MATHEMATICAL MODEL OF THE VOLUME DISSOCIATION OF GAS-PHASE HYDRATES IN A POROUS MEDIUM WITH WATER-PHASE MOBILITY

A. M. Maksimov

UDC 536.24:622.27

A mathematical model of volume dissociation of gas-phase hydrates in a porous medium is constructed. The model accounts for transport processes in the water phase. The effect of the porous medium permeability on the character of the processes of phase transition and filtration is analyzed on the basis of a self-similar solution.

The growth in studies of the processes of formation and dissociation of gas-phase hydrates in many ways is related to the problems of hydrate formation in the face zones of boreholes, in boreholes, and pipelines [1]. It is also related to the analysis of the potential of gas-phase hydrates as commercial minerals [2]. The results of numerous theoretical and experimental investigations of the thermodynamic aspects and properties of hydrate formation and dissociation in natural strata have been reviewed in [3, 4].

The process of dissociation (formation) of gas-phase hydrates is linked to the change in the governing thermodynamic parameters (pressure and temperature) and is accompanied by transport of heat, gas, and water. A mathematical model of the dynamics of the interacting processes of heat and mass transfer and phase transition in a prorous medium is constructed within the framework of continuum mechanics and the thermodynamics of phase transitions. In [1, 5-7], models were constructed based on the assumption that there exists a sharp boundary: the phase transition front (dissociation). In this case, the pressure dependence of the temperature of dissociation was taken into account. It was shown in [8, 9] that for the case of incomplete pore saturation by hydrates, these front models do not provide an adequate mathematical description, since there are thermodynamic contradictions in the permeability range of practical interest ($k > 10^{-16}$ m^2). A consistent mathematical model was proposed, which accounts for the formation of an extended phase-transition zone with the assumption that the water formed in the dissociation process can be neglected. In the present work, the model from [8] is developed to take into account the presence and mobility of the water phase. This gives a more exact mathematical description and makes possible future studies of the dynamics of gas-phase hydrate dissociation and formation processes in porous media, including the effects of water-soluble hydrate-formation inhibitors.

Statement of the Problem. We consider a one-dimensional approximation of the problem of gas-phase hydrate dissociation in a porous medium, which initially is a saturated mixture of gas, water, and hydrate in thermodynamic equilibrium. We will assume that the matrix of the porous medium and the gas-phase hydrate are incompressible and immobile, that the gas is perfect, and the water incompressible. The motion of the gas and water obeys the two-phase filtration Darcy law [10]. Capillary effects are not considered.

The fundamental equations describing the dynamics of an equilibrium mixture of gas, water, and gas-phase hydrate in a porous medium can be derived from conservation laws using the mechanics of heterogeneous media [11]. The law of conservation of mass for the water has the form:

$$m\frac{\partial}{\partial t}(\nu\varepsilon\rho_h + (1-\nu)s\rho_w) + \operatorname{div}\rho_w\mathbf{v}_w = 0; \qquad (1)$$

Institute for Gas and Oil Problems, Academy of Sciences of the USSR and GKNO of the USSR, Moscow. Translated from Inzhenerno-fizicheskii Zhurnal, Vol. 62, No. 1, pp. 76-81, January, 1992. Original article submitted February 15, 1991.

1062-0125/92/6201-0060$12.50

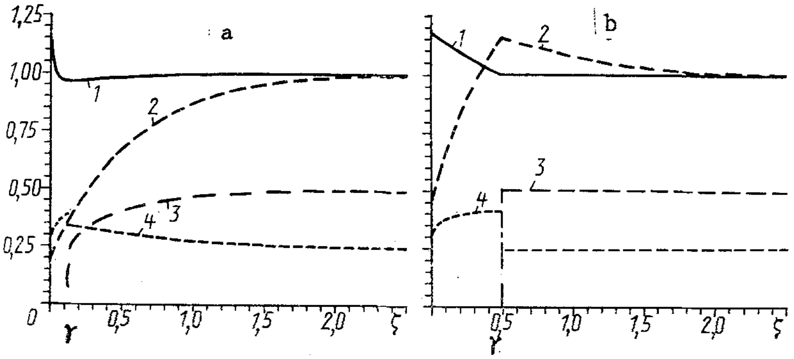

Fig. 1. Dimensionless temperature (1), pressure (2), hydrate saturation (3), and water saturation (4) as functions of the dimensionless similarity variable (a: $k = 10^{-15}$ m^2, b: $k = 10^{-17}$ m^2).

that for the gas is:

$$m\frac{\partial}{\partial t}(\nu(1-\varepsilon)\rho_h + (1-\nu)(1-s)\rho_g) + \operatorname{div}\rho_g\mathbf{v}_g = 0; \tag{2}$$

Darcy's laws for water and gas are:

$$\mathbf{v}_w = -\frac{k}{\mu_w} f_w(\nu,\ s)\operatorname{grad} P, \tag{3}$$

$$\mathbf{v}_g = -\frac{k}{\mu_g} f_g(\nu,\ s)\operatorname{grad} P; \tag{4}$$

the law of conservation of energy is:

$$(\rho C)_e\frac{\partial T}{\partial t} - mq\rho_h\frac{\partial \nu}{\partial t} - m(1-\nu)(1-s)\frac{\partial P}{\partial t} +$$
$$+ (\rho_w\mathbf{v}_w C_w + \rho_g\mathbf{v}_g C_g)\operatorname{grad} T + \mathbf{v}_w\operatorname{grad} P = \operatorname{div}\lambda_e\operatorname{grad} T, \tag{5}$$

where

$$(\rho C)_e = (1-m)\rho_m C_m + m\nu\rho_h C_h + m(1-\nu)s\rho_w C_w + m(1-\nu)(1-s)\rho_g C_g;$$
$$\lambda_e = (1-m)\lambda_m + m\nu\lambda_h + m(1-\nu)s\lambda_w + m(1-\nu)(1-s)\lambda_g;$$
$$q = \varepsilon h_w + (1-\varepsilon)h_g - h_h.$$

We write the equations of state as

$$\rho_m = \text{const}, \tag{6}$$
$$\rho_w = \text{const}, \tag{7}$$

$$\rho_g = \frac{P}{RT} \tag{8}$$

and the condition of thermodynamic equilibrium of the mixture as [12]

$$T = \alpha_1 \ln P + \alpha_2. \tag{9}$$

It is easy to see that (1)-(9) reduces to a system of four equations in the unknowns T, P, ν and s.

At the boundary x = 0 of the porous medium $0 < x < \infty$, let values of the temperature and pressure be maintained which correspond to that region of the phase diagram in which the gas and water mixture exists and the gas-phase hydrate is not present. Then it is natural to expect the development of the process of decomposition of a gaseous cylinder with the formation of two zones, separated by a moving boundary X(t). Zone I ($X(t) < x < \infty$) is an extended phase-transition region, in which equations (1)-(9) are satisfied. In zone II

($0 < x < X(t)$), the gas-phase hydrate is absent, and the equations for this zone are easily obtained from (1)-(8) by setting $\nu \equiv 0$. The two zones are separated by a moving boundary $X(t)$, at which the pressure and temperature are assumed to be continuous while the functions ν and s admit discontinuities. The conditions at this boundary can be obtained from the general jump relations [13]. Then the expression of mass balance for the water takes the form

$$m\left(s_-\rho_w - \nu_+\varepsilon\rho_h - (1-\nu)\,s_+\rho_w\right)\frac{dX}{dt} - \rho_w\left(v^n_{w_-} - v^n_{w_+}\right) = 0, \tag{10}$$

the mass balance for the gas is:

$$m\left((1-s_-)\,\rho_g - \nu_+(1-\varepsilon)\,\rho_h - (1-\nu_+)(1-s_+)\,\rho_g\right)\frac{dX}{dt} - \\ - \rho_g\left(v^n_{g_-} - v^n_{g_+}\right) = 0, \tag{11}$$

and the energy balance is:

$$m\nu_+\rho_h q\,\frac{dX}{dt} = \lambda_{e_+}(\mathrm{grad}\,T)^n_+ - \lambda_{e_-}(\mathrm{grad}\,T)^n_-. \tag{12}$$

We write the condition of thermodynamic equilibrium as

$$T_* = \alpha_1 \ln P_* + \alpha_2, \tag{13}$$

initial conditions as

$$t=0:\ T=T_0,\ P=P_0,\ \nu=\nu_0,\ s=s_0,\ X=0, \\ \text{with } T_0 = \alpha_1 \ln P_0 + \alpha_2, \tag{14}$$

and the conditions at the fixed boundary as

$$x=0:\ T=T^0,\ P=P^0,\quad \text{with } T^0 > \alpha_1 \ln P^0 + \alpha_2. \tag{15}$$

Relations (1)-(15) constitute the complete system of equations, initial and boundary conditions for determining the unknown functions $T(x, t)$, $P(x, t)$, $\nu(x, t)$, $s(x, t)$, and $X(t)$.

Self-Similar Solution. Let T_0, P_0, ν_0, s_0, T^0, P^0 be constants in conditions (14) and (15). Then problem (1)-(15) admits a self-similar solution

$$T = T(\xi),\ P = P(\xi),\ \nu = \nu(\xi),\ s = s(\xi),\ X = \beta t^{1/2},\ \xi = xt^{-1/2}. \tag{16}$$

In this case, the equations in zone I ($\beta < \xi < \infty$) take the form

$$\frac{kf_w}{m\mu_w}P'' + \nu'(\varepsilon\rho_h/\rho_w - s)\frac{\xi}{2} + (1-\nu)\,s'\,\frac{\xi}{2} + \\ + \frac{k}{m\mu_w}\left(\frac{\partial f_w}{\partial\nu}\nu' + \frac{\partial f_w}{\partial s}s'\right)P' = 0, \tag{17}$$

$$\frac{kf_g}{m\mu_g}\left(P'' + \frac{(P')^2}{P} - \frac{P'T'}{T}\right) + \frac{k}{m\mu_g}\left(\frac{\partial f_g}{\partial\nu}\nu' + \frac{\partial f_g}{\partial s}s'\right)P' + \\ + (1-\varepsilon)\frac{\rho_h}{\rho_g}\nu'\frac{\xi}{2} + (1-\nu)(1-s)\left(\frac{P'}{P} - \frac{T'}{T} - \right. \\ \left. - \frac{s'}{1-s} - \frac{\nu'}{1-\nu}\right)\frac{\xi}{2} = 0, \tag{18}$$

$$(\rho C)_e T'\frac{\xi}{2} - mq\rho_h\nu'\frac{\xi}{2} - m(1-\nu)(1-s)\,P'\frac{\xi}{2} + \\ + k\left(f_w C_w\rho_w/\mu_w + f_g k_g\rho_g/\mu_g\right)T'P' + kf_w(P')^2/\mu_w + \\ + \lambda_e T'' + \left(\frac{\partial\lambda_e}{\partial s}s' + \frac{\partial\lambda_e}{\partial\nu}\nu'\right)T' = 0, \tag{19}$$

$$T = \alpha_1 \ln P + \alpha_2. \tag{20}$$

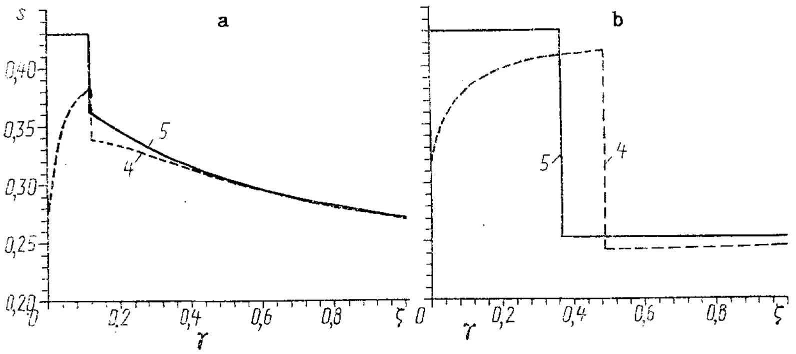

Fig. 2. Distribution of water saturation with (4); and without (5) taking water mobility into account (a: $k = 10^{-15}$ m^2, b: $k = 10^{-17}$ m^2).

The equations in zone II ($0 < \xi < \beta$) are easily obtained from (17)-(19) by setting $\nu \equiv 0$.

The conditions at the moving boundary $\xi = \beta$ are:

$$(s_- - \nu_+\varepsilon\rho_h/\rho_w - (1-\nu_+)s_+)\beta/2 + \frac{k}{m\mu_w}(f_w(s_-)P'_- - f_w(\nu_+, s_+)P'_+) = 0, \tag{21}$$

$$(1 - s_- - (1-\nu_+)(1-s_+) - \nu_+(1-\varepsilon)\rho_h/\rho_g)\beta/2 + \frac{k}{m\mu_g}(f_g(s_-)P'_- - f_g(\nu_+, s_+)P'_+) = 0, \tag{22}$$

$$m\nu_+\rho_h q\beta/2 = \lambda_e(\nu_+, s_+)T'_+ - \lambda_e(s_-)T'_-, \tag{23}$$

$$T_* = \alpha_1 \ln P_* + \alpha_2. \tag{24}$$

In addition, from (14), (15) we have:

$$\xi = 0: \quad T = T^0, \ P = P^0, \tag{25}$$

$$\xi \to \infty: \quad T = T_0, \ P = P_0, \ \nu = \nu_0, \ s = s_0. \tag{26}$$

Thus, after introduction of the similarity variable $\xi = xt^{-1/2}$, the original initial-boundary value problem for the system of partial differential equations reduces to a three-point boundary value problem for ordinary differential equations with boundary conditions at $\xi = 0$, $\xi = \beta$, and $\xi \to \infty$. Note that here, β is the unknown quantity. Numerical solution is carried out by a predictor-corrector iterative method [14] using subroutines from the NAG package.

Sample Calculations. Figure 1 shows sample calculations of the self-similar solution for a prblem with the following parameters [3, 4, 12]: $\rho_w = 1000$ kg/m^3, $\rho_m = 2000$ kg/m^3, $\rho_h = 700$ kg/m^3, $C_w = 4200$ J/(kg·K), $C_m = 920$ J/(kg·K), $C_h = 2700$ J/(kg·K), $C_g = 2093$ J/(kg·K), $\lambda_w = 0.58$ W/(m·K), $\lambda_m = 1.9$ W/(m·K), $\lambda_h = 2$ W/(m·K), $\lambda_g = 0.0072$ W/(m·K), $R = 519$ J/kg, $\alpha_1 = 10$ K, $\alpha_2 = 128.1$ K, $q = 510$ kJ/kg, $m = 0.2$, $\varepsilon = 0.87$, $\mu_w = 1.8\cdot10^{-3}$ Pa·s, $\mu_g = 1.98\cdot10^{-5}$ Pa·s.

The parameter values for the gas and the gas-phase hydrate are appropriate for methane and its hydrate. In the calculations, a linear relation was used for the phase permeabilities.

Figure 1 shows the dimensionless temperature T/T_0 (1), pressure P/P_0 (2), hydrate saturation ν (3), and water saturation s (4), as functions of the dimensionless similarity variable $\zeta = \xi(kP_0/m\mu_g)^{-1/2}$. Correspondingly, γ denotes the dimensionless version of the quantity β. The calculations correspond to the values $T_0 = 284$ K, $T^0 = 323$ K, $P^0 = 10^6$ Pa, $\nu_0 = 0.5$, $s_0 = 0.25$ with different permeabilities: $k = 10^{-15}$ m^2 (Fig. 1a), and $k = 10^{-17}$ m^2 (Fig. 1b).

It is easy to see the qualitative differences in the hydrate- and water saturation distributions for the different permeabilities. So, for high permeability (Fig. 1a), the form of curves 3 and 4 is indicative of the decomposition of gas-phase hydrate in zone I

($\zeta > \gamma$), which is accompanied by an increase in water saturation. For low permeability (Fig. 1b), there is some increase in hydrate content and a decrease in water content in zone I. In addition, either a pressure maximum (Fig. 1a) or a temperature minimum (Fig. 1b) is observed close to the moving boundary.

These results indicate that the magnitude of the permeability in many ways determines the character of those processes which accompany the decomposition of gas-phase hydrates in a porous medium.

In conclusion, further evidence is given of the need to consider the effect of filtration processes. Figure 2 shows, for comparison, distributions of water saturation obtained as a result of solving the problem with (curve 4) and without (curve 5, $v_w \equiv 0$) accounting for water mobility. The calculations of Fig. 2a and 2b correspond to the parameter values used for Fig. 1a and 1b, respectively. It is clear that there is a significant discrepancy in the value of s, especially in zone II ($0 < \zeta < \gamma$). The solution without water mobility overestimates the wave saturation and underestimates the velocity of the moving boundary. The divergence of the results increases with growing permeability.

NOTATION

x, coordinate; t, time; X, coordinate of the moving boundary; ρ, density; v, filtration velocity; T, temperature; P, pressure; ε, bulk concentration of water in the gas-phase hydrate; ν, s, volume hydrate- and water saturations, respectively; k, permeability; μ, viscosity; f, phase permeability; C, specific heat capacity; m, porosity; q, heat of dissociation of the gas-phase hydrate; λ, thermal conductivity coefficient; R, gas constant; h, enthalpy; ξ, similarity variable; ζ, dimensionless similarity variable; β, similarity coordinate of the moving boundary; γ, dimensionless similarity coordinate of the moving boundary. Indices: h, gas-phase hydrate; m, matrix of the porous medium; w, water; g, gas; e, effective value; -, +, *, quantitites to the left, right, and at the moving boundary, respectively; n denotes the projection of the normal onto the surface of the moving boundary; 0, initial and boundary values.

LITERATURE CITED

1. É. A. Bondarev, G. D. Babe, A. G. Groisman, and M. A. Kanibolotskii, Mechanics of Hydrate Formation in Gas Flows [in Russian], Novosibirsk (1976).
2. N. V. Cherskii and S. P. Nikitin, Study of Gas-Bearing Zones with Hydrate Formation in the USSR [in Russian], Yakutsk (1987).
3. Yu. F. Makogon, Gas-Phase Hydrates: Anticipating Their Development and Use [in Russian], Moscow (1985).
4. S. Sh. Byk, Yu. F. Makogon, and V. I. Fomina, Gaseous Hydrates [in Russian], Moscow (1980).
5. N. V. Cherskii and É. A. Bondarev, Dokl. Akad. Nauk SSSR, 203, No. 3, 550-552 (1972).
6. N. N. Verigin, I. L. Khabibullin, and G. A. Khalikov, Izv. Akad. Nauk SSSR, Mekh. Zhidk. Gaza, No. 1, 174-177 (1980).
7. M. S. Selim and E. D. Sloan, A. I. Chem. Eng. J., 35, No. 6, 1049-1052 (1989).
8. É. A. Bondarev, A. M. Maksimov, and G. G. Tsypkin, Dokl. Akad. Nauk SSSR, 308, No. 3, 575-577 (1989).
9. A. M. Maksimov, and G. G. Tsypkin, Izv. Akad. Nauk SSSR, Mekh. Zhidk. Gaza, No. 5, 84-87 (1990).
10. R. Collins, Fluid Flow through Porous Media [Russian translation], Moscow (1964).
11. R. I. Nigmatulin, Fundamentals of the Mechanics of Heterogeneous Media [in Russian], Moscow (1978).
12. A. G. Groisman, Thermophysical Properties of Gaseous Hydrates [in Russian], Novosibirsk (1976).
13. L. I. Sedov, Mechanics of a Continuous Medium [in Russian], Vol. 1, Moscow (1970).
14. T. Na, Computational Methods for Solving Applied Boundary-Value Problems [Russian translation], Moscow (1982).