HYDRATE FORMATION PROCESS WITH CONSIDERATION OF HEAT AND MASS EXCHANGE

V. M. Bilyushov, É. A. Bondarev,
and V. I. Maron

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Results are offered from numerical experiments involving hydrate formation in pipelines during quasisteady state flow of a moist gas.

A mathematical model describing the process of hydrate formation in pipeline transport of a moist gas was proposed in [1]. Its main difference from the model of [2, 3] is its simultaneous consideration of both factors which play an important role in hydrate formation, namely heat- and mass-transport processes. Such a treatment is possible if we assume that the temperature on the phase transition boundary depends not only on pressure in the system, but also on the water vapor concentration at the boundary.

This dependence is given by the equation of state of the vapor—gas mixture located in equilibrium with the hydrate:

$$\Theta_\omega = \left\{1 + \frac{\mu_g}{\mu_w}\,\frac{z_w(P,\ T_\omega)}{z_g(P,\ T_\omega)}\left[\frac{P}{P_w^h(P,\ T_\omega)} - 1\right]\right\}^{-1}. \tag{1}$$

The process of hydrate formation (decomposition) is controlled by heat and mass exchange between the gas and the hydrate.

If we neglect moisture transfer between the gas and hydrate, then the rate of hydrate formation or decomposition will be determined by heat exchange between the gas and hydrate:

$$\frac{dS_\omega}{dt} = \frac{4\pi\lambda_h(T_\omega - T_e)}{L_h\rho_h\left(\ln\dfrac{S_\omega}{S_0} - \dfrac{2\lambda_h}{\lambda_s G}\right)} - \frac{2\alpha\sqrt{\pi S_\omega}\,(T_\omega - T)}{L_h\rho_h}. \tag{2}$$

If we neglect the effect of heat exchange the process goes in one or the other direction depending on the ratio between the water vapor concentrations in the gas and on the phase boundary:

$$\frac{dS_\omega}{dt} = \frac{2\beta\sqrt{\pi S_\omega}}{\rho_h\Theta_h v}(\Theta_\omega - \Theta). \tag{3}$$

For simultaneous consideration of both factors, i.e., when the temperature T_ω and concentration Θ_ω on the phase boundary are interrelated, conditions (2) and (3) must be satisfied simultaneously. Then from those conditions we obtain an expression for the unknown concentration on the gas—hydrate phase boundary

$$\Theta_\omega = \Theta + \frac{\Theta_h v}{\beta L_h\sqrt{S_\omega}}\left[\frac{2\sqrt{\pi}\lambda_h(T_\omega - T_e)}{\ln\dfrac{S_\omega}{S_0} - \dfrac{2\lambda_h}{\lambda_s G}} - \alpha\sqrt{S_\omega}(T_\omega - T)\right]. \tag{4}$$

Using Eq. (1) to eliminate Θ_ω, we obtain the dependence of temperature on the gas—hydrate phase boundary upon flow parameters: pressure, gas temperature, water vapor concentration in the gas, as well as the area of the "live" channel section and the thermal resistance of the soil:

$$\Theta + \frac{\Theta_h v(P,\ T)}{\beta L_h\sqrt{S_\omega}}\left[\frac{2\sqrt{\pi}\lambda_h(T_\omega - T_e)}{\ln\dfrac{S_\omega}{S_0} - \dfrac{2\lambda_h}{\lambda_s G}} - \alpha\sqrt{S_\omega}(T_\omega - T)\right] = \tag{5}$$

$$= \frac{a(P,\ T_\omega)}{\dfrac{P}{P_w^h(P,\ T_\omega)} - 1 + a(P,\ T_\omega)},\quad a(P,\ T_\omega) = \frac{\mu_w}{\mu_g}\,\frac{z_g(P,\ T_\omega)}{z_w(P,\ T_\omega)}.$$

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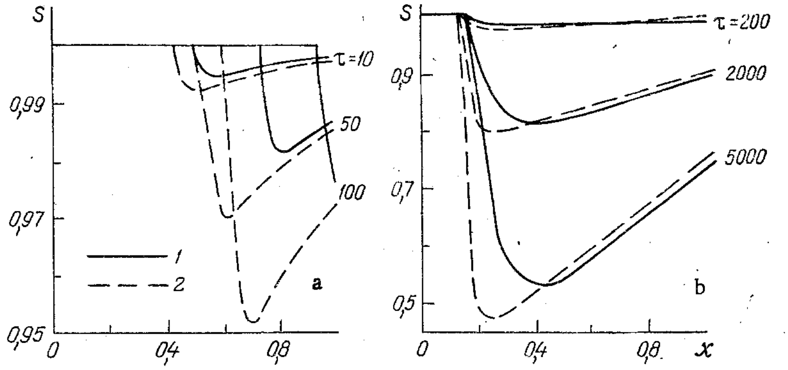

Fig. 1. Change in "live" section of pipeline (a) and well (b) with time for initial concentrations $\Theta_0=5\cdot10^{-5}$ (a) and $\Theta_0=5\cdot10^{-4}$ (b): a) 1, α = 200 W/m²·K; 2, 661; b) 1, α = 400 W/m²·K; 2, 1970.

For a quasisteady state flow regime to which we will limit our examination in the present study, the distribution of pressure, gas temperature, and water vapor concentration in the gas is found from a system of equations [1]:

$$\frac{dP}{dx}=\frac{M^2v}{S_\omega^3}\frac{dS_\omega}{dx}-\frac{g\sin\gamma}{v}-\frac{\sqrt{\pi}\psi M^2v}{4S_\omega^{2,5}},$$

$$\frac{dT}{dx}=-\frac{2\alpha\sqrt{\pi S_\omega}}{C_pM}(T-T_\omega)+\frac{\sqrt{\pi}\psi M^2v}{4C_pS_\omega^{2,5}}\left[v-T\left(\frac{\partial v}{\partial T}\right)_p\right]+\frac{T}{C_p}\left(\frac{\partial v}{\partial T}\right)_p\left[\frac{M^2v}{S_\omega^3}\frac{dS_\omega}{dx}-\frac{g\sin\gamma}{v}\right], \quad (6)$$

$$\frac{d\Theta}{dx}=\frac{2\beta\sqrt{\pi S_\omega}}{Mv}(\Theta_\omega-\Theta).$$

We calculate the water vapor pressure above the hydrate with the expression [4]

$$P_W^h=\exp\left(24{,}87-\frac{6235}{T_\omega}-0{,}1593\ln P\right). \quad (7)$$

To determine the thermal resistance of the disturbed ground G we use the method described in [5], according to which

$$G=\max\left\{\frac{1}{\ln\left(\frac{H}{R_0}+\sqrt{\frac{H^2}{R_0^2}-1}\right)};\quad\frac{R-1}{R\ln R-R+1}\right\}.$$

The radius over which the ground is perturbed is found by solution of the equation

$$\frac{dR}{dt}=\frac{\varkappa_s}{R_0^2}\,\frac{\ln R+\frac{1}{R}-1}{\frac{R\ln R}{6}\left(1+\frac{1}{R}+\frac{1}{R^2}\right)-\frac{R}{4}+\frac{1}{4R}}. \quad (8)$$

To complete the system of equations it is necessary to specify the dependence of the transport coefficients α, β, and ψ on the defining parameters. We will assume the latter to be the same as for gas flow in a pure tube with no phase transition present.

The heat liberation coefficient α from the gas to the hydrate can be calculated with Mikheev's criterial expression

$$\mathrm{Nu}=0{,}021\,\mathrm{Re}^{0.8}\,\mathrm{Pr}^{0.43}. \quad (9)$$

The mass transfer coefficient β can be defined commencing from the analogy between heat and mass exchange coefficients:

$$\beta=\frac{\alpha D(P)}{\lambda}. \quad (10)$$

We take the hydraulic resistance coefficient ψ the same as for a plain tube.

The algorithm for numerical calculation is constructed in the following manner.

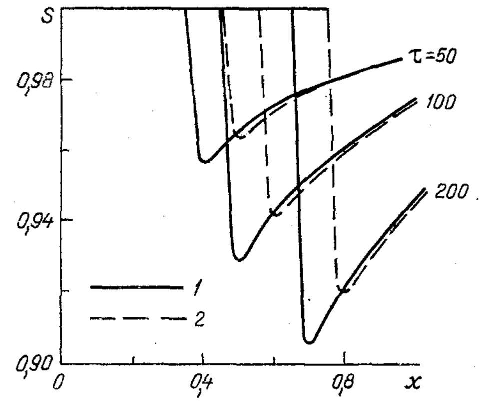

Fig. 2

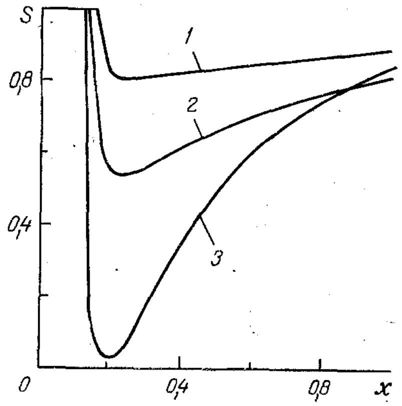

Fig. 3

Fig. 2. Effect of external temperature on hydrate formation process in pipeline. Initial concentration $\Theta_0 = 6 \cdot 10^{-5}$, heat liberation efficient $\alpha = 661$ W/m²·K: 1) external temperature $T_e = 263$ K; 2) $T_e = 266$ K.

Fig. 3. Profile of well "live" section at time $\tau = 2000$. Initial concentration $\Theta_0 = 5 \cdot 10^{-4}$; mass flow rates 5 (1), 10 (2), 15 kg/sec (3).

1. For an area of the "live" tube section and ground thermal perturbation radius fixed in time, using the initial conditions

$$P(0) = P_0, \quad T(0) = T_0, \quad \Theta(0) = \Theta_0 \tag{11}$$

and Eqs. (1) and (5), by integration of Eq. (6) we find the distribution of pressure, gas temperature, and water vapor concentration in the gas over tube length.

2. Integration of Eqs. (8) and (3) using the distributions of pressure, temperature, and concentration and initial conditions

$$R(0) = R_0, \quad S_\omega(0) = S_0 \tag{12}$$

lets us find the radius of ground thermal perturbation and the distribution of the "live" tube section $S_\omega(x)$ for the following moment in time.

3. Returning to step 1, we find the distribution of pressure, temperature, and concentration over tube length for the following moment in time. Then again substituting the values obtained for $P(x)$, $T(x)$, and $\Theta(x)$ in Eq. (3), we make the following step in time, etc.

Below we will present results of numerical calculations of the process of hydrate formation in wells and pipelines. Calculations were performed for the following parameters:

for a well: diameter 0.1 m, mass flow rate 5 kg/sec, well depth 2000 m, input pressure 20 MPa, input temperature 320 K, surrounding rock temperature at well face 323 K, geothermal gradient 0.025 deg/m;

for pipeline: diameter 1.4 m, mass flow rate 500 kg/sec, input pressure 5.5 MPa, pipeline length 100 km, installation depth 1.8 m, thermal conductivity and diffusivity of soil, 1.7 W/m·K and $7.7 \cdot 10^{-7}$ m²/sec.

The calculation results are presented in the dimensionless coordinates $\bar{x} = \frac{x}{l}$, $\tau = t4\lambda_h T_0/\rho_h L_h R_0^2$, $\bar{S} = S_\omega/\pi R_0^2$.

Analysis of the results shows that hydrate formation in wells and pipelines is possible if the input concentration of water vapor in the gas exceeds the minimum required for the given conditions $\Theta_0^{\min}$, which depends on a number of parameters such as the external temperature (for a well, the face temperature and geothermal gradient), the heat liberation coefficient, and the thermal conductivities of the hydrate and surrounding soil. For example, for an increase in the temperature of the ground surrounding the pipeline from 263 to 270 K the smallest input concentration at which hydrate formation will commence increases from $4 \cdot 10^{-5}$ to $7.7 \cdot 10^{-5}$. The gas dew point then increases from −21 to −14°C.

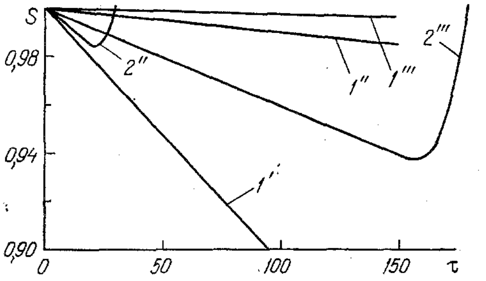

Fig. 4

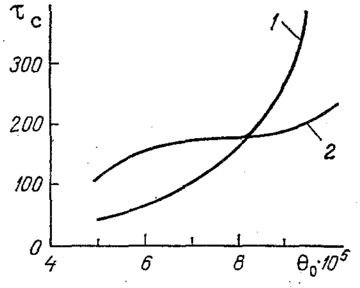

Fig. 5

Fig. 4. Profile of pipeline "live" section for various mass flow rates. Initial concentration $\Theta_0 = 5 \cdot 10^{-5}$, gas mass flow rates M = 156 (1), 500 kg/sec (2), coordinate X = 0.1 (1'); 0.5 (1", 2"); 0.8 (1'", 2'").

Fig. 5. Self cleaning time of well and pipeline vs initial water vapor concentration in gas: 1) well, α = 1970 W/m²·K; 2) pipeline, α = 200 W/m²·K.

The hydrate layer is distributed nonuniformly over the length of the tube (Fig. 1). For a given time there is a clearly expressed maximum in the hydrate layer thickness. The position of the maximum does not coincide with the position of the forward edge of the hydrate layer. As time passes the leading edge and the maximum in hydrate layer thickness move down the flow. The velocity of this motion depends on the input concentration, decreasing with increase in the latter. For significant concentrations there is practically no displacement of the leading edge or maximum (Fig. 1b). The hydrate layer then grows monotonically with time, which in the case of long-term use of a pipeline with unchanging gas parameters can lead to total blockage of the tube.

Increase in temperature of the surrounding soil leads not only to increase in the dew point of the gas transportable without hydrate formation, but also to a slowing of the hydrate formation rate. With increase in temperature of the surrounding ground the hydrate layer moves more rapidly toward the mouth of the pipe while it has a lower thickness (Fig. 2).

The coefficient of heat liberation from the gas to the hydrate α (see Fig. 1) has a significant effect on the process of hydrate formation and decomposition in wells and pipelines. In the presence of phase conversions the transport coefficients in the tube will differ from the transport coefficients in a simple tube. However, there are no experimental data or reliable methods for calculation of heat and mass transport and hydraulic resistance coefficients under phase change conditions. Therefore, the calculations basically used values of the transport coefficients obtained for gas flow in a tube without phase transitions. In addition the heat liberation coefficient and related mass liberation coefficient were subjected to variation.

The calculations showed that with increase in the heat liberation coefficient the leading edge of the hydrate layer is located closer to the input section and the thickness of the hydrate layer increases significantly.

Hydrate formation in tubes depends significantly on the heat and mass liberation coefficients, which in turn are determined by the mass flow rate of the gas. On the other hand the gas flow rate determines the gas flow parameters and through them affects the hydrate formation process. In connection with this calculations of the hydrate formation process were performed for a well (Fig. 3) and pipeline (Fig. 4) for various gas flow rates.

The calculations show that increase in gas flow rate in the well leads to an insignificant displacement of the leading edge and maximum thickness of the hydrate layer up the flow. The rate of hydrate formation then increases abruptly and the danger of complete blockage of the tube "live" section rises rapidly. On the other hand, increase in flow rate in a pipeline leads to a decrease in hydrate formation rate and complete decomposition of the hydrates formed over time. At low gas flow rates hydrate formation occurs continuously and the hydrates do not decompose over time, which can lead to complete blockage of the pipeline section, making it unusable.

The different effects on hydrate formation of increase in gas flow rate in a well and a pipeline can be explained in the following manner. On the one hand, increase in gas flow rate intensifies mass exchange between the gas and hydrate, which for constant thermodynamic parameters of the gas flow should lead to an increase in hydrate formation rate. On the other hand, increase in gas flow rate to the well known limit [6] causes an increase in temperature of the gas flow and consequently, a decrease in the hydrate formation rate.

The calculations show that for low input water vapor concentrations in the gas self-cleaning of previously formed hydrate residue is possible in pipelines and wells (Fig. 5). For significant water vapor concentrations in the gas the well or pipelines will not be cleaned of hydrates, if the parameters of the gas transported are not changed. To clean the pipeline of hydrates in this case it is necessary to either increase the gas flow rate or supply to the input section a gas with much lower dew point.

NOTATION

P, T, v, M, pressure, temperature, specific volume, and mass flow rate of gas; Θ, Θ_ω, Θ_h, water vapor concentrations in gas flow, on phase change boundary, and in hydrate; T_ω, temperature on phase change boundary; C_p, specific heat of gas; α, β, ψ, heat exchange, mass exchange, and hydraulic resistance coefficients; S_ω, tube "live" section area; R_0, S_0, l, radius, cross sectional area, and length of tube; ρ_h, λ_h, L_h, density, thermal conductivity coefficient, and heat of formation of hydrate; λ_s, $\varkappa_s$, G, thermal conductivity, diffusivity, and resistance of soil; t, x, time and coordinate along tube axis; H, pipeline installation depth; R, dimensionless (referenced to R_0) radius of ground thermal perturbation; T_e, external temperature; λ, gas thermal conductivity; p^h_w, water vapor pressure above hydrate; D, water vapor diffusion coefficient in gas; μ_g, z_g, μ_w, z_w, molecular weight and supercompressibility coefficient of gas and water vapor respectively.

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