipe, and the ground and equilibrium hydration temperature distribution upon the introduction into the pipe of methanol with a mass content  $m_{\rm m0} = 30$  kg/day.  $t_{\rm g}$ ,  $t_{\rm G}$ ,  $t_{\rm G}$ ,  $t_{\rm m,s}$ , <sup>o</sup>C. z, km.

struction is due to the decrease in the equilibrium hydration temperature  $T_{m,s}$  (and, consequently, in the surface temperature of the phase transitions  $T_{\sigma}$  as well) because of the presence of methanol in the liquid droplets present in the gas flow. It is seen that in the cross-section (Fig. 2b) corresponding to the left boundary of the hydrate layer (in the following, we will denote the cross-section coordinate as  $z = z_h$ ) the mass content is  $k_{m,liq} \approx 0.1$ , which, according to the data of [7], leads to a decrease in the equilibrium hydration temperature at  $k_{m,liq} = 0.1$  from  $t_{m,s} = 9^{\circ}$ C to  $t_{m,s} = 5^{\circ}$ C. As a result of this, inflow of heat to the surface of the layer of solid deposits from the gas flow and the ground arises and promotes the dissociation of hydrates near the cross-section  $z = z_h$ .

The second feature is the fact that in the parts situated down the pipeline the thickness of the gas hydrate plaque increases with time (Fig. 2a). The reasons for this fact are explained by the character of the curves in Fig. 3 presenting the distributions of the gas temperature  $t_g$ , the temperature of the inner surface of the pipe  $t_{\sigma}$ , and the equilibrium hydration temperature  $t_{m,s}$  that reached a steady-state value ten days after the beginning of feeding methanol. Dissociation of gas hydrates leads to an exudation of water which, entering the flow, decreases the concentration of methanol in droplets and thus leads to a decrease in the  $k_{m,liq}$  value (this fact is illustrated in Fig. 2b below the cross-section  $z = z_h$ ). Then, according to Eq. (16), the value of temperature  $t_{m,s}$  increases. This leads to the fact that in some cross-section the temperature of the inner surface of the gas hydrate layer  $t_{\sigma}$  ( $t_{\sigma} = t_{m,s}$ ) increases to the ground temperature  $t_G$  (see Fig. 3) and then exceeds it. This means that the heat flow here is directed from the surface into the ground.

At the same time, because of the heat outflow from the gas its cooling occurs. This leads to the fact that after the cross-section  $z = z_s$  the gas and surface temperatures become equal, and the heat transfer between the gas and the hydrate layer terminates. Thus, it is seen that after the cross-section  $z = z_s$  the heat flow  $q_{\sigma G}$  is directed into the



Fig. 4. Change with time in the hydrate layer thickness (a) and in the content of methanol in droplets (b) upon the introduction into the pipe of methanol  $(m_{\rm m0} = 70 \text{ kg/day})$ .  $\delta$ , cm; z, km.



Fig. 5. Distribution of the temperatures of the gas, the inner surface of the pipe, and the ground, and equilibrium hydration temperature distribution upon the introduction into the pipe of methanol with a mass content  $m_{\rm m0} = 70$  kg/day that reached steady-state values after 10 days.  $t_{\rm g}$ ,  $t_{\rm G}$ ,  $t_{\rm m,s}$ , <sup>o</sup>C. *z*, km.

ground, and  $q_{g\sigma} = 0$ . This, according to (7), leads to a repeated formation of a gas hydrate layer on the pipe walls after the cross-section  $z = z_s$ .

Such behavior of the curves in Fig. 2 is likely to be due to the fact that the value of the mass flow of methanol  $m_{m0}$  taken in the calculations does not provide the required concentration of methanol in droplets  $k_{m,liq}$ . Therefore, it is necessary to take a larger value of  $m_{m0}$ , at which the gas hydrate would dissociate along the full length of the pipeline and there would be no repeated formation of gas hydrates in the lower parts of the pipeline. The investigation performed indicates that at  $m_{m0} = 70 \text{ kg/day}$  this is feasible. Figure 4 shows the change with time in the gas hydrate layer thickness  $\delta$  and in the mass content of methanol. Judging by the behavior of the curves, dissociation of gas hydrates occurs within the limits of the initial boundaries of gas hydrate deposits and their repeated formation outside the boundaries of this region is not observed. In so doing, the process is faster in the initial part of gas hydrate deposits where the dissociation intensity is determined by the heat inflow from both the gas and the ground (Fig. 5), whereas in the lower parts, only from the ground.

The calculations by formula (23) show that the value of the minimal flow rate of methanol at which the formation of gas hydrates is excluded is  $m'_{m0} = 63 \text{ kg/day}$ . Note that under operating conditions with continuous feeding of the inhibitor during two months the total consumption of methanol is 3780 kg.

In practice periodic injection of inhibitors (by certain portions) is more suitable. The point of this technique is that methanol is pumped into the gas flow at regular intervals, during which there occurs an insignificant build-up



Fig. 6. Change in the gas hydrate layer thickness in the regime of periodic injection of methanol. Numbers by the curves denote the time in hours from the beginning of injecting methanol into the pipe.  $\delta$ , cm; *z*, km.

of gas-hydrate deposits (for our example, of thickness about 1 mm), i.e., the thus formed layer of gas hydrates has no appreciable influence on the thermodynamic characteristics of the gas flow.

Figure 6 gives curves illustrating the change in the gas hydrate layer thickness in the case of periodic injection of methanol. The operating period of the pipeline without injection of methanol is two days. During this time a layer of solid deposits is formed on the pipe walls (dashed lines in Fig. 6). The duration of feeding the inhibitor with  $m_{\rm m0} = 70$  and 150 kg/day (Fig. 6) is 48 and 24 hours, respectively. In both cases, in the allotted time the gas hydrates are completely removed from the pipe walls. In such a regime of feeding the inhibitor, over a period of two months the total consumption of methanol will be 2100 kg in the first case and 3000 kg in the second case, i.e., this regime of feeding methanol permits decreasing the total consumption of the inhibitor used.

**Conclusions.** A mathematical model of the processes proceeding in a gas pipeline during its operation with account for the phase transitions, hydration, and heat transfer between the pipe and the surrounding ground has been developed. The efficiency of removing gas hydrate deposits by injecting inhibitors (methanol) into the gas flow has been shown. It has been established that in this case there occurs destruction of the layer of gas hydrate deposits in the front part and subsequent displacement of the front edge of gas hydrates to the mouth of the pipe; in its lower parts repeated build-up of gas hydrate deposits occurs.

## NOTATION

a, radius of the flow section of the pipeline, m;  $a_0$ , inner radius of the pipe, m;  $a_1$ , outer radius of the pipe, m;  $a_2$ , outer radius in the presence of heat insulation, m;  $c_g$ , specific heat capacity of the gas, J/(kg·K); D, diffusion coefficient, m<sup>2</sup>/sec; f, hydraulic friction force per unit length, N/m; h, depth of laying the pipeline, m;  $j_w$  and  $j_h$ , absorption (exudation) intensity of water upon the formation (dissociation) of gas hydrates and formation (dissociation) intensity of gas hydrates, kg/m<sup>2</sup>;  $k_w$  and  $k_{g,h}$ , mass content of water in the gas flow and gas molecules forming gas hydrates;  $k_{w,v}$ , mass content of water vapors;  $k_{w0}$  and  $k_{w,v0}$ , mass contents of water and water vapors at the inlet to the pipe;  $k_{\text{liq}}$ ,  $k_{\text{m}}$ ,  $k_{\text{m,v}}$ , and  $k_{\text{m,v}}$ , mass concentrations of droplets, the mixture of methanol vapors and moisture in the flow, methanol in droplets, and methanol in the mixture of water vapors and methanol, respectively; K, thermal diffusivity, m<sup>2</sup>/sec;  $l_w$ ,  $l_m$ , and  $l_h$ , specific heat capacities of vaporization, methanol vaporization, and hydration, J/kg; L, pipeline length, km;  $m_w$ ,  $m_g$ ,  $m_{m0}$ , and  $m_{v0}$ , mass rates of flow of water, gas, methanol, and water vapors at the inlet to the pipe, kg/sec;  $N_{m,lia}$ , molar concentration of methanol in droplets; Nu, Nusselt criterion; p, pressure, Pa;  $p_0$ , pipe inlet pressure, Pa;  $p_{w,v}$ ,  $p_{m,s}(T)$ , and  $p_{w,s}(T_g)$ , partial pressure of water vapors in the flow, equilibrium pressures of water and methanol saturation, Pa;  $p_{w^*}$ ,  $p_{s^*}$ ,  $p_{m^*}$ , empirical parameters, Pa; Pr, Prandtl number;  $Q_{g\sigma}$ , intensity of heat transfer from the gas flow to the wall, J/m;  $q_{g\sigma}$  and  $q_{\sigma G}$ , intensity of heat transfer from the gas flow to the pipe wall and from the wall to the surrounding ground,  $J/m^2$ ;  $R_g$ ,  $R_{w,v}$ ,  $R_m$ , and  $R_w$ , reduced gas constants for the gas flow, water vapor, methanol, and water, J/(kg·K); Re, Reynolds number; S, pipe cross-section area, m<sup>2</sup>; Sh, Sherwood number; T, temperature, K; t, temperature, <sup>o</sup>C;  $T_{g0}$ , gas temperature at the inlet to the pipe, K;  $T_{w*}$ ,  $T_{m*}$ ,  $T_{m,s*}$ ,  $T_{s*}$ ,  $T_{h*}$ ; empirical parameters, K;  $V_g$ , gas flow rate, m<sup>3</sup>/sec;  $w_g$ , gas velocity, m/sec; z, coordinate, m;  $z_s$ , coordinate in which equilibrium hydration conditions are fulfilled, m;  $\alpha_{\sigma G}$ , coefficient of heat transfer form the wall to the ground, J/(m<sup>2</sup>·sec·K);  $\chi$ , hydraulic friction force per unit area, N/m<sup>2</sup>;  $\delta$ , thickness of the layer of gas hydrate deposits, m;  $\eta_g$ , dynamic viscosity, kg/(sec·m);  $\lambda$ , hydraulic resistance coefficient, kg/(m·sec);  $\lambda_g$ ,  $\lambda_b$ ,  $\lambda_1$ ,  $\lambda_2$ ,  $\lambda_G$ , heat conductivity coefficients of the gas, gas hydrates, pipe wall material, heat insulation, and ground, J/(m·sec·K);  $\mu_m$  and  $\mu_w$ , molecular masses of methanol and water, kg/mole; v, kinematic viscosity, m<sup>2</sup>/sec;  $\rho_g$ ,  $\rho_h$ , and  $\rho_{w,v}$ , density of the gas, gas hydrates, and water vapors in the flow, kg/m<sup>3</sup>;  $\tau$ , time, sec. Superscripts: ', parameters used in calculating the minimal flow rate of methanol preventing the formation of gas hydrates; \*, empirical parameter. Subscripts: g, gas; G, ground; h, gas hydrate; liq, liquid in the form of droplets; m, methanol; s, equilibrium parameter value; v, vapor; w, water;  $\sigma$ , inner surface of the pipe; 0, parameter value at the inlet to the pipe.

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