4. G. I. Abramov and K. A. Ivanov, Inzh.-fiz. Zh., 60, No. 3, 379-385 (1991).
5. P. I. Geshev, Inzh.-fiz. Zh., 35, No. 2, 292-296 (1978).
6. A. F. Polyakov, Teplofiz. Vys. Temp., 12, No. 2, 328-336 (1974).
7. B. S. Petukhov, A. F. Polyakov, Yu. L. Shekhter, and Yu. V. Tsypulev, Turbulent Boundary-Layer Flow [in Russian], Novosibirsk (1975), Part 2, pp. 162-177.
8. D. A. Labuntsov and Yu. B. Zudin, Periodic Heat-Transfer Processes [in Russian], Moscow (1984).
9. R. Cheesewright and K. S. Doan, Int. J. Heat Mass Transfer, 21, No. 7, 911-921 (1978).
10. V. P. Ivakin, A. G. Kirdyashkin, and L. I. Chernyavskii, Turbulent Boundary-Layer Flow [in Russian], Novosibirsk (1975); Part 2, pp. 256-269.
11. S. Klein, W. Reynolds, F. Shroub, et al., Mekhanika, No. 4, 42-78 (1969).
12. E. Corino and R. Brodky, Mekhanika, No. 1, 56-82 (1971).
13. L. C. Thomas, Int. J. Heat Mass Transfer, 25, No. 8, 1127-1136 (1982).
14. K. Kutamura, M. Koike, I. Fukuoka, and T. Saito, Int. J. Heat Mass Transfer, 28, No. 4, 837-850 (1985).
15. E. M. Khabakhpasheva, Problems of Heat Physics and Hydrodynamics [in Russian], Novosibirsk (1974), pp. 223-235.
16. S. S. Kutateladze, B. P. Mironov, V. E. Nakoryakov, and E. M. Khabakhpasheva, Experimental Studies of Turbulent Boundary-Layer Flow [in Russian], Novosibirsk (1975).
17. S. S. Kutateladze, A. G. Kirdyashkin, and V. P. Ivakin, Dokl. Akad. Nauk SSSR, 214, No. 6, 1270-1273 (1974).
18. S. S. Kutateladze, E. M. Khabakhpasheva, and B. V. Perepelitsa, Heat Transfer, 1978. Soviet Research [in Russian], Moscow (1980), pp. 5-13.
19. R. Cheesewright and E. Ierokipiotis, Proc. 7th Int. Heat Trans. Conf., Vol. 2 (1982), pp. 305-309.
20. I. G. Kozhevnikov and L. A. Novitskii, Thermal and Physical Properties of Materials at Low Temperatures [in Russian], Moscow (1982).
21. N. B. Vargaftik, Thermal and Physical Properties of Gases and Liquids [in Russian], Moscow (1972).
22. P. L. Kirillov, Inzh.-fiz. Zh., 50, No. 3, 501-512 (1986).

DISSOCIATION OF GASEOUS HYDRATES IN BEDS

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A mathematical model which accounts for the mobility of the liquid phase is constructed to describe the dissociation of gaseous hydrates in beds.

1. The extraction of gaseous hydrates from beds presumes that these compounds break down in the beds. The dissociation process, accompanied by the evolution of substantial volumes of gas and absorbed heat, is controlled to a considerable extent by the initial state of the bed system. Three different mathematical models corresponding to different states have been constructed to describe the breakdown of a gaseous hydrate in a porous medium. The model in [1] is based on the proposition that the pores in the bed are completely saturated with gaseous hydrate. The authors of [2] examined the case when the gas in the porous medium is in the two-phase state at the initial moment of time. In [3], it was assumed that the bed initially contains the gaseous hydrate, gas, and water in a state of thermodynamic equilibrium. These models make it possible to obtain quantitative estimates of processes occurring in beds when gas is being extracted from a gas—hydrate deposit by the pressure-reduction method in combination with heating of the well region.

The above three models are all based on the assumption that the effect of water on the given physical process (dissociation of hydrates) is small enough to be ignored. In those cases in which the level of hydrate saturation is high and, thus, a proportionately large

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volume of water is obtained as a result of the dissociation, the validity of this assumption must be questioned. Moreover, excluding the liquid phase from consideration makes it impossible to study one problem of great practical interest – the problem of the effect of catalysts on a hydrate-containing bed, with the liquid phase being responsible for their transport [4].

Another class of problems in which it is necessary to consider the mobility of both components is the problem of the formation and dissociation of gaseous hydrates in oceanic deposits [5]. It is noted that the given process usually takes place with a deficit of gas, which leads to a reduction of degree of occupation of the pore space. Also, phase transformations lead to a change in the salt regime of interstitial water, which to a large extent determines the mobility of water in marine deposits.

Mathematical formulations of problems involving unknown moving boundaries are quite complicated, so it is natural to first examine a generalization for the simplest situation which arises in the dissociation of a gaseous hydrate completely filling a pore space.

In the present investigation, we establish the conditions at the dissociation front with allowance for the presence of the liquid phase and its mobility. We use a unidimensional formulation to obtain a similarity solution that allows us to analyze the effect of the parameters of the system on the dissociation of a hydrate in porous medium.

2. By a hydrate-bearing bed, we will mean a porous medium completely saturated with a hydrate of a gas. Let the conditions for pressure and temperature at a certain stationary boundary be such that the gas and water are in the free state. Then we will have a dissociation boundary with hydrate on one side and gas and water in the free state on the other side. For simplicity, we will assume [1-3] that the skeleton of the porous medium and the gaseous hydrate are incompressible and stationary, that the water is an incompressible fluid, that the gas satisfies the Clapeyron equation, and that capillary effects are small. Then the below heat-conduction equation is valid in the region of the hydrate

$$\frac{\partial T}{\partial t} = a_0 \Delta T. \tag{1}$$

Here

$$a_0 = \frac{m\lambda_{gh} + (1-m)\lambda_c}{m\rho_{gh}C_{gh} + (1-m)\rho_c C_c}.$$

In the region containing gas and water, we have system of equations representing the mass conservation laws for the gas and water, the generalized Darcy's laws, the law of energy conservation, and the equation of state:

$$\begin{gathered}
m\frac{\partial}{\partial t}(1-S)\rho_g + \operatorname{div}\rho_g \mathbf{v}_g = 0, \\
m\frac{\partial}{\partial t}S + \operatorname{div}\mathbf{v}_w = 0, \\
\mathbf{v}_g = -\frac{kf_g(S)}{\mu_g}\operatorname{grad}P, \quad \mathbf{v}_w = -\frac{kf_w(S)}{\mu_w}\operatorname{grad}P, \\
\frac{\partial}{\partial t}(\rho e)_{ef} + \operatorname{div}(\rho_g h_g \mathbf{v}_g + \rho_w h_w \mathbf{v}_w) = \operatorname{div}(\lambda_{ef}\operatorname{grad}T), \\
P = \rho_g RT.
\end{gathered} \tag{2}$$

Here $(\rho e)_{ef} = mS\rho_w e_w + m(1-S)\rho_g e_g + (1-m)\rho_c C_c$, $\lambda_{ef} = mS\lambda_w + m(1-S)\lambda_g + (1-m)\lambda_c$.

In order to formulate the problem of the dissociation of gaseous hydrates, it is necessary to assign boundary conditions for the moving phase boundary. We will do this on the basis of balance equations. For the sake of specificity, we will examine a hydrate of methane with the occupation factor n = 6 (the number of water molecules per molecule of gas) [6]. To derive the mass-balance relations, it is sufficient to represent the gaseous hydrate as a homogeneous mixture of gas and water. This means that we can introduce effective densities for the gas and water in the hydrate-saturated region, calculating them as the masses of the corresponding components referred to the entire volume occupied by the gaseous hydrate. Then using the known molecular weights of methane and water, we find that 1 m^3 of hydrate with a weight of 900 kg and a value n = 6 contains 783.87 kg water and 116.13 kg gas. Thus, we can set the effective densities of water and gas in the hydrate-containing region equal to ρ_{w0} = 783.87 kg/m^3 and ρ_{g0} = 116.13 kg/m^3, respectively.

Using universal discontinuity equations [7], we obtain the balance relations for the energy and the masses of the water and gas. In the present case, these relations take the form:

$$\begin{gathered}\lambda_-(\operatorname{grad}T)_{n-}-\lambda_+(\operatorname{grad}T)_{n+}-\rho_{g-}h_{g-}(\mathbf{v}_g)_{n-}-\rho_{w-}h_{w-}(\mathbf{v}_w)_{n-}=\\=mV_n\{\rho_{gh}h_{gh}-\rho_{g-}h_{g-}(1-S_-)-\rho_{w-}h_{w-}S_-\},\\\rho_{w-}(\mathbf{v}_w)_{n-}=mV_n(\rho_{w-}S_--\rho_{w0}),\\\rho_{g-}(\mathbf{v}_g)_{n-}=mV_n\{\rho_{g-}(1-S_-)-\rho_{g0}\}.\end{gathered}\tag{3}$$

We augment the system of conservation laws at the dissociation front with the condition of equilibrium phase transformation [1-4]:

$$T_*=A\ln P_*+B.\tag{4}$$

Here, A = 10 K, B = 128 K. Equations (3) and (4) constitute the complete system of conditions for the moving boundary.

Systems (2) and boundary conditions (3-4) can be transformed by using thermodynamic relations and identity substitutions relative to the temperature T, pressure P, and water saturation S. We thus obtain the following system of basic equations in the gas—water region:

$$\begin{gathered}m\frac{\partial S}{\partial t}=\frac{k}{\mu_w}\operatorname{div}(f_w\operatorname{grad}P),\\(1-S)\frac{\partial P}{\partial t}-P\frac{\partial S}{\partial t}-(1-S)\frac{P}{T}\frac{\partial T}{\partial t}=\frac{k}{m\mu_g}\operatorname{div}(f_gP\operatorname{grad}P)+\frac{kf_g}{m\mu_g}\frac{P}{T}\operatorname{grad}T\operatorname{grad}P,\\(\rho C)_{ef}\frac{\partial T}{\partial t}-k\operatorname{div}\left[P\left(\frac{f_g}{\mu_g}+\frac{f_w}{\mu_w}\right)\operatorname{grad}P\right]-\\-\left(\rho_wC_w\frac{f_w}{\mu_w}+\frac{C_V}{R}\frac{P}{T}\frac{f_g}{\mu_g}\right)\operatorname{grad}P\operatorname{grad}T=\operatorname{div}(\lambda_{ef}\operatorname{grad}T).\end{gathered}\tag{5}$$

Here

$$(\rho C)_{ef}=mS\rho_wC_w+m(1-S)\rho_gC_p+(1-m)\rho_cC_c.$$

The conditions on the phase boundary take the form:

$$\begin{gathered}\frac{k}{\mu_w}f_w(S_-)(\operatorname{grad}P)_{n-}=m\left(\frac{\rho_{w0}}{\rho_w}-S_-\right)V_n,\\\frac{k}{\mu_g}f_g(S_-)(\operatorname{grad}P)_{n-}=\left(\frac{\rho_{g0}}{P_*}RT_*-1+S_-\right)V_n,\\mq\rho_{gh}V_n=\lambda_+(\operatorname{grad}T)_{n+}-\lambda_-(\operatorname{grad}T)_{n-},\\T_*=A\ln P_*+B.\end{gathered}\tag{6}$$

3. Let us examine a hydrate-saturated bed with the temperature T. Let the bed have a certain fixed boundary. We assign values of pressure P^0 and temperature T^0 on this boundary which, on phase diagram, lie within the region in which the gas exists in the free state. We will examine the problem in a linear approximation, when the changes in the sought functions are small compared to their absolute values. We represent the sought functions in the gas—water region in the form of unperturbed values and perturbations:

$$T=T^0+T',\ P=P^0+P',\ S=S^0+S',$$

Then system (5) will have the following form in the linear approximation:

$$\begin{gathered}\frac{\partial S'}{\partial t}=\varkappa_w\Delta P',\\\frac{\partial P'}{\partial t}+\delta\frac{\partial T'}{\partial t}=\varkappa\Delta P',\\\frac{\partial T'}{\partial t}+\omega\frac{\partial P'}{\partial t}=a\Delta T'.\end{gathered}\tag{7}$$

Here

$$a = \frac{\lambda_{ef}}{(\rho C)_{ef}}, \quad \omega = -\frac{m(1-S^0)}{(\rho C)_{ef}},$$

$$\varkappa = \frac{kP^0}{m(1-S^0)}\left(\frac{f_w}{\mu_w} + \frac{f_g}{\mu_g}\right), \quad \delta = -\frac{P^0}{T^0}, \quad \varkappa_w = \frac{kf_w}{m\mu_w}.$$

We define the unperturbed value of water saturation S^0 around which the linearization is performed as the zeroth approximation for S_*. To do this, in Eqs. (6) we replace the sought values at the front by the values of the unperturbed quantities. Excluding mass from the conservation laws $(\mathrm{grad}\ P)_{n-}$ and assuming for simplicity in the linear approximation that $f_w(S^0) = S^0$, $f_g(S^0) = 1 - S^0$, we finally obtain:

$$S^0 = Q - \sqrt{Q^2 - \rho_{w0}/\rho_w},$$

$$Q = \frac{1}{2}\left[\frac{\mu_g}{\mu_w}\frac{\rho_{g0}}{P^0}RT^0 + \left(1 + \frac{\rho_{w0}}{\rho_w}\right)\right].$$

It should be noted that the given expression for S^0 was obtained from the solution of a quadratic equation. The second root is discarded as physically meaningless, since it is always greater than unity. If the functions of relative phase permeabilities have a different form, then the problem can be reduced to the solution of a transcendental equation.

In the hydrate region separated by a moving boundary from the gas—water region, linear heat-conduction equation (1) is valid. Following [1-3], we will examine a unidimensional semi-infinite problem. Let T_0, T^0 and P^0 be constants. Then the formulated problem has a similarity solution of the form

$$T' = T'(\xi), \quad P' = P'(\xi), \quad X(t) = \beta\sqrt{t}, \quad \xi = x/\sqrt{t}. \tag{8}$$

The solution in both regions can be expressed through probability integrals. In the gas—water region $(0 < \xi < \beta)$ we have:

$$T(\xi) = \frac{\omega}{\alpha_1 - \alpha_2}\left[b_1E_1(\xi) - b_2E_2(\xi)\right] + T^0,$$

$$P(\xi) = \frac{1}{\alpha_2 - \alpha_1}\left[(1-\alpha_1)b_1E_1(\xi) - (1-\alpha_2)b_2E_2(\xi)\right] + P^0,$$

$$S(\xi) = \varepsilon\left(\frac{P - P_*}{P^0} - \frac{T - T_*}{T^0}\right) + S_-.$$

Here

$$\begin{gathered}
\alpha_{1,2} = \frac{1}{2}\left(1 + \frac{a}{\varkappa}\right) \pm \sqrt{\frac{1}{4}\left(1 - \frac{a}{\varkappa}\right)^2 + \frac{a}{\varkappa}\delta\omega}; \\
b_1 = \frac{1-\alpha_2}{\omega}(T_* - T^0) + P_* - P^0; \quad E_1(\xi) = \frac{\mathrm{erf}\left(\frac{\xi}{2}\sqrt{\frac{\alpha_1}{a}}\right)}{\mathrm{erf}\left(\frac{\beta}{2}\sqrt{\frac{\alpha_1}{a}}\right)}; \\
b_2 = \frac{1-\alpha_1}{\omega}(T_* - T^0) + P_* - P^0; \quad E_2(\xi) = \frac{\mathrm{erf}\left(\frac{\xi}{2}\sqrt{\frac{\alpha_2}{a}}\right)}{\mathrm{erf}\left(\frac{\beta}{2}\sqrt{\frac{\alpha_2}{a}}\right)}; \\
\varepsilon = \frac{(1 - S^0)f_w(S^0)\mu_g}{\mu_g f_w(S^0) + \mu_w f_g(S^0)}.
\end{gathered} \tag{9}$$

In the hydrate-containing region $(\beta < \xi < \infty)$ the temperature distribution is determined by the expression

$$T = (T_* - T_0)\frac{\mathrm{erfc}\left(\frac{\xi}{2\sqrt{a_0}}\right)}{\mathrm{erfc}\left(\frac{\beta}{2\sqrt{a_0}}\right)} + T_0. \tag{10}$$

Exact solution (9-10) contains the unknowns P_*, T_*, S_-, β. Differentiating the pressure and temperature distributions that have been found, we find the heat and mass flows to

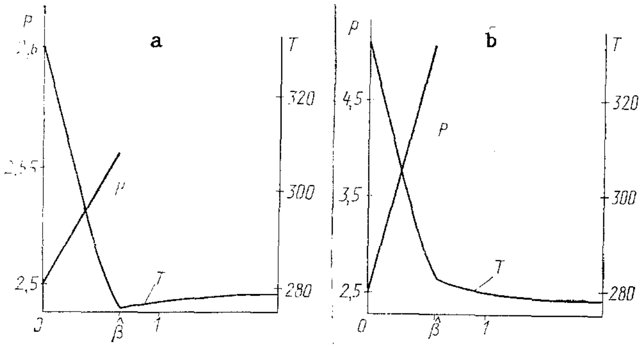

Fig. 1. Dependence of temperature and pressure on the dimensionless similarity variable (T_0 = 278 K, T^0 = 333 K, P^0 = 2.5 MHz); a) $k = 10^{-15}$ m^2; b) $k = 10^{-17}$ m^2. P, MHz; T, K

the right and left of the moving boundary. Inserting these expressions into (6) and considering that $V_n \equiv \dot{X}(t) = \beta/2\sqrt{t}$, we obtain a system of equations to determine the sought quantities P_*, T_*, S_-, β. This system was solved numerically.

4. The calculations were carrried out for the following values of the parameters: $m = 25$; $R = 520$ J/(kg·K), $\rho_w = 10^3$ kg/m^3, $\rho_{gh} = 9 \cdot 10^2$ kg/m^3, $\rho_c = 2 \cdot 10^3$ kg/m^3, $\mu_g = 1.8 \cdot 10^{-5}$ Pa·sec, $\mu_w = 1.8 \cdot 10^{-3}$ Pa·sec, $\lambda_c = 2$ W/(m·K), $\lambda_w = 0.58$ W/(m·K), $\lambda_g = 3.4 \cdot 10^{-2}$ W/(m·K), $\lambda_{gh} = 2.11$ W/(m·K), $C_w = 4.2 \cdot 10^3$ J/(kg·K), $C_c = 10^3$ J/(kg·K), $C_{gh} = 2.5 \cdot 10^3$ J/(kg·K), $C_p = 2 \cdot 10^3$ J/(kg·K), $q = 5 \cdot 10^5$ J/kg.

The characteristic regimes of dissociation of the gaseous hydrates are shown in Fig. 1. The results of the numerical experiments show that an increase in temperature T^0 or a decrease in pressure P^0 on the stationary wall leads to an increase in the velocity of the dissociation boundary. The exact hydrate dissociation regime also depends on permeability. Thus, with a relatively high permeability $k = 10^{-15}$ m^2 (see Fig. 1a), the value of P_* at the dissociation front is close to P^0. At small $k = 10^{-17}$ m^2, the flow of gas from the front is impeded. This leads to a decrease in the velocity of the dissociation front and a substantial increase in pressure at the boundary (see Fig. 1b).

There are also differences in the temperature distributions. For example, in the first case the minimum temperature is seen on the dissociation surface. This minimum is a consequence of the pressure drop, which intensifies dissociation of the hydrate. In this case, heat for the phase transformation is also removed from the region ahead of the front. At low permeabilities (see Fig. 1b) the temperature distribution is nonmonotonic, since an increase in pressure at the boundary leads to an increase in dissociation temperature. In the given case, this temperature turns out to be lower than the initial temperature.

It should be noted that the pressure distribution in the gas—water region is almost a physically linear function. This shows that the solution of the problem can be simplified in the given region. However, such a simplification does not always introduce any significant changes in the procedure that must be used to solve the system of transcendental equations.

As was noted in the introduction, the presence of the liquid phase was not taken into account in previous studies. If the degree of hydration is low [2] and, thus, so is the degree of saturation with water, then its presence can be ignored when the motion of the gas is calculated. If hydrate saturation is initially equal to unity, then it can be assumed that the water is stationary [1] (in the sense that all of the water from dissociation of the hydrate remains in place), and the phase permeability of the gas can easily be determined on the basis of molecular considerations. In this case, water saturation in the gas—water region is unambiguously determined by the effective density of the water in the hydrate region. Assuming that the water is incompressible and stationary, its saturation for the given case $S_0 = 0.783$. Calculations performed with allowance for mobility show that $S_- = 0.65$ for the solution shown in Fig. 1a and $S_- = 0.7$ for Fig. 1b, i.e., a decrease in permeability leads to a decrease in the amount of water removed from the dissociation region. In this case, the latter quantity approaches S_0. An increase in permeability increases water flow from the gas—water region, and there may be a twofold difference in the gas permeabilities determined by different methods. Thus, to evaluate gas flows in the case of high permeabilities, it is necessary to consider the mobility of the liquid phase.

It should also be noted that, as follows from the solution (9), water saturation in the region changes only slightly. This is a consequence of the chosen approximation (ignoring capillary pressure), in which the entire change in saturation is in essence referred to the boundary.

If we examine a problem corresponding to the recovery of gas from a gas–hydrate deposit by the pressure-reduction method and assume that the temperature at the outlet T^0 is equal to the initial temperature T_0, then in this case water saturation S_- depends only slightly on permeability k and differs appreciably from S_0. Thus, in this case, it is necessary to allow for the mobility of water in estimates of the amount of gas that can be recovered from the bed. Thus, with $k = 10^{-14}$ m^2, we obtain $S_- = 0.656$, $\hat{\beta} = 0.179$, $P_* = 2.5004$ MPa, $T_* = 275.3$ K, while at $k = 10^{-17}$ m^2 $S_- = 0.66$, $\hat{\beta} = 0.142$, $P_* = 2.74$ MPa, $T_* = 276.24$ K.

We should point out the fourfold decrease in the velocity of the dissociation front compared to the regimes shown in Fig. 1a.

The above examples correspond to a high value of the occupation factor (n = 6), the exact value of this quantity depending on the conditions of hydrate formation and possibly being lower than six due to incomplete occupation. The results of our calculations show that an increase in the degree of occupation (a decrease in the number of gas molecules in the structure of the gaseous hydrate) leads to a decrease in pressure and temperature at the dissociation front with an increase in water saturation in the gas-water region and the velocity of the boundary. Thus, at n = 12, calculations performed for the case corresponding to that shown in Fig. 1b yield the following values for the sought quantities: $S_- = 0.73$, $\beta = 0.6$, $P_* = 4.31$ MPa, $T_* = 280.77$ K.

NOTATION

T, temperature; a, diffusivity; m, porosity; λ, thermal conductivity; ρ, density; C, heat capacity; S, water saturation; v, filtration velocity; k, permeability; f, relative phase permeability; P, pressure; μ, viscosity; e, internal energy density; h, enthalpy; R, gas constant; V, X(t), velocity and law of motion of the dissociation surface; ξ, similarity variable; β, self-similar velocity; $\hat{\beta} = \beta/2\sqrt{a}$. Indices: gh, gaseous hydrate; g, gas; w, water; n, normal; +, −, values to the right and left of the boundary; *, value on the boundary.

LITERATURE CITED

1. N. V. Cherskii and E. A. Bondarev, Dokl. Akad. Nauk SSSR, 203, No. 3, 550-552 (1972).
2. N. N. Verigin, I. L. Khabibullin, and G. A. Khalikov, Izv. Akad. Nauk SSSR Mekh. Zhidk. Gaza, No. 1, 174-177 (1980).
3. E. A. Bondarev, A. M. Maksimov, and G. G. Tsypkin, Dokl. Akad. Nauk SSSR, 308, No. 3, 575-577 (1989).
4. V. A. Kamath and S. P. Godbole, J. Pet. Technol., No. 11, 1379-1388 (1987).
5. V. A. Solov'ev and G. D. Ginsburg, Litol Polezn. Iskop., No. 5, 121-125 (1987).
6. Yu. F. Makagon, Gaseous Hydrates, the Prerention of Their Formation and the Utilization of Their Formation and the Utilization [in Russian], Moscow (1985).
7. L. I. Sedov, Cintinuum Mechanics [in Russian], Vol. 1, Moscow (1970).