HYDRATE FORMATION DURING GAS FLOW IN PIPES

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The problem of crystalline hydrate formation during nonisothermal stationary flow of an ideal gas in a circular inclined pipe is studied. A model is proposed for the growth of the hydrate layer on the pipe walls.

In the practice of extraction and transport of natural gases, there is observed plugging of wells and pipelines by crystalline compounds of these gases with water (hydrates) [1].

It is well known [1] that the existence of a gas hydrate of given composition is determined by certain critical temperatures T_F and pressures p which are related by the semiempirical expression

$$T_{\rm F} = \beta_1 \ln p + \beta_2. \tag{1}$$

It is obvious that the formation of hydrates during gas flow in pipes is associated with cooling of the wet gas below the critical temperature $T_{\rm F}$.

We consider hydrate formation during flow of an ideal gas in a circular pipe when the external temperature T_{ex} is definitely lower than T_F and the gas is completely saturated with moisture.

Let the gas temperature T_0 in the entrance section be constant and greater than T_F . Then cooling of the gas during its motion leads to a situation where, starting at some distance from the entrance, formation of a hydrate layer begins on the walls of the pipe reducing the open cross section.

The specific heat of hydrate formation is of the same order of magnitude as the specific heat of ice formation so that the rate of growth of the hydrate layer is markedly lower than the gas velocity in the pipe. One can therefore assume one has steady-state motion of a gas in a pipe of variable cross section S(x). Equations describing such motion are [2]

$$S\frac{dp}{dx} + S\gamma\sin\varphi + \frac{\pi}{4}\psi\left(\frac{S}{\pi}\right)^{1/2}\frac{\gamma\omega^2}{g} = 0,$$
 (2)

$$\frac{d}{dx}\left[S\left(z+c_{p}T\right)\right]=2\pi R_{0}\frac{K_{ex}}{S\gamma\omega},$$
(3)

$$\frac{\partial}{\partial x} (S\gamma w) = m^*(x, t), \tag{4}$$

$$p = RT\gamma/g.$$
 (5)

The quantity $m^*(x, t)$ is the amount of gas converted into hydrate per unit time. It is clear that m^* is proportional to the rate of formation of the hydrate layer and is consequently a quantity which is negligibly small in comparison with the mass flow of gas. We then have from Eq. (4)

$$S\gamma w = G = \text{const.}$$
 (6)

The absence of convective terms in Eqs. (2) and (3) is justified by the fact that the gas velocity is ordinarily much below the velocity of sound [2].

We consider a cross section of the pipe in which a hydrate layer is formed. To determine the law for its motion, it is necessary to solve a problem with moving boundaries for the equation of thermal conductivity under the following boundary conditions:

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Fig. 1. Variation of hydrate thickness along pipeline for a gas flow rate of $1 \cdot 10^6 \text{ m}^3/\text{day}$: 1) t = 300 sec; 2) t = 43,740 sec; 3) t = 131,220 sec.

Fig. 2. Variation of hydrate thickness along pipeline at t = 4860 sec: 1) flow rate of $5 \cdot 10^6 \text{ m}^3/\text{day}$; 2) flow rate of $1 \cdot 10^6 \text{ m}^3/\text{day}$.

$$T_1 = T_{\text{ex}} \text{ for } r = R_0, \tag{7}$$

$$T_{1} = T_{F} \text{ for } r = R_{0} - \xi,$$

$$L\rho_{1} \frac{d\xi}{dt} = \lambda_{1} \frac{\partial T_{1}}{\partial r} + \alpha_{1}(T_{ex} - T)$$
(9)
for $r = R_{0} - \xi$

The coefficient of heat transfer α_1 , which takes into account the thermal resistance of the cylindrical hydrate layer is given by

$$\alpha_{1} = \left[\frac{1}{\alpha} - \frac{R_{0} \ln (1 - \xi/R_{0})}{\lambda_{1}}\right]^{-1}.$$
 (10)

In this formulation, the thermal resistance of the pipe material is assumed negligibly small in comparison with the thermal resistance of the growing hydrate layer.

To solve the problem (7)-(9), we use the method of quasistationary states [3] according to which the temperature of the hydrate layer is

$$T_1 = c_1 \ln r + c_2 \quad (R_0 > r > R_0 - \xi).$$

We determine the integration constants c_1 and c_2 through the boundary conditions (7) and (8). Substituting the value found for T_1 in Eq. (9), we obtain an equation for the law of motion for the boundary of the hydrate layer,

$$\frac{d\xi}{dt} = -\frac{\lambda_1 (T_F - T_{ex})}{L\rho_1 R_0} \frac{1}{\left(1 - \frac{\xi}{R_0}\right) \ln\left(1 - \frac{\xi}{R_0}\right)} + \frac{\alpha_1 (T_{ex} - T)}{L\rho_1}, \quad \xi(0) = 0.$$
(11)

One should keep in mind that T and T_{F} , are unknown functions which must be determined from the system of equations (1), (3), (5), and (6).

We shall assume that heat exchange between the flow and the surrounding medium is in accordance with Newton's law. Then

$$K_{ex} = \alpha_1 S \left(T_{ex} - T \right). \tag{12}$$

In such a case, the original system can be reduced to two differential equations for the pressure and temperature.

As the result of simple calculations, we obtain

$$\frac{dp^{2}}{dx} + \frac{2\sin\varphi}{RT}p^{2} + \frac{\pi}{2}\psi\left(\frac{S}{\pi}\right)^{1/2}\frac{G^{2}RT}{S^{3}g^{2}} = 0, \qquad (13)$$

$$\frac{dT}{dx} + \frac{2\pi R_0 \alpha_1}{c_p G} \left(T_0 - T_{\text{ex}} \right) + \frac{\sin \varphi}{c_p} = 0.$$
(14)



pressure along pipeline for a gas flow rate of $5 \cdot 10^6 \text{ m}^3/\text{day: 1}$ t = 120 sec: 2) t = 4860 sec.

We add to the system (13), (14) the boundary conditions

$$p(0) = p_0,$$

$$T(0) = T_0.$$
(15)
(16)

The relations between the variable cross section of the pipe and the thickness of the hydrate layer is given by

$$S = \pi R_0^2 \left(1 - \frac{\xi}{R} \right)^2. \tag{17}$$

The considerations noted above regarding the difference of the time scales in the gas flow and in the hydrate layer make it possible to solve the system (13), (14) and Eq. (11) separately in each time step. The computational algorithm has the following form. The system (13), (14) is integrated numerically at the initial time. Then a time step is taken and S(x) is calculated from Eqs. (11) and (17). In this case, the values of p(x) and T(x) are taken from the previous step.

It should be noted that integration of Eq. (11) is carried out only in those cross sections of the pipe where the gas temperature is below the critical temperature T_F , i.e., where the condition

$$T < \beta_1 \ln p + \beta_2$$

is satisfied.

Having obtained the relationship S(x) for a given time step in this way, we once again solve the system (13), (14) and then take a time step, etc.

Numerical calculations were made for natural gas transport along a pipeline 0.534 m in diameter and 100 km long at various flow rates. In this case, the heat transfer coefficient α was calculated from the criterial relation [4]

$$Nu = 0.023 Re^{0.8} Pr^{0.4}$$
,

where Nu = $2\alpha R / \lambda$.

The values of the initial parameters were: $p_0 = 55 \text{ kg/cm}^2$; $T_0 = 40^{\circ}\text{C}$; $T_{ex} = -10^{\circ}\text{C}$. Special experimental studies were made to determine the thermophysical characteristics of the hydrate.

The results of the calculations reveal a complex picture for the growth of the hydrate layer. Thus at moderate gas flow rates, the maximum thickness of the layer is ordinarily reached at the exit section. However, with increasing pipeline operating time, this maximum is shifted toward the entrance section (Fig. 1).

At high flow rates, the maximum thickness of the hydrate layer is displaced toward the entrance section even after a short period of time (about 1.5 h in the example considered (Fig. 2)).

This is explained by the fact that with an increase in gas flow rate, the pressure falls more intensely, especially near the exit section, which leads to a reduction in the critical temperature for hydrate formation because of Eq. (1) and therefore to a reduction in the rate of growth of the hydrate layer (Fig. 3).

We note in conclusion that this interesting effect is revealed only through joint consideration of the equation system for gas dynamics and of the equation of thermal conductivity in the hydrate layer, which significantly distinguishes this problem from the problem of ice formation during the flow of water in pipes (for example, see [5]).

NOTATION

β_1, β_2	are the empirical coefficients being constant for gas of given composition;
S(x)	is the area of tube section;
γ	is the specific weight of gas;
φ	is the angle between tube axis and horizontal plane;
ψ	is the hydraulic resistance coefficient of tube;
R ₀	is the tube radius;
g	is the free falling acceleration;
w, c _p , T	are the velocity, specific heat capacity, and temperature of gas;
Kex	is the heat power supplied from without;
R	is the gas constant;
ξ	is the thickness of hydrate layer;
L	is the latent heat of hydration;
r	is the radius of cross section;
ρι	is the hydrate density;
t	is the time;
λ	is the hydrate thermal conductivity;
T_1	is the temperature of hydrate layer;
α	is the heat transfer coefficient from gas to tube wall without hydrate;
λ	is the gas thermal conductivity;
l	is the length of conduit;
$\mathbf{S}_0 = \pi \mathbf{R}_0^2;$	
$z = x \sin \varphi$.	

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