



Gas injection into a moist porous medium with the formation of a gas hydrate[☆]

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ABSTRACT

The model problem of the formation of a gas hydrate when a gas is injected into a porous medium, filled in the initial state with a gas and water, is considered in the one-dimensional approximation. A detailed pattern of the seepage flow with phase transitions for different modes of gas injection is obtained. Three seepage modes in a porous medium are possible, which differ qualitatively in the temperature and hydrate saturation fields. At low boundary pressures no hydrate is formed and the temperature distribution increases monotonically. As the boundary pressure increases, when the corresponding values of the pressure and temperature on the phase diagram lie in the region of gas-hydrate stability (below the equilibrium curve), a purely frontal pattern of hydrate formation is obtained with a monotonic temperature distribution. When the boundary pressure is increased further, an extended region of hydrate formation appears with a convex temperature profile, where, depending on the values of the boundary pressure, the hydrate saturation may be continuous (at high boundary pressures) or change abruptly at lower boundary pressures.

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The interest in analysing processes related to the formation of gas hydrates is due to the development of safe and economic methods of natural-gas conservation.^{1,2} The equilibrium temperature of phase transitions for gas hydrates depends quite strongly on the pressure, and hence their formation and expansion when thermal and force fields act on a porous medium may occur on frontal boundaries, and also within the volume;^{3–6} therefore, the theory of these processes is an extension of Stefan's problem.

1. Formulation of the problem

To describe processes of heat and mass transfer when a gas is pumped into a porous stratum we will use the following assumptions. A single-temperature mode is considered, i.e., the temperatures of the porous medium and of the saturating substance (gas, hydrate or water) are identical. The hydrate is a two-component system with a mass concentration of gas G . The skeleton of the porous medium, the gas hydrate and the water are incompressible and fixed, the porosity is constant and the gas is calorically perfect.

With these assumptions, we will write the equations of conservation of mass, Darcy's law and the equation of state of the gas and the heat flux equation for the one-dimensional problem as follows:

$$\begin{aligned} \frac{\partial}{\partial t}(mS_g\rho_g) + \frac{\partial}{\partial x}(mS_g v_g \rho_g) &= -mG\rho_h \frac{\partial S_h}{\partial t}, \quad \frac{\partial}{\partial t}(mS_l\rho_l) = -m(1-G)\rho_h \frac{\partial S_h}{\partial t} \\ mS_g v_g &= -\frac{k_g}{\mu_g} \frac{\partial p}{\partial x}, \quad p = \rho_g R_g T \\ \rho c \frac{\partial T}{\partial t} + \rho_g c_g m S_g v_g \frac{\partial T}{\partial x} &= \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right) + m\rho_h L_h \frac{\partial S_h}{\partial t} \\ \left(\rho c = (1-m)\rho_{sk}c_{sk} + m \sum_{j=g,l,h} S_j \rho_j c_j, \quad \lambda = (1-m)\lambda_{sk} + m \sum_{j=g,l,h} S_j \lambda_j, \quad S_g + S_l + S_h = 1 \right) \end{aligned} \quad (1.1)$$

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Here m is the porosity, p is the pressure, T is the temperature, ρ_j and S_j are the true density and saturation of the j -th phase ($j = g, \ell, h, sk$), the subscripts g, ℓ, h and sk relate to the parameters of the gas, water, hydrate and skeleton of the porous medium, v_g, k_g and μ_g are the velocity, permeability and dynamic viscosity of the gas phase, L_h is the specific heat of the hydrate formation, c_j and λ_j are the specific heat capacity and thermal conductivity of the phases, and ρc and λ are the specific volume heat capacity and thermal conductivity of the system. Since, in the majority of cases, the thermal conductivity and heat capacity of the stratum are determined by the porous skeleton, the variability of the thermal diffusivity will be neglected. Moreover, it follows from estimates given previously in Ref. 3, that the term in the heat-flux equation, related to the work of the pressure forces, makes an unimportant contribution.

We have the following equality for the ratio of the rates of seepage of the water and gas

$$mS_\ell v_\ell / (mS_g v_g) = \mu_g k_\ell / (\mu_\ell k_g)$$

where $k_i (i = \ell, g)$ are the phase permeabilities. Since the gas viscosity μ_g is considerably less than the water viscosity μ_ℓ , this ratio is always usually small (with the exception of cases when the initial water saturation $S_{\ell 0}$ is close to a certain limit value $S_{\ell*}$, which will be determined later). Hence, in the majority of cases of practical interest, the assumption that the liquid is at rest $v_\ell = 0$ is justified.

The dependence of the permeability for the gas k_g on the actual porosity mS_g will be specified using Kozeny's formula.⁷ We then obtain the following relation between the permeability and the gas saturation

$$k_g = k_* \frac{(mS_g)^3}{(1 - mS_g)^2} \approx k_0 S_g^3, \quad k_0 = k_* m^3 \quad (1.2)$$

The quantity k_0 corresponds to the permeability of the skeleton.

The values of the temperature and pressure in the region in which the hydrate is formed are related to the phase equilibrium condition²

$$T = T_0 + T_* \ln(p/p_{s0}) \quad (1.3)$$

where T_0 is the initial temperature of the system, p_{s0} is the equilibrium pressure, corresponding to the initial temperature, and T_* is an empirical parameter, the value of which depends on the form of the gas hydrate.

According to modern ideas,⁸ the formation of hydrate particles is accompanied by non-equilibrium processes, due to diffusion of the hydrate-forming gas towards the water-hydrate contact surface through the layer of water and hydrate. Assuming that the characteristic thicknesses of these layers is of the order of the dimensions of the pore channels $\sqrt{k_g/m}$, we obtain the estimate $t_D = k_g/(mD)$ for the characteristic relaxation times t_D of diffusion non-equilibrium, where D is the diffusion coefficient. For porous media of interest in practice, the permeability and diffusion coefficient lie in the ranges $k_g \sim 10^{-14} - 10^{-12} \text{ m}^2$ and $D \sim 10^{-11} - 10^{-9} \text{ m}^2/\text{s}$, while the value of the porosity $m \sim 10^{-1}$. Hence, we have $t_D \leq 1 \text{ s}$ for the characteristic times of diffusion non-equilibrium. Consequently, compared with the times that are of interest in the problem being considered here, these characteristic times, as a rule, are short.

Three characteristic regions may arise when a gas hydrate is formed in a porous stratum. In the region close to the boundary $x=0$ the pores are filled with gas and hydrate. In the second (intermediate) region gas hydrate is formed, and hence here the pores are filled with gas, water and hydrate. In the third (far) region gas and water are present. At the boundaries of these regions the conditions of mass and heat balance must be satisfied⁴

$$\begin{aligned} [m(S_h \rho_h (1 - G) + S_l \rho_l) \dot{x}_{(i)}] &= 0, \quad [m(\rho_g S_g (v_g - \dot{x}_{(i)}) - \rho_h S_h G \dot{x}_{(i)})] = 0 \\ \left[\lambda \frac{\partial T}{\partial x} \right] &= [m \rho_h L_h S_h \dot{x}_{(i)}] \end{aligned} \quad (1.4)$$

Here $[\psi]$ is the jump in the parameter ψ at the boundary $x = x_{(i)}$ ($i = n, d$) between the regions, $\dot{x}_{(i)}$ is the velocity of motion of this boundary, the value $i = n$ relates to the boundary between the near and intermediate regions, and $i = d$ relates to the boundary between the intermediate and far regions. The temperature and pressure in these regions will be assumed to be continuous.

Suppose the stratum, at the initial instant of time, is saturated with gas ($S_g = S_{g0}$) and water ($S_\ell = S_{\ell 0}$), the pressure p_0 and the temperature T_0 of which in the initial state correspond to the thermodynamic conditions for their existence in a free state ($p_0 \leq p_{s0}$) and are the same over the whole stratum. These conditions can be written as follows

$$t = 0: \quad S_\ell = S_{\ell 0} \quad (S_g = 1 - S_{\ell 0}, S_h = 0), \quad T = T_0, \quad p = p_0 \quad (x \geq 0) \quad (1.5)$$

When $t > 0$ gas (similar to the initial gas) at a temperature T_e at constant pressure p_e begins to enter through the boundary $x=0$. The boundary condition then has the form

$$x = 0: \quad T = T_e, \quad p = p_e \quad (t > 0) \quad (1.6)$$

The problem has a self-similar solution. As already noted, there are two ways in which the hydrate can be formed. In the first, the hydrate is formed completely on the front boundary. In the second an extended region with phase transitions is formed. Consequently, the first mode can be regarded as the limiting situation, when the intermediate region degenerates into a phase-transition surface ($x_{(n)} = x_{(d)} = x_{(s)}$).

In Fig. 1 we show, in the phase plane (p, T), these two ways in which a hydrate can be formed for the same initial state (0) in a porous medium. The boundary conditions at $x=0$, corresponding to the two regimes, are denoted by the points (e_1) and (e_2). The point (s) on the gas-water-hydrate (g, ℓ, h) system phase equilibrium line corresponds to the frontal boundary of the phase transitions for the first mode. The part of the line on the phase-equilibrium curve between the points $s_{(n)}$ and $s_{(d)}$ corresponds to an intermediate region for the second mode, while the points themselves correspond to the near and far boundaries of the intermediate region.

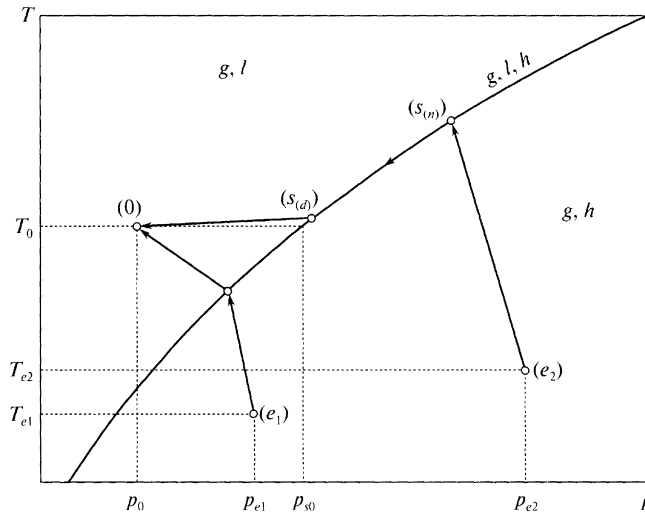


Fig. 1.

2. Solutions in the near and far regions

We will introduce the self-similar variable

$$\xi = x / \sqrt{\aleph^{(T)} t} \quad (\aleph^{(T)} = \lambda / \rho c)$$

where $\aleph^{(T)}$ is the thermal diffusivity of the stratum.

The second equation of (1.1) can be integrated, taking into account the initial condition for S_ℓ (1.5). As a result we obtain the relations

$$S_h = \frac{\rho_\ell}{\rho_h(1-G)}(S_{\ell 0} - S_\ell), \quad S_g = 1 - S_{\ell 0} + \left(1 - \frac{\rho_\ell}{\rho_h(1-G)}\right)(S_{\ell 0} - S_\ell) \tag{2.1}$$

Hence, in the light of these assumptions, assuming $S_\ell = 0$, we have for the near region ($0 \leq x \leq x_{(n)}$) from relations (2.1)

$$S_{he} = \frac{\rho_\ell S_{\ell 0}}{\rho_h(1-G)}, \quad S_{ge} = 1 - S_{he} \tag{2.2}$$

Hence, in the far and near regions gas seepage in the porous medium occurs with constant but different values of the actual porosity and permeability in each region.

In view of the fact that the density of the hydrate is less than the density of water, the transfer of water into the composition of the hydrate will reduce the actual porosity of the system. Since the hydrate saturation cannot exceed unity ($S_{he} < 1$), the assumed scheme is applicable for an initial water saturation, which satisfies the condition

$$S_{\ell 0} < S_{\ell 0*}, \quad S_{\ell 0*} = \rho_h(1-G) / \rho_\ell$$

In fact, to satisfy the hypothesis that the liquid is at rest, as was pointed out, the value of $S_{\ell 0}$ must be somewhat lower than $S_{\ell 0*}$, in order for the following condition to be satisfied over the seepage region

$$k_\ell / k_g \ll \mu_g / \mu_\ell$$

Usually, the characteristic pressure drop $\Delta p = p_e - p_0$ and the characteristic temperature drop $\Delta T = T_e - T_0$ in the seepage region satisfy the conditions

$$|\Delta p| / p_0 \gg |\Delta T| / T_0$$

The following estimates then follow from the equation of state for a calorifically perfect gas

$$\Delta \rho_g / \rho_{g0} \approx \Delta p / p_0 - \Delta T / T_0 \approx \Delta p / p_0$$

Hence, the change in density due to the variability of the temperature can be neglected. Using Leibenzon's linearization method,⁷ we obtain the following solution for the dimensionless pressure $P = p/p_0$ and temperature $\theta = T/T_0$ in the near and far regions:

when $0 < \xi < \xi_{(n)}$

$$\begin{aligned}
 P^2 &= P_{(n)}^2 + (P_e^2 - P_{(n)}^2) \frac{\Phi_{(n)}^{(p)}(\xi)}{\Phi_{(n)}^{(p)}(0)}, \quad \theta = \theta_{(n)} + (\theta_e - \theta_{(n)}) \frac{\Phi_{(n)}^{(T)}(\xi)}{\Phi_{(n)}^{(T)}(0)} \\
 \Phi_{(n)}^{(p)}(\xi) &= \int_{\xi}^{\xi_{(n)}} E_{(n)}^{(p)}(\xi) d\xi, \quad E_{(n)}^{(p)}(\xi) = \exp\left(-\frac{\xi^2}{4\eta_{(n)}}\right) \\
 \Phi_{(n)}^{(T)}(\xi) &= \int_{\xi}^{\xi_{(n)}} E_{(n)}^{(T)}(\xi) d\xi, \quad E_{(n)}^{(T)}(\xi) = \exp\left(-\frac{\xi^2}{4} - \frac{\alpha_{(n)} P^2}{2}\right)
 \end{aligned} \tag{2.3}$$

when $\xi_{(d)} < \xi < \infty$

$$\begin{aligned}
 P^2 &= 1 + (P_{(d)}^2 - 1) \frac{\Phi_{(d)}^{(p)}(\xi)}{\Phi_{(d)}^{(p)}(\xi_{(d)})}, \quad \theta = 1 + (\theta_{(d)} - 1) \frac{\Phi_{(d)}^{(T)}(\xi)}{\Phi_{(d)}^{(T)}(\xi_{(d)})} \\
 \Phi_{(d)}^{(p)}(\xi) &= \int_{\xi}^{\infty} E_{(d)}^{(p)}(\xi) d\xi, \quad E_{(d)}^{(p)}(\xi) = \exp\left(-\frac{\xi^2}{4\eta_{(d)}}\right) \\
 \Phi_{(d)}^{(T)}(\xi) &= \int_{\xi}^{\infty} E_{(d)}^{(T)}(\xi) d\xi, \quad E_{(d)}^{(T)}(\xi) = \exp\left(-\frac{\xi^2}{4} - \frac{\alpha_{(d)} P^2}{2}\right)
 \end{aligned} \tag{2.4}$$

Here $\xi_{(i)} = x_{(i)} / \sqrt{\aleph^{(T)} t}$ ($i = n, d$) are the self-similar coordinates of the frontal boundaries. For the dimensionless coefficients, occurring in these solutions, and also in the solutions derived later, we have

$$\begin{aligned}
 \eta_{(i)} &= \frac{\aleph_{(i)}^{(p)}}{\aleph^{(T)}}, \quad \alpha_{(i)} = \frac{\rho_{g0} c_g k_{(i)} p_0}{\lambda \mu_g}, \quad \aleph_{(i)}^{(p)} = \frac{k_{(i)} p_0}{m S_{g(i)} \mu_g}, \quad k_{(i)} = k_0 S_{g(i)}^3; \quad i = n, d \\
 \theta_{(i)} &= 1 + \theta_* \ln \frac{P_{(i)}}{P_{s0}}, \quad i = n, d, s; \quad \theta_* = \frac{T}{T_{0*}}, \quad P_{s0} = \frac{p_{s0}}{p_0}, \\
 S_{g(d)} &= S_{g0} = 1 - S_{\ell 0}, \quad S_{g(n)} = S_{ge}
 \end{aligned} \tag{2.5}$$

3. The equation of piezoconductivity in the intermediate region

The first equation of (1.1), taking equalities (2.1) into account, can be reduced to the form

$$\frac{\partial}{\partial t} (m S_g (\rho_g - \rho_{gh})) + \frac{\partial}{\partial x} (m S_g v_g \rho_g) = 0 \quad \left(\rho_{gh} = \frac{G \rho_h \rho_\ell}{\rho_\ell - (1 - G) \rho_h} \right) \tag{3.1}$$

In particular, for methane gas hydrate² we have

$$\rho_h = 0.9 \cdot 10^3 \text{ kg/m}^3, \quad \rho_\ell = 10^3 \text{ kg/m}^3, \quad G = 0.12$$

and, consequently, $\rho_{gh} \approx \rho_h/2$. Since in the majority of cases $\rho_g \ll \rho_{gh}$, in the first term on the left-hand side of Eq. (3.1) we can neglect the quantity ρ_g compared with ρ_{gh} . Then, the first equation of (1.1) takes the form

$$m G \rho_h \frac{\partial S_h}{\partial t} + \frac{\partial}{\partial x} (m S_g v_g \rho_g) = 0 \tag{3.2}$$

Eliminating $\partial S_h / \partial t$ from the heat flux equation (the fifth equation of (1.1)) and Eq. (3.2), and also taking Darcy's law into account (the third equation of (1.1)), we can obtain

$$\rho_c \frac{\partial T}{\partial t} - \rho_g c_g \frac{k_g \partial p \partial T}{\mu_g \partial x \partial x} = \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} + \frac{L_h}{G} \rho_g \frac{k_g \partial p}{\mu_g \partial x} \right) \tag{3.3}$$

Using the phase-equilibrium condition (1.3), we can write this equation in the form

$$\rho_c \frac{\partial T}{\partial t} - \rho_g c_g \frac{k_g T_* (\partial p)^2}{\mu_g p} = \frac{\partial}{\partial x} \left(\left(\frac{\lambda T_*}{p} + \frac{L_h}{G} \rho_g \frac{k_g}{\mu_g} \right) \frac{\partial p}{\partial x} \right) \tag{3.4}$$

We will compare the effects of conductive thermal conductivity and piezoconductivity when pressure fields propagate. It can be seen from the expression for the coefficient in front of $\partial p / \partial x$ in Eq. (3.4) that the thermal conductivity is unimportant if the permeability k_g

satisfies the condition

$$k_g \gg k_{g*}; \quad k_{g*} = \frac{\lambda T_* G \mu_g}{\rho_0 \rho_{g0} L_h} \tag{3.5}$$

For practical systems this critical permeability is very small: $k_{g*} \approx 10^{-18} \text{ m}^2$, and hence in the intermediate region the thermal conductivity can also be neglected.

We will compare the second term on the left-hand side of Eq. (3.4), corresponding to convective heat transfer due to seepage of the gas, with the right-hand side of this equation neglecting conductive thermal conductivity. We have for their ratio

$$\chi = G \frac{c_g T_* \Delta p}{L_h p_0} \tag{3.6}$$

This quantity is small for practical systems (when $\Delta p \sim p_0$ for methane gas hydrates it amounts to $\chi \approx 2 \times 10^{-2}$). Consequently, convective heat transfer in the intermediate region is also unimportant. The heat flux equation can then be simplified and reduced to the form

$$\rho c \frac{\partial T}{\partial t} = m \rho_h L_h \frac{\partial S_h}{\partial t} \tag{3.7}$$

Equation (3.7) can be integrated in the intermediate region ($x_{(n)} \leq x \leq x_{(d)}$). We obtain

$$S_h = \frac{\rho c}{m \rho_h L_h} (T - T_{(d)}) \tag{3.8}$$

where $T_{(d)}$ is the value of the temperature on the far boundary.

Substituting $\partial S_h / \partial t$ from Eq. (3.7) into Eq. (3.2), taking Darcy’s law (the third equality of (1.1)) and the phase-equilibrium condition (1.3) into account, we obtain a non-linear equation for the dimensionless pressure

$$\begin{aligned} \frac{\partial P}{\partial t} &= \aleph_{(m)} P \frac{\partial}{\partial x} \left(\frac{P S_g^3 \partial P}{\theta \partial x} \right) \\ \aleph_{(m)} &= \frac{k_0 \rho_{g0} p_0 L_h}{G \mu_g \rho c T_*}, \quad S_g = 1 - S_{\ell 0} - \left(1 - \frac{(1-G)\rho_h}{\rho_\ell} \right) S_h, \\ S_h &= \frac{1}{m} \frac{\rho c T_*}{\rho_h L_h} \ln \frac{P}{P_{(d)}}, \quad \theta = 1 + \theta_* \ln \frac{P}{P_{s0}} \end{aligned} \tag{3.9}$$

We will compare Eq. (3.9) with the usual linearized seepage equation⁹ with piezoelectric coefficient $\aleph = k \rho_0 C^2 / (m \mu)$ (where C is the velocity of sound for a fluid, defining its compressibility). It follows from a comparison of the formula for \aleph and the expression for $\aleph_{(m)}$ from Eq. (3.9), that the effective velocity of sound for the system considered in the intermediate region is given by the expression

$$C = \sqrt{\frac{m S_g^3 p_0 L_h}{G \rho c T_*}} \tag{3.10}$$

For methane gas hydrate with $p_0 = 3 \text{ MPa}$ and $m S_g \approx 10^{-10}$ this quantity amounts to $C \approx 250 \text{ m/s}$. Hence, the compressibility of the fluid in the intermediate region is determined by phase-transition effects. Hence, expression (3.10) for the porous skeleton – gas hydrate – gas – water system can be considered as an analogue of the Landau velocity of sound.¹⁰

Equation (3.9) takes the following form in self-similar variables

$$-\frac{\xi dP}{2 d\xi} = \eta_{(m)} P \frac{d}{d\xi} \left(\frac{P S_g^3 dP}{\theta d\xi} \right); \quad \eta_{(m)} = \frac{\aleph_{(m)}}{\aleph_{(T)}} \tag{3.11}$$

It can be seen from this equation that the non-linearity related to the change in the actual porosity (defined by the quantity S_g) is unimportant if the following condition is satisfied

$$S_{g0} - S_{ge} \ll S_{g0} \tag{3.12}$$

Taking the expressions for S_{g0} and S_{ge} into account (the last two expressions of Eq. (2.5)), we hence obtain the following critical condition for the initial water saturation

$$S_{\ell 0} \ll S_{\ell*}; \quad S_{\ell*} = \frac{\rho_h (1-G)}{\rho_\ell} \tag{3.13}$$

For methane gas hydrate $S_{\ell*} \approx 0.8$. When condition (3.13) is satisfied, and also, in more general cases, when we can neglect the variability of S_g , and also assuming $\theta \approx 1$ in Eq. (3.11), we can obtain the Leibenzon linearized solution

$$P^2 = P_{(d)}^2 + (P_{(n)}^2 - P_{(d)}^2) \frac{\Phi_{(m)}^{(p)}(\xi)}{\Phi_{(m)}^{(p)}(\xi_{(n)})}$$

$$\Phi_{(m)}^{(p)}(\xi) = \int_{\xi}^{\xi_{(d)}} E_{(m)}^{(p)}(\xi) d\xi \quad E_{(m)}^{(p)}(\xi) = \exp\left(-\frac{\xi^2}{4\tilde{\eta}_{(m)}}\right), \quad \tilde{\eta}_{(m)} = \tilde{S}_g^3 \tilde{\eta}_{(m)} \tilde{P}^2 \tag{3.14}$$

where \tilde{S}_g and \tilde{P} are certain mean values of the gas saturation and the dimensionless pressure in the intermediate region ($P_{(d)} \leq \tilde{P} \leq P_{(n)}$).

4. The conditions on the boundary between the regions

Taking Darcy's law into account (the third equality of (1.1)) for the near boundary ($x=x_{(n)}$) we can obtain from conditions (1.4)

$$-\frac{k_{(n)}^- (\partial p)^-}{\mu_g (\partial x)_{(n)}} + \frac{k_{(n)}^+ (\partial p)^+}{\mu_g (\partial x)_{(n)}} = m (S_{h(n)}^- - S_{h(n)}^+) \left(1 - \frac{G \rho_h}{\rho_{g(n)}} - \frac{\rho_h (1-G)}{\rho_f}\right) \dot{x}_{(n)}$$

$$-\lambda (\partial T)^- + \lambda (\partial T)^+ = m \rho_h L_h (S_{h(n)}^- - S_{h(n)}^+) \dot{x}_{(n)}$$

$$\left(S_{h(n)}^- = S_{he}, \quad k_{(n)}^- = k_{(n)} = k_0 S_{ge}^3, \quad k_{(n)}^+ = k_0 (S_{g(n)}^+)^3, \quad S_{g(n)}^+ = 1 - S_{\ell 0} - \left(1 - \frac{\rho_h (1-G)}{\rho_f}\right) S_{h(n)}^+\right) \tag{4.1}$$

The superscripts plus and minus correspond to the value of the parameters which undergo discontinuities before and after the boundary. On the far boundary we assume that the hydrate saturation undergoes no discontinuity $S_{h(d)}^- = S_{h(d)}^+ = 0$. From similar conditions for $x=x_{(d)}$ we obtain

$$-\left(\frac{\partial p}{\partial x}\right)_{(d)}^- + \left(\frac{\partial p}{\partial x}\right)_{(d)}^+ = 0, \quad -\left(\frac{\partial T}{\partial x}\right)_{(d)}^- + \left(\frac{\partial T}{\partial x}\right)_{(d)}^+ = 0 \tag{4.2}$$

In the intermediate region, the temperature and pressure are related by phase-equilibrium condition (1.3), and hence the derivatives of the pressure and temperature on the boundary $x=x_{(n)}$ and $x=x_{(d)}$ must be related respectively by the relations

$$\left(\frac{\partial T}{\partial x}\right)_{(n)}^+ = \frac{T_*}{p_{(n)}} \left(\frac{\partial p}{\partial x}\right)_{(n)}^+, \quad \left(\frac{\partial T}{\partial x}\right)_{(d)}^- = \frac{T_*}{p_{(d)}} \left(\frac{\partial p}{\partial x}\right)_{(d)}^- \tag{4.3}$$

Using solutions (2.3) and condition (4.1) and taking the first relation of (4.3) into account we obtain

$$-(\theta_e - \theta_{(n)}) \frac{E_{(n)}^{(T)}(\xi_{(n)})}{\Phi_{(n)}^{(T)}(0)} + \frac{\theta_* (P_e^2 - P_{(n)}^2)}{2P_{(n)}^2} \left(\frac{S_{g(n)}^-}{S_{g(n)}^+}\right)^3 \frac{E_{(n)}^{(p)}(\xi_{(n)})}{\Phi_{(n)}^{(p)}(0)} =$$

$$= \left(m \tilde{\rho}_h J a_h + \left(1 - \frac{G \theta_{(n)}}{\tilde{\rho}_{g0} P_{(n)}} - \frac{1-G}{\tilde{\rho}_\ell}\right) \frac{\theta_*}{P_{(n)} S_{g(n)} \eta_{(n)}} \left(\frac{S_{g(n)}^-}{S_{g(n)}^+}\right)^3\right) \frac{(S_{h(n)}^- - S_{h(n)}^+) \xi_{(n)}}{2}$$

$$\left(\tilde{\rho}_h = \frac{\rho_h}{\rho}, \quad \tilde{\rho}_{g0} = \frac{\rho_{g0}}{\rho_h}, \quad \tilde{\rho}_\ell = \frac{\rho_\ell}{\rho_h}, \quad J a_h = \frac{L_h}{c T_0}\right) \tag{4.4}$$

Equation (4.4) for specified values of the pressure and temperature on the boundary, defined by the dimensionless quantities P_e and θ_e , connects the three quantities $\xi_{(n)}$, $P_{(n)}$ and $S_{(n)}^+$, while all the remaining quantities occurring here ($S_{g(n)}^-$ and $S_{h(n)}^-$, for example) are uniquely defined by the initial values p_0 , T_0 and $S_{\ell 0}$. Similarly from the condition on the far boundary ($\xi = \xi_{(d)}$), taking solution (2.4) into account, we obtain

$$\frac{P_{(d)}^2 - 1 E_{(d)}^{(p)}(\xi_{(d)})}{2P_{(d)} \Phi_{(d)}^{(p)}(\xi_{(d)})} + \left(\frac{dP}{d\xi}\right)_{(d)}^- = 0, \quad (\theta_{(d)} - 1) \frac{E_{(d)}^{(T)}(\xi_{(d)})}{\Phi_{(d)}^{(T)}(\xi_{(d)})} + \left(\frac{d\theta}{d\xi}\right)_{(d)}^- = 0 \tag{4.5}$$

Eliminating $(dP/d\xi)_{(d)}^-$ and $(d\theta/d\xi)_{(d)}^-$ and taking the second equality of (4.3) into account we have the equation

$$\theta_* \frac{P_{(d)}^2 - 1 E_{(d)}^{(p)}(\xi_{(d)})}{2P_{(d)} \Phi_{(d)}^{(p)}(\xi_{(d)})} - (\theta_{(d)} - 1) \frac{E_{(d)}^{(T)}(\xi_{(d)})}{\Phi_{(d)}^{(T)}(\xi_{(d)})} = 0 \tag{4.6}$$

It relates the unknown quantities $\xi_{(d)}$ and $P_{(d)}$, which, in addition to the initial properties of the porous medium, depend on the conditions for gas injection through the boundary $x=0$.

When the purely frontal mode of phase transitions occurs (the intermediate region degenerates to a surface $\xi_{(n)} = \xi_{(d)} = \xi_{(s)}$), we obtain from the mass and heat balance conditions (1.4), using analytic solutions (2.3) and (2.4),

$$\frac{P_e^2 - P_{(s)}^2}{2P_{(s)}} \frac{E_{(n)}^{(p)}(\xi_{(s)})}{\Phi_{(n)}^{(p)}(0)} - \left(\frac{S_{ge}}{S_{g0}}\right)^3 \frac{P_{(s)}^2 - 1}{2P_{(s)}} \frac{E_{(d)}^{(p)}(\xi_{(s)})}{\Phi_{(d)}^{(p)}(\xi_{(s)})} = \left(1 - \frac{G}{\tilde{\rho}_{g0} P_{(s)}} \theta_{(s)} - \frac{1-G}{\tilde{\rho}_\ell}\right) \frac{S_{he} \xi_{(s)}}{2S_{ge} \eta_{(n)}} \tag{4.7}$$

$$-(\theta_e - \theta_{(s)}) \frac{E_{(n)}^{(T)}(\xi_{(s)})}{\Phi_{(n)}^{(T)}(0)} + (\theta_{(s)} - 1) \frac{E_{(d)}^{(T)}(\xi_{(s)})}{\Phi_{(d)}^{(T)}(\xi_{(s)})} = \frac{1}{2} m \tilde{\rho}_h J a_h S_{he} \xi_{(s)} \tag{4.8}$$

For the functions $\Phi_{(n)}^{(p)}(\xi)$, $\Phi_{(n)}^{(T)}(\xi)$ and $\Phi_{(d)}^{(p)}(\xi)$, $\Phi_{(d)}^{(T)}(\xi)$, defined by formulae (2.3) and (2.4), we put $\xi_{(n)} = \xi_{(s)}$ and $\xi_{(d)} = \xi_{(s)}$.

Equations (4.7) and (4.8) for known values of the parameters of the system in the initial state, and also values of the pressure and temperature on the boundary, enable us to determine the hydrodynamic and temperature fields in the porous medium. In order for the solutions obtained not to be thermodynamically contradictory, the values of the temperature in the region $x_{(s)} < x < \infty$ must be no higher than its equilibrium values, defined by formula (1.3) for the current values of the pressure in this region. In particular, the necessary condition for this is that the following inequalities should be satisfied for $x = x_{(s)}$

$$-\left(\frac{dT}{dx}\right)_{(s)}^+ \leq -\left(\frac{dT}{dp}\right)_{(s)} \left(\frac{dp}{dx}\right)_{(s)}^+ \left(\left(\frac{dT}{dp}\right)_{(s)} = \frac{T_*}{p_{(s)}}\right) \tag{4.9}$$

or

$$\left(\frac{d\theta}{d\xi}\right)_{(s)}^+ \geq \frac{\theta_*}{P_{(s)}} \left(\frac{dP}{d\xi}\right)_{(s)}^+ \tag{4.10}$$

The derivatives $(d\theta/d\xi)_{(s)}^+$ and $(dP/d\xi)_{(s)}^+$ must be calculated from solution (2.4).

Taking inequality (4.10) as the critical condition, which ensures that the solutions for $\xi > \xi_{(s)}$ are not physically contradictory, we can write the equation of the line which is the boundary of the region in the (P_e, θ_e) plane, when a purely frontal gas hydrate formation mode is obtained, in the form

$$\begin{aligned} & -(\theta_e - \theta_{(s)}) \frac{E_{(n)}^{(T)}(\xi_{(s)})}{\Phi_{(n)}^{(T)}(0)} + \theta_* \frac{P_e^2 - P_{(s)}^2}{2P_{(s)}^2} \left(\frac{S_{ge}}{S_{g0}}\right)^3 \frac{E_{(n)}^{(p)}(\xi_{(s)})}{\Phi_{(n)}^{(p)}(0)} \\ & = \left(m \tilde{\rho}_h J a_h + \left(1 - \frac{G}{\tilde{\rho}_{g0} P_{(s)}} \theta_{(s)} - \frac{1-G}{\tilde{\rho}_\ell}\right) \frac{\theta_*}{P_{(s)} S_{ge} \eta_{(n)}} \left(\frac{S_{ge}}{S_{g0}}\right)^3 \right) \frac{S_{he} \xi_{(s)}}{2} \end{aligned} \tag{4.11}$$

This equation, together with equalities (4.7) and (4.8) gives the relation between P_e and θ_e .

Note that problems touching on the existence and evolution of abrupt changes in the hydrate saturation can be investigated using the method described earlier in Refs 11 and 12.

5. The solution in the intermediate region

Hence, we have arrived at the boundary-value problem for Eq. (3.11) in the interval $\xi_{(n)} \leq \xi \leq \xi_{(d)}$. Here the unknown coordinates of the boundaries $\xi_{(n)}$ and $\xi_{(d)}$, and also the values of the pressures $P_{(n)}$ and $P_{(d)}$ at these boundaries must satisfy system of transcendental equations (4.4) and (4.6). A numerical solution of this problem can be obtained by ranging the value of the pressure $P_{(d)}$ on the right boundary of the intermediate region. By choosing the value of $P_{(d)} > 1$, we start counting from the right boundary $\xi = \xi_{(d)}$, the coordinates of which are defined uniquely by Eq. (4.6) in terms of $P_{(d)}$. Here the value of the first derivative $P'_{(d)}$, necessary to realize Cauchy's problem for Eq. (3.11), is determined using the first equation of (4.5). The Cauchy problem is then solved in the direction to the boundary $\xi = \xi_{(n)}$ (with a negative step) for Eq. (3.11) with the "initial" conditions

$$P = P_{(d)}, \quad dP/d\xi = P'_{(d)} \text{ when } \xi = \xi_{(d)}$$

until Eq. (4.4) is satisfied for the current values of the self-similar coordinate ξ and the dimensionless pressure P . Here the corresponding quantities $S_{h(n)}^+$ and $S_{g(n)}^+$, occurring in Eq. (4.4), according to the third and fourth equalities of (3.9) are determined from the formulae

$$S_{h(n)}^+ = \frac{1}{m} \frac{\rho c T_*}{\rho_h L_h} \ln \frac{P_{(n)}}{P_{(d)}}, \quad S_{g(n)}^+ = 1 - S_{\ell 0} - \left(1 - \frac{\rho_h (1-G)}{\rho_\ell}\right) S_{h(n)}^+ \tag{5.1}$$

The values of $P_{(d)}$ are chosen until Eq. (4.4) is satisfied with the specified accuracy.

As numerical calculations show, in the majority of cases of practical interest, in the far region the variability of the temperature can be neglected and one can assume $T = T_0$. Hence, taking condition (1.3) into account, we will have $P_{(d)} = P_{s0}$. In this case ranging is necessary along the self-similar coordinate $\xi_{(d)}$ of the far boundary.

If we use solution (3.14) for the intermediate region, boundary conditions (4.1) for $\xi = \xi_{(n)}$ can be written in the form

$$\begin{aligned} & \frac{P_e^2 - P_{(n)}^2}{P_{(n)}} \frac{E_{(n)}^{(p)}(\xi_{(n)})}{\Phi_{(n)}^{(p)}(0)} - \frac{P_{(n)}^2 - P_{(d)}^2}{P_{(n)}} \left(\frac{S_{g(n)}^+}{S_{g(n)}} \right)^3 \frac{E_{(m)}^{(p)}(\xi_{(n)})}{\Phi_{(m)}^{(p)}(\xi_{(n)})} = \\ & = \left(1 - \frac{G}{\tilde{\rho}_{g0}} \frac{\theta_{(n)}}{P_{(n)}} - \frac{1-G}{\tilde{\rho}_\ell} \right) \frac{(S_{h(n)}^- - S_{h(n)}^+) \xi_{(n)}}{S_{g(n)} \eta_{(n)}} \\ & - (\theta_e - \theta_{(n)}) \frac{E_{(n)}^{(T)}(\xi_{(n)})}{\Phi_{(n)}^{(T)}(0)} + \theta_* \frac{P_{(n)}^2 - P_{(d)}^2}{2P_{(n)}^2} \frac{E_{(m)}^{(p)}(\xi_{(n)})}{\Phi_{(m)}^{(p)}(\xi_{(n)})} = \frac{1}{2} m \tilde{\rho}_h J a_h (S_{h(n)}^- - S_{h(n)}^+) \xi_{(n)} \end{aligned} \quad (5.2)$$

Boundary conditions (4.5) on the far boundary ($\xi = \xi_{(d)}$) take the form

$$\begin{aligned} & \frac{P_{(d)}^2 - 1}{P_{(d)}} \frac{E_{(d)}^{(p)}(\xi_{(d)})}{\Phi_{(d)}^{(p)}(\xi_{(d)})} - \frac{P_{(n)}^2 - P_{(d)}^2}{P_{(d)}} \frac{E_{(m)}^{(p)}(\xi_{(d)})}{\Phi_{(m)}^{(p)}(\xi_{(n)})} = 0 \\ & (\theta_{(d)} - 1) \frac{E_{(d)}^{(T)}(\xi_{(d)})}{\Phi_{(d)}^{(T)}(\xi_{(d)})} - \frac{\theta_* (P_{(n)}^2 - P_{(d)}^2)}{2P_{(d)}^2} \frac{E_{(m)}^{(T)}(\xi_{(d)})}{\Phi_{(m)}^{(T)}(\xi_{(n)})} = 0 \end{aligned} \quad (5.3)$$

Since the quantities $\theta_{(n)}$ and $\theta_{(d)}$ are determined, on the basis of condition (1.3), by the values of the dimensionless pressures $P_{(n)}$ and $P_{(d)}$, Eqs (5.2) and (5.3) enable us to determine completely the four unknown parameters $\xi_{(n)}$, $\xi_{(d)}$, $P_{(n)}$, $P_{(d)}$ from the known P_e and θ_e . The values of these parameters, in turn, according to the analytical solutions (2.3) and (2.4), and also (3.14), enable the structure of the flow and the temperature field in the porous medium to be determined.

6. The results of calculations

We carried out numerical calculations using the equations obtained above and also the analytical solutions. We took the following values for the parameters defining the properties of the porous medium (unless otherwise stated), the water, gas and hydrate

$$\begin{aligned} m &= 0.1, \quad k_0 = 10^{-13} \text{ m}^2, \quad \rho c = 2.5 \cdot 10^6 \frac{\text{J}}{\text{kg} \cdot \text{K}}, \quad \lambda = 2 \frac{\text{W}}{\text{m} \cdot \text{K}}, \\ \rho_\ell &= 10^3 \frac{\text{kg}}{\text{m}^3}, \quad R_g = 520 \frac{\text{J}}{\text{kg} \cdot \text{K}}, \quad \mu_g = 10^{-5} \frac{\text{kg}}{\text{m} \cdot \text{s}}, \\ \rho_h &= 900 \frac{\text{kg}}{\text{m}^3}, \quad L_h = 5 \cdot 10^5 \frac{\text{J}}{\text{kg}}, \quad T_0 = 280 \text{ K}, \quad T_e = 278 \text{ K}, \\ T_* &= 10 \text{ K}, \quad p_{s0} = 5.5 \text{ MPa} \end{aligned}$$

In Fig. 2 we show the most typical patterns of the pressure, temperature and hydrate saturation fields as the boundary pressure p_e increases; on the right we show the coordinate increased fragments of the pattern of the near zone of the porous medium. For the initial state of the moist porous medium we have assumed that $p_0 = 4 \text{ MPa}$ and $S_{\ell 0} = 0.5$. For $p_e = 4.4 \text{ MPa}$, when the value of the boundary pressure is lower than $p_e^{(1)}$ ($p_e^{(1)} \approx 4.5 \text{ MPa}$), no gas hydrate forms in the porous medium. For $p_e = 5 \text{ MPa}$ we obtain the frontal phase transition mode. However, ¹³ when p_e increases, beginning with a certain value $p_e = p_e^{(2)}$ (for the system in question $p_e^{(2)} \approx 5.5 \text{ MPa}$), for the solution with the frontal boundary the temperature in the porous medium behind the hydrate formation front drops below the equilibrium temperature, corresponding to the pressure distribution according to condition (1.3). Consequently, supercooling of the water and gas in the pores is observed here, and hence this solution is physically contradictory. This in turn indicates that when $p_e > p_e^{(2)}$ it is necessary to construct a solution with an intermediate zone of hydrate formation. These solutions correspond to $p_e = 12 \text{ MPa}$ and $p_e = 20 \text{ MPa}$. There is a basic difference between these two solutions. Whereas for the solution corresponding to $p_e = 12 \text{ MPa}$, on the boundary $\xi = \xi_{(n)}$ the hydrate saturation undergoes an abrupt change, for the solution $p_e = 20 \text{ MPa}$ there is no such abrupt changes. The characteristic value of the pressure $p_e = p_e^{(3)}$, when this abrupt change disappears, can be determined using the expression for S_h (the penultimate equation of (3.9), assuming $S_h = S_{he}$). As a result, taking relations (2.2) into account, we obtain

$$p_e^{(3)} = p_{(d)} e^\gamma, \quad \gamma = m S_{\ell 0} \frac{\rho_\ell L_h}{\rho c T_* (1 - G)}$$

For the example considered this characteristic value of the pressure is $p_e^{(3)} = 17 \text{ MPa}$.

Numerical analysis shows that when $p_e > p_e^{(3)}$ the solution of the problem is simplified considerably. First, in the analytical solutions (2.3) and (2.4) we can approximately assume that $p_{(n)} > p_e^{(3)}$ and $p_{(d)} = p_{s0}$. Then these solutions will only contain two unknown parameters: $\xi_{(n)}$ and $\xi_{(d)}$. If we use the analytic solutions (3.14) for the intermediate zone, then, from the first equations of systems (5.2) and (5.3), assuming

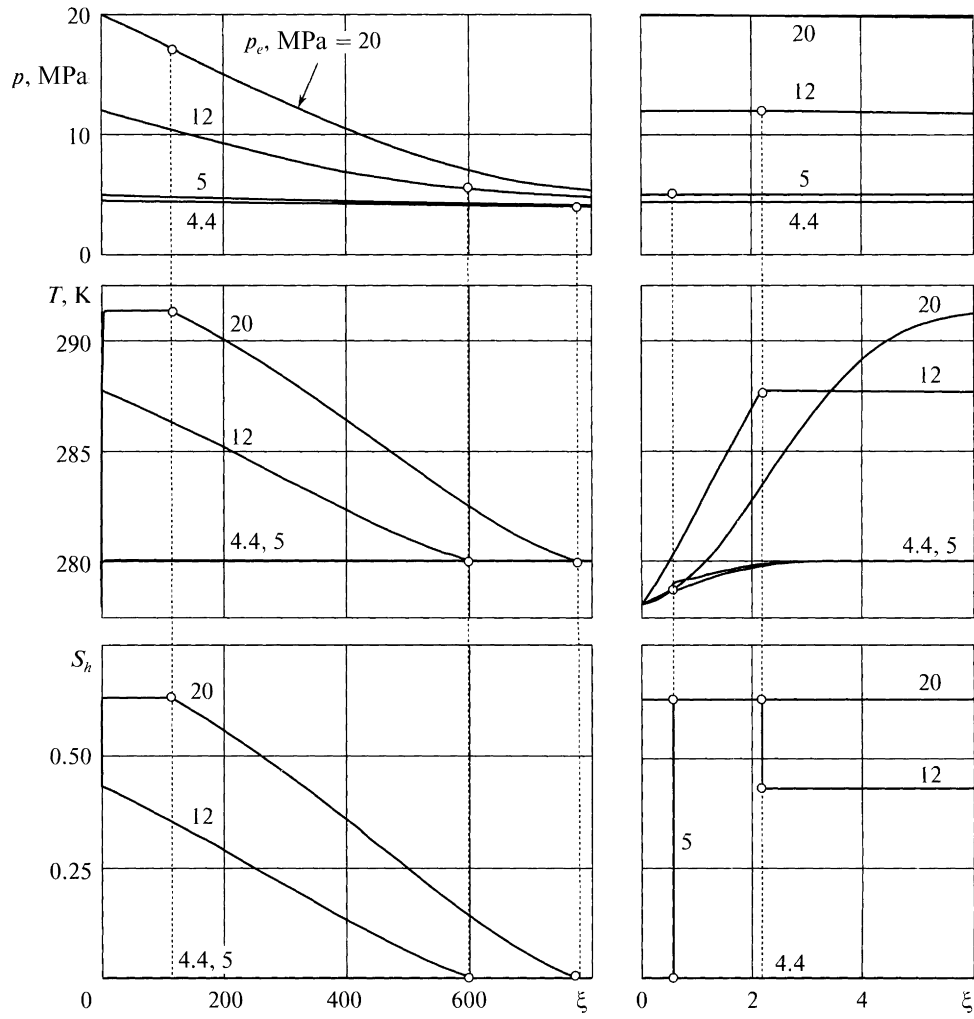


Fig. 2.

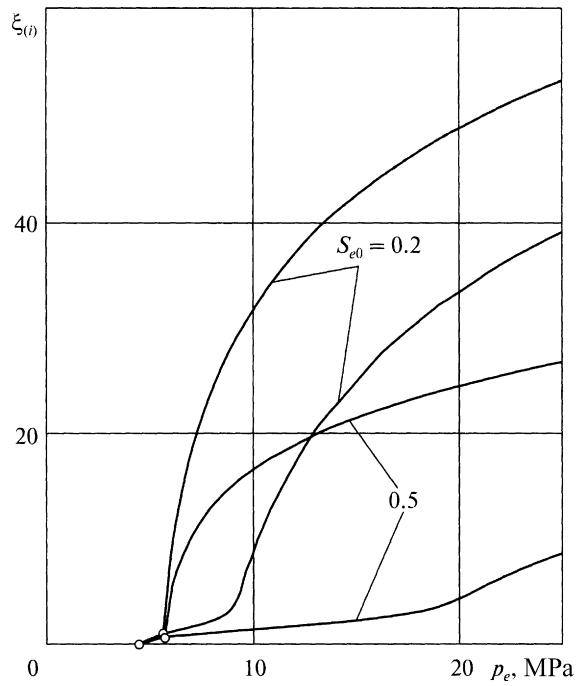


Fig. 3.

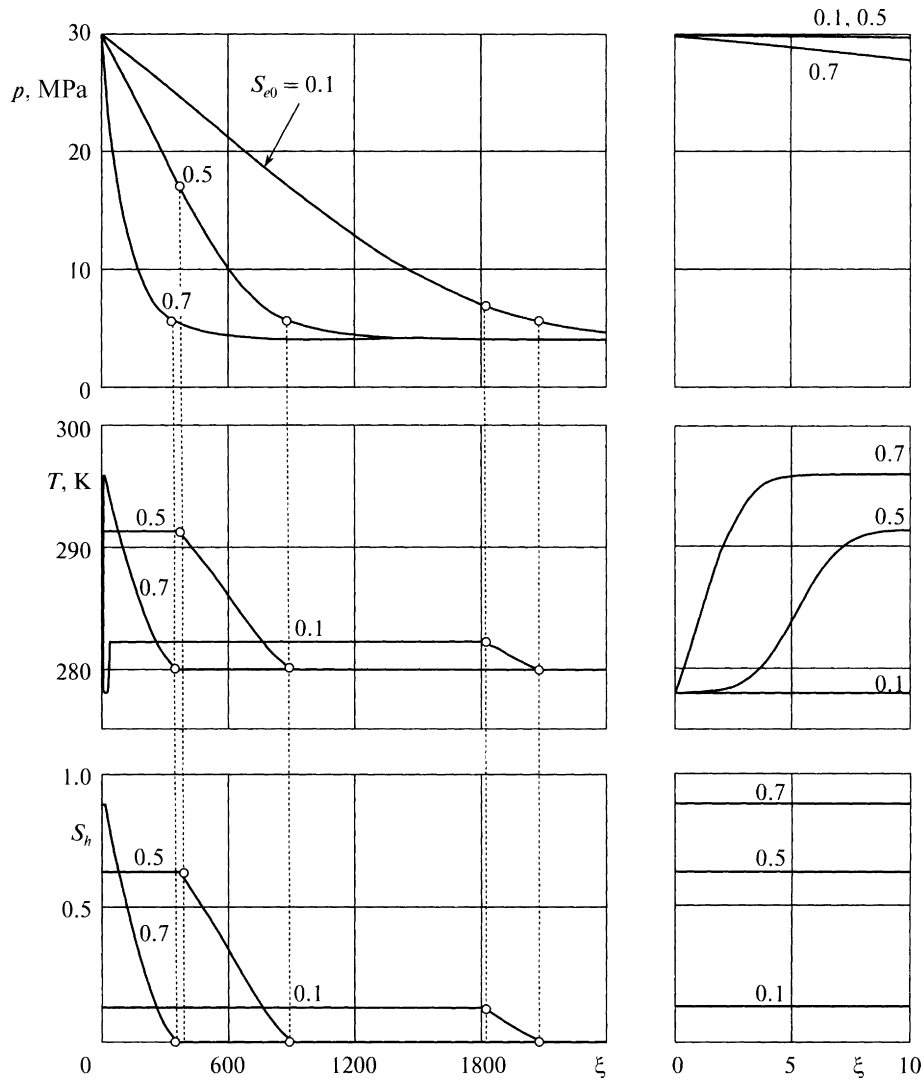


Fig. 4.

that $S_{h(n)}^- = S_{h(n)}^+$, we obtain the equations

$$\frac{P_e^2 - P_e^{(3)2} E_{(n)}^{(p)}(\xi_{(n)})}{P_e^{(3)} \Phi_{(n)}^{(p)}(0)} - \frac{P_e^{(3)2} - P_{s0}^2 E_{(m)}^{(p)}(\xi_{(n)})}{P_e^{(3)} \Phi_{(m)}^{(p)}(\xi_{(n)})} = 0$$

$$\frac{P_{s0}^2 - 1 E_{(d)}^{(p)}(\xi_{(d)})}{P_{s0} \Phi_{(d)}^{(p)}(\xi_{(d)})} + \frac{P_e^{(3)2} - P_{s0}^2 E_{(m)}^{(p)}(\xi_{(d)})}{P_{s0} \Phi_{(m)}^{(p)}(\xi_{(n)})} = 0$$

In Fig. 3 we show graphs of the self-similar coordinates of the frontal boundaries as a function of the boundary pressure. We took $k_0 = 10^{-14} \text{ m}^2$ for the permeability of the skeleton. It can be seen that as the boundary pressure p_e increases, beginning from a certain value p_0 , three characteristic parts of the relation are observed. On the first part ($p_0 \leq p_e \leq p_e^{(1)}$) no hydrate is formed in the porous medium (here we have formally assumed that $\xi_{(s)} = 0$). For the values of $S_{\ell 0}$ of 0.2 and 0.5 assumed, the value of the boundary pressure $p_e^{(1)} \approx 4.5 \text{ MPa}$. On the second part $p_e^{(1)} < p_e \leq p_e^{(2)}$ the formation of the gas hydrate occurs in accordance with the frontal scheme, and here $p_e^{(2)} \approx 5.5 \text{ MPa}$. When there is a further increase in p_e ($p_e > p_e^{(2)}$) hydrate is formed in the volume.

Graphs of the pressure, temperature and hydrate saturation fields against the initial moisture content are shown in Fig. 4, constructed in the same way as Fig. 2. We took $p_e = 30 \text{ MPa}$ as the boundary pressure, while the values of all the remaining parameters were as before. For these results of the calculations, the temperature of the flowing gas T_e does not exceed the initial temperature T_0 of the porous medium ($T_e \leq T_0$). Hence, the temperature of the porous medium cannot be higher than the equilibrium value, given by formula (1.3) for the corresponding pressure fields. It can be seen that the maximum temperature of the porous medium occurs for an initial water saturation of $S_{\ell 0} = 0.7$. This is due to the fact that, for a fixed value of the permeability k_0 , the permeability falls considerably as the initial water saturation increases, particularly in the region close to the boundary of the porous medium, where, in particular, the value of the hydrate saturation for the above values of the initial water saturation is $S_{he} = 0.13, 0.63$ and 0.88 . Also, as a consequence of this, the convective heat transfer is reduced.

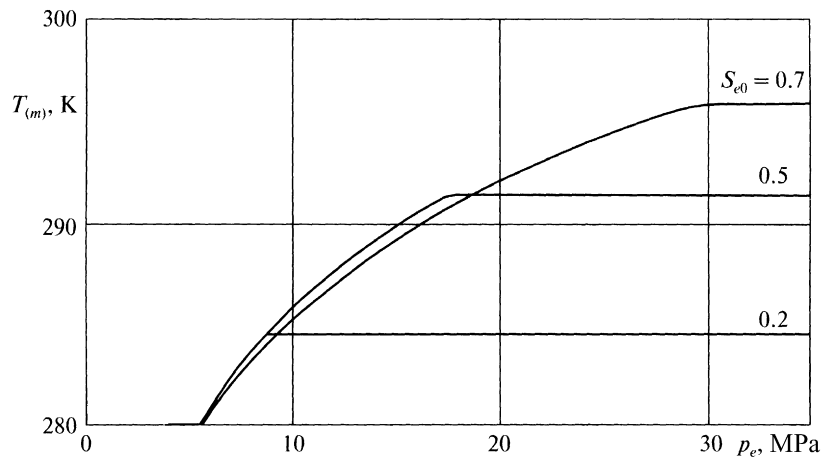


Fig. 5.

In Fig. 5 we show the effect of the initial water saturation of the porous medium on the value of the maximum temperature which can be obtained in the porous medium. Hence, due to the hydrate formation in the volume, the gas injected into the moist porous medium becomes a unique heat transfer medium although its temperature may be lower than the initial temperature of the porous medium.

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