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DISSOCIATION OF HYDRATES IN A POROUS MEDIUM UNDER DEPRESSIVE EFFECTS

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Considerable attention has recently been given to the dissociation of hydrates in porous media [1–8]. This paper is devoted to some aspects of the depression-induced dissociation of hydrates completely filling a porous volume in the initial state. Criteria are proposed for parameters of the system where a hydrate is dissociable in the volume zone.

1. Fundamental Assumption. Let us consider hydrodynamic and thermophysical processes that occur in porous media during dissociation of hydrates. The system of equations describing these processes has the most general form for a three-phase region [4], where a solid hydrate and the products of its dissociation [liquid (water) and gas] are present. For the subsequent consideration we assume that: 1) the gas, liquid, solid hydrate, and porous medium have the same temperature at each point, 2) in addition, the porous medium skeleton, the hydrate, and water are incompressible, 3) the porosity is constant, and the gas is calorifically perfect:

$$\rho_s^0, \rho_h^0, \rho_l^0, \quad m = \text{const}, \quad p = \rho_g^0 RT, \tag{1.1}$$

where ρ_i^0 $(i = s, h, g, l)$ is the true density, p is the pressure, T is the temperature, R is the gas constant, and m is the porosity. Hereafter the subscripts s, h, g, and l mean that a given parameter belongs to the porous medium skeleton, hydrate, gas, and water, respectively. The porous medium skeleton and the hydrate are immovable $(\mathbf{v}_s = \mathbf{v}_h = 0)$. The presence of liquid vapors in the gas phase and the gas solubility in the liquid as well as diffusion in the hydrate are neglected. The hydrate is a two-component system having mass concentration of gas g (mass concentration of the liquid $1 - g$). We will neglect diffusion in the hydrate.

2. Fundamental Equations. Taking into account the above assumptions, we write the mass conservation equations for gas and water as follows:

$$\frac{\partial}{\partial t}[m((1-\nu)\rho_g^0 S_g + \nu\rho_h^0 g)] + \nabla\cdot[m(1-\nu)\rho_g^0 S_g \mathbf{v}_g] = 0; \tag{2.1}$$

$$\frac{\partial}{\partial t}[m((1-\nu)\rho_l^0 S_l + \nu\rho_h^0(1-g))] + \nabla\cdot[m(1-\nu)\rho_l^0 S_l \mathbf{v}_l] = 0, \tag{2.2}$$

$$S_g + S_l = 1,$$

where ν is the hydrate saturation, $m(1-\nu)$ is the "quick" mobile porosity, i.e., a portion of the porous medium volume filled with mobile phases — liquid and gas, S_g and S_l are the gas and water saturation, respectively, $\mathbf{v}_i$ $(i = gl)$ is the velocity of the phases.

For the gas and liquid filtration we use the Darcy law:

$$m(1-\nu)S_i\mathbf{v}_i = -\frac{kK_i}{\mu_i}\nabla p \quad (i = g, l), \tag{2.3}$$

where k, K_i are the coefficients of absolute permeability and relative phase permeability, respectively, and μ_i $(i = g, l)$ is the dynamic viscosity. The heat supply equation for the system under consideration, with the

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above assumptions, can be written as follows:

$$\rho c \frac{\partial T}{\partial t} + m(1-\nu)(\rho_g^0 S_g c_g v_g + \rho_l^0 S_l c_l v_l) \cdot \nabla T = \nabla \cdot (\lambda \nabla T) + m(1-\nu) S_g \left(\frac{\partial p}{\partial t} + \mathrm{v}_g \cdot \nabla p \right) + m \rho_h^0 l \frac{\partial \nu}{\partial t}, \quad (2.4)$$

$$\rho c = (1-m)\rho_s^0 c_s + m(\nu \rho_h^0 c_h + (1-\nu)(\rho_g^0 S_g c_g + \rho_l^0 S_l c_l)),$$

where c_i ($i = s, h, g, l$) is the specific heat (with c_g being the specific heat of the gas at constant pressure), λ is the thermal conductivity coefficient, and l is the specific heat of the hydrate dissociation.

In the dissociation region, where the gas, liquid, and hydrate are present, the temperature and pressure on the saturation line satisfy the condition

$$T = T_* \ln(p/p_*), \quad (2.5)$$

where T_* and P_* are empirical parameters.

We assume that the mass concentration of the gas in the hydrate does not depend on the temperature and pressure ($g = \text{const}$).

The "quick" mobile porosity in the processes under consideration is variable due to the hydrate dissociation. Therefore, the absolute permeability depends on the hydrate saturation. This dependence can be obtained on the basis of the Kozeny formula

$$k = k_0 \frac{m'^3}{(1-m')^2}, \quad m' = m(1-\nu). \quad (2.6)$$

In general, relative phase permeability coefficients do not universally depend on phase saturation and other physical parameters that describe the flow of a gas–liquid mixture in capillaries. Under certain hypotheses for each particular case, these coefficients may be determined. In particular, in the limiting case where the liquid produced during hydrate dissociation completely remains in the porous medium, the phase permeability for the liquid is $K_l = 0$, and the permeability coefficient for the gas phase can be determined as in (2.6):

$$k_g = kK_g = k_0 \frac{m''^3}{(1-m'')^2}, \qquad m'' = m(1-\nu)S_g. \quad (2.7)$$

It is significant that this scheme, as demonstrated below, is equivalent to the assumption that gas is the only product of hydrate dissociation with normalized density and other thermophysical parameters. In addition, it is possible to determine the relative phase permeability coefficient accepting the "gas bearing" scheme which assumes that the related gas phase flows primarily along the pore walls. According to this assumption, the relative phase permeability coefficient takes the form [9]

$$K_g = S_g^2, \quad K_l = (1-S_g)[\bar{\mu} + (2-\bar{\mu})S_g]/\bar{\mu}, \quad \bar{\mu} = \mu_g/\mu_l.$$

If the equilibrium scheme of filtration flow is accepted, which means that the gas and the liquid move at the same velocity, then the relative phase permeability coefficient can be written as

$$K_g = \mu_g S_g/\mu_{gl}, \quad K_l = \mu_l S_l/\mu_{gl},$$

where μ_{gl} is the normalized viscosity for the gas–liquid mixture in equilibrium.

3. Immovable Liquid ($K_l = 0$). According to the first scheme of filtration flow, from Eqs. (2.1)–(2.4) we have for a one-dimensional case:

$$\frac{\partial}{\partial t}[m((1-\nu)\rho_l^0 S_l + \nu\rho_h^0(1-g))] = 0; \quad (3.1)$$

$$\frac{\partial}{\partial t}[m((1-\nu)\rho_g^0 S_g + \nu\rho_h^0 g)] + \frac{\partial}{\partial x}[m(1-\nu)S_g \rho_g^0 v_g] = 0; \quad (3.2)$$

$$\rho c \frac{\partial T}{\partial t} + m(1-\nu)\rho_g^0 S_g c_g v_g \frac{\partial T}{\partial x} = \frac{\partial}{\partial x}\left(\lambda \frac{\partial T}{\partial x}\right) + m(1-\nu)S_g\left(\frac{\partial p}{\partial t} + v_g \frac{\partial p}{\partial x}\right) + m\rho_h^0 l \frac{\partial \nu}{\partial t}. \quad (3.3)$$

If we assume that the porous medium is initially completely filled with a hydrate ($\nu = 1$), it can be concluded from Eq. (3.1) that

$$(1-\nu)\rho_l^0 S_l + \nu\rho_h^0(1-g) = \rho_h^0(1-g),$$

which gives

$$S_l = \frac{\rho_h^0(1-g)}{\rho_l^0}, \quad S_g = \frac{\rho_l^0 - \rho_h^0(1-g)}{\rho_l^0}. \tag{3.4}$$

It follows from these equations that under the above assumptions for ρ_h^0, ρ_l^0, and g, the water saturation (as well as gas saturation) remains constant in the dissociation region. Since the water saturation value must be less than unity, the liquid and hydrate density must satisfy the following inequality in order for the accepted scheme to be meaningful:

$$\rho_l^0 > \rho_h^0(1-g).$$

This condition for the systems under consideration is usually satisfied. Using Eq. (3.4), we can reduce Eq. (3.1) to the form

$$\frac{\partial}{\partial t}[(\rho_g^0 - \tilde{\rho}_h^0)(1-\nu)] = \frac{\partial}{\partial x}\left(\frac{\rho_g^0 \tilde{k}_g}{m\mu_g}\frac{\partial p}{\partial x}\right), \tag{3.5}$$

where $\tilde{\rho}_h^0 = g\rho_h^0/S_g$; $\tilde{k}_g = k_g/S_g$. It follows from Eq. (3.5) that, based on the accepted simplifications, the problem becomes equivalent to the case where gas is the only product of hydrate dissociation, with hydrate density $\tilde{\rho}_h^0$ and porous medium saturation $\tilde{k}_g$.

To clear up the principal features of the process at actual values of the thermophysical parameters of the system under consideration, we may neglect, in most cases, terms related to the barothermic effect in (3.3) (the second term on the right-hand side) and terms related to the convective transfer of heat caused by gas filtration. Taking into account that for the parameters of gas–liquid systems the relation $\rho_g^0 \ll \tilde{\rho}_h^0$ usually holds, we write Eqs. (3.3) and (3.4) as follows:

$$\frac{\partial \nu}{\partial t} = \frac{\partial}{\partial x}\left(\frac{\tilde{k}_g \rho_g^0}{m\mu_g\tilde{\rho}_h^0}\frac{\partial p}{\partial x}\right); \tag{3.6}$$

$$\rho c\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\lambda\frac{\partial T}{\partial x}\right) + m\rho_h^0 l\frac{\partial \nu}{\partial t}. \tag{3.7}$$

Eliminating $\partial\nu/\partial t$ from these equations, we obtain

$$\rho c\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\frac{\tilde{k}_g\rho_g^0\rho_h^0 l}{\mu\tilde{\rho}_h^0}\frac{\partial p}{\partial x} + \lambda\frac{\partial T}{\partial x}\right). \tag{3.8}$$

In the region where a gas, a liquid, and a hydrate are present, the pressure uniquely determines the current temperature according to relation (2.5), hence

$$\frac{\partial p}{\partial x} = p'\frac{\partial T}{\partial x}, \quad p' = \frac{dp}{dT}. \tag{3.9}$$

Now Eq. (3.8) takes the form

$$\rho c\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left[\left(\frac{\tilde{k}_g\rho_g^0\rho_h^0 l p'}{\mu_g\tilde{\rho}_h^0} + \lambda\right)\frac{\partial T}{\partial x}\right]. \tag{3.10}$$

It follows from Eq. (3.10) that when temperature (or pressure) fields propagate in a porous medium which is filled with a hydrate and products of its dissociation, the thermal conductivity is negligible at sufficiently high values of the permeability coefficient defined by the condition

$$k_g \gg k_g^*, \quad k_g^* = \tilde{k}_g^* S_g, \quad \tilde{k}_g^* = \frac{\mu_g\,\tilde{\rho}_h^0\,\lambda T'}{\rho_g^0\,\rho_h^0\,l}, \quad T' = \frac{dT}{dp}. \tag{3.11}$$

In view of (2.5), we may rewrite the expression for the normalized critical permeability as

$$\tilde{k}_g^* = \frac{\mu_g\, \tilde{\rho}_h^0\, T_* \lambda}{\rho_g^0\, \rho_h^0\, p\, l} = \text{æ}_g \left(\frac{\tilde{\rho}_h^0}{\rho_h^0}\right)\left(\frac{\lambda T_*}{pl}\right), \qquad \text{æ}_g = \frac{\mu_g}{\rho_g^0},$$

where æ_g is the kinematic gas viscosity. In particular, for a porous medium filled with a hydrate, having $g = 0.1$, $\rho_h^0 = 900$ kg/m^3, $T_* = 10$ K, $l = 5 \cdot 10^5$ J/kg, $p = 10$ MPa, $\lambda = 2$ kg·m/(sec^3·K), $\mu_g = 2 \cdot 10^{-5}$ Pa·sec, we obtain $k_g^* = 10^{-18}$ m^2.

Consequently, the influence of thermal conductivity must be taken into account only at very small values of the gas permeability coefficient k_g. At low values ($k_g \ll k_g^*$), the terms of Eq. (3.6) related to piezo conductivity may be neglected. However, it should be noted that Eqs. (3.6) and (3.7) in this case have only the trivial solution $\nu = 1$ for hydrate saturation. This means that at low permeability there cannot exist volume regions containing a hydrate and products of its dissociation simultaneously.

In other words, the pressure gradients uniquely determined by the temperature field according to Eq. (2.5) are not sufficient to transfer gas that is released during the hydrate dissociation. In particular, when the absolute permeability [defined by (2.7) at $\nu = 0$]

$$k = k_0 m^3 S_g^3/(1 - mS_g)^2$$

satisfies the condition $k \ll k_g^*$, the volume regions where the hydrate dissociation takes place are completely absent. Hydrate dissociation will occur on the phase transition surface.

Below we consider the cases where it is possible to neglect thermal conductivity ($\lambda = 0$) and to consider the thermal capacity constant in a unit volume of the system ($\rho c = \text{const}$).

Let us assume that a porous medium in the initial state is completely filled with a hydrate ($\nu = 1$) at temperature T_0 (dissociation pressure at this temperature $p_0 = p_* \exp(T_0/T_*)$). We consider a self-similar regime of gas filtration which is characterized by a sudden drop of pressure on the porous medium boundary to the value determined by the condition $p_e < p_0$. Under this assumption, the initial and boundary conditions take the form

$$p = p_0, \quad \nu = 1 \quad (t = 0,\ x \geqslant 0), \ p = p_e \quad (t > 0,\ x = 0). \tag{3.12}$$

From Eqs. (3.6) and (3.7), in view of (1.1), (2.5), and (2.7), we obtain

$$\frac{\partial p}{\partial t} = \frac{\Delta_h T}{T'(p)} \frac{\partial}{\partial x}\left[\frac{k_0 m^2 S_g^2 \rho_g^0(p)}{\mu_g \tilde{\rho}_h^0 (1 - m'')^2}(1 - \nu)^3 \frac{\partial p}{\partial x}\right], \tag{3.13}$$

where

$$1 - \nu = (T_0 - T(p))/\Delta_h T; \quad T(p) = T_* \ln(p/p_*); \quad T'(p) = T_*/p;$$
$$\rho_g^0(p) = p/RT(p); \quad m'' = m(1 - \nu)S_g; \quad \Delta_h T = m\rho_h^0 l/\rho c;$$

$\Delta_h T$ is the temperature change of the system, provided that the amount of heat supplied to the system is equal to the heat produced by dissociation of the total hydrate present in the porous medium.

Hence, for the piezoconductivity in a porous medium filled with a hydrate and products of its dissociation we have one nonlinear parabolic equation. To determine the features of the processes described by Eq. (3.9), let us consider the case where the pressure p_e on the porous medium boundary differs little from p_0 ($p_0 - p_e \ll p_0$). After partial linearization of Eq. (3.13), in particular, assuming that ρ_g^0 and T' are constant and that

$$\rho_g^0 \simeq \rho_{g0}^0 = \rho_g^0(p_0), \quad T'(p) \simeq T'(p_0) = T_*/p_0,$$

we have

$$\frac{\partial p}{\partial t} = \text{æ}_p^{(f)} \frac{\partial}{\partial x}\left[\left(\frac{p_0 - p}{p_0}\right)^3 \frac{\partial p}{\partial x}\right], \quad \text{æ}_p^{(f)} = \frac{k_0}{\text{æ}_g} \frac{p_0}{\tilde{\rho}_h^0}\left(\frac{\rho}{\rho_l^0}\right)^2\left(\frac{cT'(p_0)p_0}{l}\right)^2 S_g^2, \quad \text{æ}_g = \mu_g/\rho_{g0}^0. \tag{3.14}$$

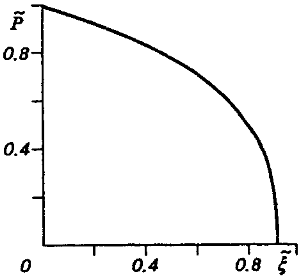

Fig. 1

It follows from (2.5) that

$$\text{æ}_p^{(f)} = \frac{k_0}{\text{æ}_g} \frac{p_0}{\tilde{\rho}_h^0} \left(\frac{\rho}{\rho_h^0}\right)^2 \left(\frac{cT_*}{l}\right)^2 S_g^2. \tag{3.15}$$

In deriving (3.14), we considered that $m'' \ll 1$. Entering the dimensionless normalized parameter for pressure

$$\tilde{P} = \frac{p_0 - p}{p_0 - p_e} = \frac{1 - P}{1 - P_e}, \quad P = p/p_0$$

into Eq. (3.14), we obtain

$$\frac{\partial \tilde{P}}{\partial t} = \tilde{\text{æ}}_p^{(f)} \frac{\partial}{\partial x}\left(\tilde{P}^3 \frac{\partial \tilde{P}}{\partial x}\right), \quad \tilde{\text{æ}}_p^{(f)} = \left(\frac{p_0 - p_e}{p_0}\right)^3 \text{æ}_p^{(f)}. \tag{3.16}$$

With these substitutions the initial and boundary conditions (3.12) become

$$\tilde{P} = 0 \quad (t = 0,\ \text{æ} \geqslant 0), \quad \tilde{P} = 1 \quad (t > 0,\ x = 0). \tag{3.17}$$

In terms of the self-similar variables $\tilde{\xi} = x/\sqrt{\tilde{\text{æ}}_p^{(f)} t}$, Eq. (3.16) and condition (3.17) take the form

$$-\frac{\tilde{\xi}}{2} \frac{d\tilde{P}}{d\tilde{\xi}} = \frac{d}{d\tilde{\xi}}\left(\tilde{P}^3 \frac{d\tilde{P}}{d\tilde{\xi}}\right), \quad \tilde{P}(\infty) = 0, \quad \tilde{P}(0) = 1. \tag{3.18}$$

A solution to Eq. (3.18) satisfying the given boundary conditions is illustrated in Fig. 1. Note that the solution curve intersects the abscissa axis at the point $\tilde{\xi}_0 = 0.91$ with a vertical tangent line. Hence, it may be concluded that the region where the hydrate dissociation occurs is finite. We write an equation for the movement of the right boundary of this region in the form

$$x_0^{(f)} = \tilde{\xi}_0 \sqrt{\tilde{\text{æ}}_p^{(f)} t}.$$

For a porous medium completely filled with a hydrate in the initial state, with $m = 0.1$, $\rho_s^0 = 2.6 \cdot 10^3$ kg/m^3, $\rho_l^0 = 10^3$ kg/m^3, $c_s = 10^3$ J/(kg·K), $p_0 = 10$ MPa, $p_0 - p_e = 1$ MPa, $k_0 = 10^{-9}$ m^2, $S_g = 0.21$, we obtain $\tilde{\text{æ}}_p^{(f)} = 8 \cdot 10^{-5}$ m^2/sec.

It can easily be shown that near the boundary of the hydrate dissociation region the pressure curve is defined by the following asymptotic expression:

$$\tilde{P} = \sqrt[3]{\frac{3}{2} \tilde{\xi}_0 (\tilde{\xi}_0 - \tilde{\xi})}.$$

When making specific estimations, in particular, determining the rate of a gas flow through the porous medium boundary, it should be taken into account that an important feature of the curve in Fig. 1 is its slope,

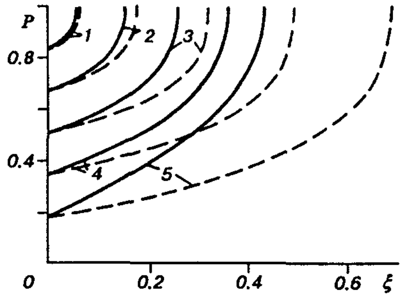

Fig. 2

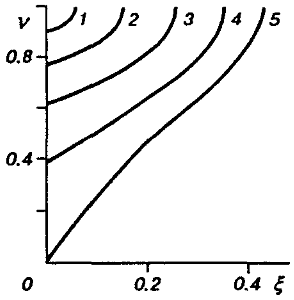

Fig. 3

which is determined by the value of the derivative $d\tilde{P}/d\tilde{\xi}$ at $\tilde{\xi} = 0$. For this case it can be estimated as

$$\left(\frac{d\tilde{P}}{d\tilde{\xi}}\right)_{\tilde{\xi}=0} = \tilde{P}'_e \simeq -0.31.$$

The asymptotic expression for the pressure distribution in the vicinity of the porous medium boundary can be written as

$$\tilde{P} = (1 + 4\,\tilde{P}'_e\,\tilde{\xi})^{1/4}.$$

For the rate of a three-dimensional gas flow through a porous medium boundary which is defined by the expression

$$Q_e = -m(1-\nu_e)S_g v_{ge} = \frac{k_{ge}}{\mu_g}\left(\frac{\partial p}{\partial x}\right)_{x=0},$$

we can write

$$Q_e = \frac{k_0 p_0 S_g^3}{\mu_g}\left(\frac{\rho}{\rho_h^0}\right)^3\left(\frac{cT'(p_0)p_0}{l}\right)^3\left(\frac{p_0-p_e}{p_0}\right)^{5/2}\frac{\tilde{P}'_e}{\sqrt{\text{æ}_p^{(f)}t}}.$$

In general, introducing the dimensionless parameters

$$P = p/p_0, \quad \Theta = T/T_0, \quad \mathcal{R}_g = \rho_g^0/\rho_{g0}^0$$

and self-similar variable $\xi = x/\sqrt{\text{æ}_p^{(f)}t}$ to Eq. (3.13), we can rewrite it in the form

$$-\frac{\xi}{2}\frac{dP}{d\xi} = \chi\frac{\Delta_h\Theta}{\Theta'(P)}\frac{d}{d\xi}\left[\frac{\mathcal{R}_g(1-\nu)^3}{(1-m'')^2}\frac{dP}{d\xi}\right],$$

$$\mathcal{R}_g = P/\Theta(P), \quad 1-\nu = (1-\Theta(P))/\Delta_h\Theta, \quad \Theta(P) = \Theta_*\ln(P/P_*), \quad \Theta'(P) = \Theta_*/P,$$

$$m'' = (1-\nu)mS_g, \quad \Delta_h\Theta = \Delta_h T/T_0, \quad \Theta_* = \frac{T_*}{T_0}, \quad P_* = p_*/p_0, \quad \chi = (\Delta_h\Theta/\Theta'(1))^2 = (\Delta_h\Theta/\Theta_*)^2.$$

The initial and boundary conditions for this equation are as follows:

$$P(\infty) = 1, \qquad P(0) = P_e < 1.$$

Figures 2 and 3 show a typical pressure and hydro-saturation distribution for various values of the pressure difference $\Delta p = p_0 - p_e$. The following values have been accepted for parameters governing the physical properties of the hydrate–porous medium system: $m = 0.1$, $\rho_s^0 = 2.6\cdot 10^3$ kg/m^3, $\rho_l^0 = 10^3$ kg/m^3, $\rho_h^0 = 900$ kg/m^3, $c_s = 10^3$ J/(kg·K), $c_l = 4.2\cdot 10^3$ J/(kg·K), $T_* = 10$ K, $c_h = 2.5\cdot 10^5$ J/(kg·K), $l = 5\cdot 10^5$ J/kg, $T_0 = 293$ K, $p_* = 2.6\cdot 10^{-6}$ Pa, $p_0 = 13.8$ MPa.

Curves *1–5* (Figs. 2 and 3) correspond to the pressure on the porous medium boundary (p_e = 11.5, 9.3, 7.1, 4.7, 2.5 MPa); curve *5* refers to the complete hydrate dissociation on the boundary, and the dashed lines refer to the solution of the simplified Eq. (3.16). It follows from Figs. 2 and 3 that the region of hydrate dissociation is limited in size. Also, it is evident that the curves corresponding to the simplified equation (from the viewpoint of obtaining basic relationships for the region of hydrate dissociation and making quantitative estimates) agree well with the solution in the case of a more general statement of the problem. Since for the solutions presented here the hydrate saturation is always greater than zero ($0 \leqslant \nu \leqslant 1$), a condition for the pressure on the porous region boundary (for which the solution is meaningful) can be obtained on the basis of expression (3.13) for ν. This condition takes the form

$$p_0 \exp\left(-\frac{\Delta_h T}{T_*}\right) \leqslant p \leqslant p_0.$$

It should be noted that this solution obtained by neglecting the thermal conductivity implies that near the hydrate dissociation boundary the permeability tends to zero. Therefore, in the vicinity of the boundary there exists a region where the condition $k_g \ll k_g^*$ holds, which, in turn, means that the thermal conductivity near the dissociation region boundary cannot be neglected. Hence, a new solution should be found which would take account of thermal conductivity. It can be concluded that if the thermal conductivity is taken into account, the dissociation region boundary will be formed as the interface in the partial dissociation of hydrates.

4. Equilibrium Flow. Let us suppose that the products of hydrate dissociation (gas and liquid) move in a porous medium at an equal velocity ($\mathbf{v}_g = \mathbf{v}_l = \mathbf{v}$). Then it follows from Eqs. (2.1) and (2.2) that

$$\begin{gathered}\frac{\partial}{\partial t}[m(1-\nu)(\rho_{gl}^0 - \rho_h^0)] + \nabla \cdot [m(1-\nu)\rho_{gl}^0 \mathbf{v}] = 0, \\ \rho_{gl}^0 = \rho_g^0 S_g + \rho_l^0 S_l.\end{gathered} \tag{4.1}$$

It was assumed above that there is no dissolved gas in the liquid phase and that the gas phase does not contain evaporated liquid. Within the framework of these assumptions the density ρ_{gl}^0 of the gas–liquid mixture can be defined by the equation

$$\frac{1}{\rho_{gl}^0} = \frac{g}{\rho_g^0} + \frac{1-g}{\rho_l^0}. \tag{4.2}$$

In deriving this equation it was also taken into account that, in the initial state, the porous media was completely filled with the hydrate. Using Eq. (1.1) for the gas phase, we obtain the following state equation for the gas–liquid mixture:

$$\frac{1}{\rho_{gl}^0} = \frac{gRT}{p} + \frac{1-g}{\rho_l^0}. \tag{4.3}$$

The Darcy law can be rewritten for the equilibrium mixture in the form

$$m(1-\nu)\mathbf{v} = -\frac{k}{\mu_{gl}}\nabla p. \tag{4.4}$$

To determine the permeability coefficient, expression (2.6) can be used. Applying the same assumptions that were used for Eq. (3.13) to the equation of heat transfer, we can reduce Eqs. (4.1)–(4.4) to the form

$$\left[\frac{(\rho_{gl}^0 - \rho_h^0)T'}{\Delta_h T} + (1-\nu)g\left(\frac{\rho_{gl}^0}{\rho_g^0}\right)^2 \rho_g^{0\prime}\right]\frac{\partial p}{\partial t} = \frac{\partial}{\partial x}\left[\frac{k_0 m^2 \rho_{gl}^0}{\mu_{gl}(1-m')^2}(1-\nu)^3\frac{\partial p}{\partial x}\right], \tag{4.5}$$

$$\rho_g^{0\prime} = \frac{d\rho_g^0}{dp} = \frac{1}{RT}\left(1 - \frac{T'(p)}{T}\right), \quad m' = m(1-\nu).$$

Here the hydrate saturation depends on temperature and pressure in the same way as in (3.13). If $\rho_{gl}^0 \ll \rho_h^0$ (for the dissociation products), a simpler equation can be obtained instead of (4.5):

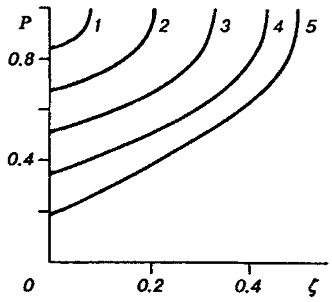

Fig. 4

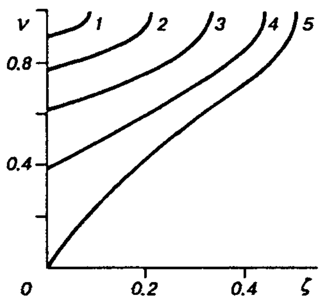

Fig. 5

$$\frac{\partial p}{\partial t} = \frac{\Delta_h T}{T'(p)}\frac{\partial}{\partial x}\left(\frac{k_0 m^2 \rho_{gl}^0}{\mu_{gl}(1-m')^2}(1-\nu)^3\frac{\partial p}{\partial x}\right).$$

Now an analog of Eq. (3.14) can be derived. In this case the coefficient analogous to $\ae_p^{(f)}$ has the form

$$\ae_p^{(e)} = \frac{k_0}{\ae_{gl}}\frac{p_0}{\rho_h^0}\left(\frac{\rho}{\rho_h^0}\right)^2\left(\frac{cT'(p_0)p_0}{l}\right)^2, \quad \ae_{gl} = \mu_{gl}/\rho_{gl0}.$$

According to (3.15), the relation of expressions describing the movement of the right boundary of the hydrate dissociation region for an immovable liquid $x_0^{(f)}$ and for an equilibrium flow $x_0^{(e)}$ can be written as follows:

$$\frac{x_0^{(f)}}{x_0^{(e)}} = \sqrt{\frac{\ae_{gl}}{\ae_g}\frac{\rho_h^0}{\tilde{\rho}_h^0}S_g}. \tag{4.6}$$

If the dynamic viscosity of the mixture is taken equal to the viscosity of the gas phase ($\mu_{gl} \approx \mu_g$) (for example, when the dissociation products are a gas–droplet mixture), this relation takes the form

$$\frac{x_0^{(f)}}{x_0^{(e)}} = \sqrt{\frac{\rho_{g0}^0}{\rho_{gl0}^0}\frac{\rho_h^0}{\tilde{\rho}_h^0}S_g}, \tag{4.7}$$

If, on the contrary, the viscosity of the liquid phase ($\mu_{gl} = \mu_l$) is taken as the dynamic viscosity of the mixture, we obtain

$$\frac{x_0^{(f)}}{x_0^{(e)}} = \sqrt{\frac{\mu_l}{\mu_g}\frac{\rho_{g0}^0}{\rho_{gl0}^0}\frac{\rho_h^0}{\tilde{\rho}_h^0}S_g}. \tag{4.8}$$

It follows from (4.6)–(4.8) that for actual parameters of the hydrate and the products of its dissociation (in particular, it is assumed that $S_g \ll 1$ as a rule) the relation $x_0^{(f)} \ll x_0^{(e)}$ is true for the movement of the hydrate dissociation region boundary. Hence, when the first scheme takes place with the liquid phase being stuck to the porous medium, the boundary moves much slower.

For the problem of a sudden pressure drop on the boundary of a porous medium, Eq. (4.5) in the self-similar variables $\zeta = x/\sqrt{\ae_p^{(e)}t}$ has the form

$$\left[(\tilde{\rho}_{gl0}^0\mathcal{R}_{gl}-1) + \eta(1-\nu)\left(\frac{\mathcal{R}_{gl}}{\mathcal{R}_g}\right)^2\left(\frac{\mathcal{R}_g'(P)}{\Theta'(P)}\right)\right]\frac{\zeta}{2}\frac{dP}{d\zeta} = \chi\frac{\Delta_h\Theta}{\Theta'(P)}\frac{d}{d\zeta}\left(\frac{\mathcal{R}_{gl}(1-\nu)^3}{(1-m')^2}\frac{dP}{d\zeta}\right),$$

$$\tilde{\rho}_{gl0}^0 = \rho_{gl0}^0/\rho_h^0, \quad \rho_{gl0}^0 = \rho_{gl}^0(p_0), \quad \eta = g\Delta_h\Theta\left(\frac{\rho_{gl0}^0}{\rho_{g0}^0}\right)\left(\frac{\rho_{gl0}^0}{\rho_l^0}\right), \quad \mathcal{R}_g'(P) = (1-\Theta_*/\Theta(P))/\Theta(P).$$

Figures 4 and 5 present the pressure and hydrate saturation distribution for various values of the pressure difference $\Delta p = p_0 - p_e$ (curves *1–5* correspond to p_e equal to 11, 9, 7, 5, and 2 MPa, respectively). The characteristic parameters of the gas–hydrate system in this case have the same values as for the first scheme.

It is obvious from Figs. 2 and 4 that the pressure distribution remains qualitatively the same as for the "immovable fluid" scheme. However, the boundary of the dissociation region moves much faster. In the cases where the viscosity of the gas–liquid mixture is taken as the gas viscosity and as the liquid viscosity, the ratio of the boundary coordinates is as follows:

$$\frac{x_0^{(e)}(\mu_g)}{x_0^{(e)}(\mu_l)} = \sqrt{\frac{\mu_l}{\mu_g}}.$$

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