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MATHEMATICAL MODEL OF GAS HYDRATE FORMATION OF SULFUR DIOXIDE BY INJECTING LIQUID SULFUR DIOXIDE INTO A LAYER SATURATED WITH METHANE AND WATER

This paper presents the results of a theoretical study for the gas hydrate formation of sulfur dioxide by injecting liquid sulfur dioxide into a layer saturated with water and methane. Self-similar solutions of a straight-line parallel problem are constructed. The dependences of the temperature and the coordinates of the formation front of sulfur dioxide gas hydrate on the layer permeability are explored. It is established that, as the layer permeability increases, the temperature of the phase transition increases on the surface. As a result, at sufficiently large values of layer permeability, the temperature at the hydrate formation border may exceed the equilibrium decomposition temperature of sulfur dioxide gas hydrate, which will correspond to the appearance of an intermediate region saturated with a mixture of water, sulfur dioxide and its gas hydrate in a state of thermodynamic equilibrium. It is established that at sufficiently high values of injection pressure and permeability, the gas hydrate formation of sulfur dioxide will occur in the extended region.

Keywords: mathematical model, self-similar solution, porous area, filtration, gas hydrates, sulfur dioxide.

Introduction

One of the ways to reduce the emission of sulfur dioxide into the atmosphere is the utilization of sulfur dioxide produced by industrial facilities in gas fields depleted [1–3]. However, there is a risk of leakage of sulfur dioxide in fluid form to the surface during its long-term underground storage. This risk can be minimized by converting sulfur dioxide into a gas hydrate state, which, in comparison with its free state, allows storing the same amount of gas at much lower pressures [4–7]. The mathematical models of hydrate formation in a porous medium are formulated, in particular, in [8–10]. The mathematical model of sulfur dioxide gas hydrate formation by injection of liquid sulfur dioxide into a porous medium saturated with water and methane is explored. It explores the conditions under which an extended area of the hydrate formation of sulfur dioxide occurs.

§1. Problem statement

The thermobaric existence conditions of the formation of sulfur dioxide hydrate are represented in the phase diagram (Fig. 1) [4]. In this diagram, the curve 1 corresponds to the three-phase equilibrium between gaseous sulfur dioxide, its gas hydrate and water, the curve 2 shows the two-phase equilibrium between gaseous and liquid sulfur dioxide, and the curve 3 represents the equilibrium between liquid sulfur dioxide, its gas hydrate and water. SO_2 gas hydrate exists above the curve 1 and to the left of the curve 3, i. e., at sufficiently high pressures and low temperatures. At the upper quadrupole point Q_2 ($T_Q = 285{,}1\,\text{K}$ and $p_Q = 0{,}233\,\text{MPa}$) gaseous and liquid sulfur dioxide, as well as its gas hydrate and water are in equilibrium. Let's assume that the semi-infinite horizontal layer in its initial state is saturated with water with the initial saturation S_{w0} and water. We assume that the layer initial temperature T_0 is lower than the temperature T_Q

corresponding to the quadrupole point, and the initial pressure p_0 corresponds to the thermodynamic conditions of the sulfur dioxide existence in its liquid state and its gas hydrate (i. e., above the curve 2 in Fig. 1). Therefore, in the case under consideration the initial state of the system corresponds to the thermobaric conditions of SO_2 gas hydrate existence. Let's assume that liquid sulfur dioxide is injected through the border ($x = 0$), the pressure p_e and the temperature T_e of which correspond to the conditions of sulfur dioxide gas hydrate existence.
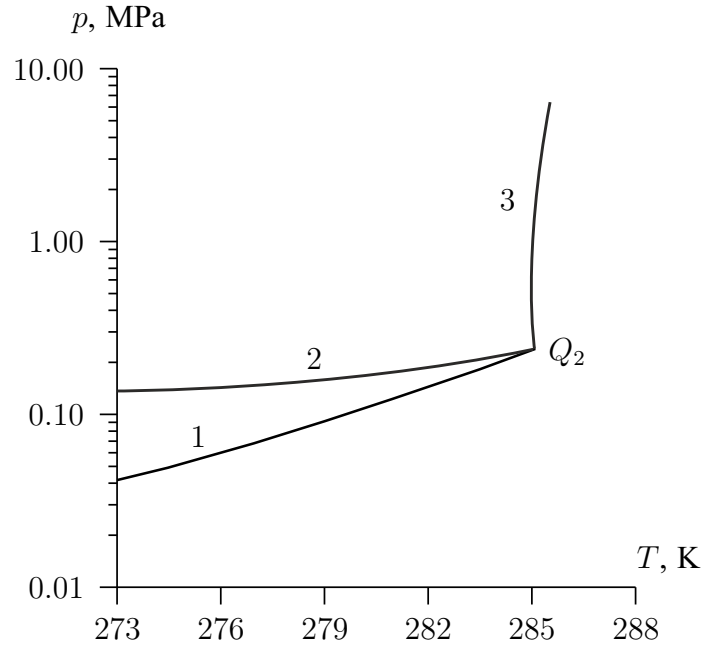

Fig. 1. Phase diagram of the system «SO_2-H_2O»

The initial and border conditions have the form:

$$
\begin{aligned}
t = 0 : S_w = S_{w0}, \quad T = T_0, \quad p = p_0 \quad (x \geq 0), \\
x = 0 : T = T_e, \quad p = p_e \quad (t > 0)
\end{aligned}
\tag{1.1}
$$

In this work we consider a model with the piston displacement of methane by liquid sulfur dioxide. This is due to the fact that the viscosity of liquid sulfur dioxide is much higher than the viscosity of methane. In addition, the flows in natural strata are laminar in nature. Then we can assume that the formation of sulfur dioxide gas hydrate occurs on the front surface coinciding with the surface of methane displacement by sulfur dioxide. In this case, two typical areas are formed in the layer. In the first (nearest) zone, sulfur dioxide and its gas hydrate are present in the pores, in the second (remote) zone are water and methane. In this case, there is a mobile interfacial surface between the first and second areas, where water completely passes into the gas hydrate state (hydrate formation front). The work considers a one-dimensional model which assumes that there is no heat inflow to the formation through its roof and sole from surrounding rocks. This approximation is valid for the case of a large thickness of the reservoir.

§ 2. Basic equations

Let's assume the value of the initial water saturation of the porous layer does not exceed 0.2, and then the water can be considered stationary. So the system of basic equations in the rectilinear-parallel case has the form [8–10]:

$$\frac{\partial}{\partial t}\left(\rho_i m S_i\right) + \frac{\partial}{\partial x}\left(\rho_i m S_i \upsilon_i\right) = 0$$

$$\rho c \frac{\partial T}{\partial t} + \rho_i c_i m S_i \upsilon_i \frac{\partial T}{\partial x} = \frac{\partial}{\partial x}\left(r\lambda \frac{\partial T}{\partial x}\right)$$

$$m S_i \upsilon_i = -\frac{k_i}{\mu_i}\frac{\partial p}{\partial x}, \quad k_i = k_0 S_i^3, \quad (i = s, g)$$

$$\rho_s = \rho_{0s} \exp\left(\beta_s\left(p - p_0\right)\right), \quad p = \rho_g R_g T. \tag{2.1}$$

where x is the coordinate; t is the time; m is the porosity; p is the pressure; T is the temperature; the subscripts $i = s$, g denote, respectively, the settings of sulfur dioxide and methane; S_i is the saturation of the pores; ρ_i is the density; υ_i is the actual average speed; k_0 is the absolute permeability of the porous medium; k_i is the phase permeability; β_s is the coefficient of compressibility of liquid sulphur dioxide; c_i is the specific heat capacity; μ_i is the dynamic viscosity; R_g is the gas constant of methane; ρc and λ are the effective values of the volumetric heat capacity and heat capacity for a saturated layer. The main contribution to the values of the coefficients of thermal conductivity and specific volumetric heat capacity of a saturated formation is made by the parameters of the solid skeleton. Therefore, we will consider them constant.

The relations arising from the conditions of the water mass balance, sulfur dioxide and methane, as well as the balance of heat are performed at the border between the zones:

$$-\frac{k_s}{\mu_s}\frac{\partial p_1}{\partial x} = m\left(\frac{\rho_h}{\rho_s}S_h G + S_s\right)V_n,$$

$$-\frac{k_g}{\mu_g}\frac{\partial p_2}{\partial x} = m S_g V_n,$$

$$m S_h \rho_h (1 - G) V_n = m S_{w0} \rho_w V_n,$$

$$\lambda \frac{\partial T_1}{\partial x} - \lambda \frac{\partial T_2}{\partial x} = m \rho_h L_h S_h V_n, \tag{2.2}$$

G is the relative mass concentration of sulfur dioxide in the gas hydrate; S_{w0} is the initial water saturation of the layer; L_h is the specific heat of SO_2 gas hydrate formation from liquid sulfur dioxide and water; the subscripts $j = 1, 2$ denote, respectively, the parameters in the first and second zones; V_n is the speed of the formation border of sulfur dioxide gas hydrate. Here and in what follows, the subscript n denotes the parameters on the surface between the zones, and the subscripts h and w, respectively, the parameters of gas hydrate and water.

According to the water mass balance (the third ratio of the system (2.2)) for the value of hydrate saturation in the first zone we have:

$$S_h = \frac{\rho_w S_{w0}}{\rho_h (1 - G)}. \tag{2.3}$$

Using (2.1) the equations of piezoconductivity and temperature conductivity in each layer zone will be written in the form:

$$\frac{\partial p_{(1)}}{\partial t} = \chi_{(i)}^{(p)}\frac{\partial}{\partial x}\left(\frac{\partial p_{(1)}}{\partial x}\right), \quad \frac{\partial T_{(1)}}{\partial t} = \chi^{(T)}\frac{\partial}{\partial x}\left(\frac{\partial T_{(1)}}{\partial x}\right) + \chi^{(T)}\mathrm{X}_{(1)}\frac{\partial p_{(1)}}{\partial x}\frac{\partial T_{(1)}}{\partial x},$$

$$\frac{\partial p_{(2)}^2}{\partial t} = \chi_{(2)}^{(p)}\frac{\partial}{\partial x}\left(\frac{\partial p_{(2)}^2}{\partial x}\right), \quad \frac{\partial T_{(2)}}{\partial t} = \chi^{(T)}\frac{\partial}{\partial x}\left(\frac{\partial T_{(2)}}{\partial x}\right) + \chi^{(T)}\mathrm{X}_{(2)}\frac{\partial p_{(2)}^2}{\partial x}\frac{\partial T_{(2)}}{\partial x}, \tag{2.4}$$

where $\chi_{(1)}^{(p)} = \frac{k_s}{\mu_s m (1 - S_h)\beta_s}$, $\chi_{(2)}^{(p)} = \frac{k_g p_0}{\mu_g m (1 - S_{w0})}$, $\chi^{(T)} = \frac{\lambda}{\rho c}$, $\mathrm{X}_{(1)} = \frac{\rho_{0s} c_s k_s}{\lambda \mu_s \beta_s}$, $\mathrm{X}_{(2)} = \frac{c_g k_g}{2\lambda R_g T_0 \mu_g}$.

To reduce the system of nonlinear differential equations (2.1) to the system of linear differential equations (2.4), the Leibenzon linearization method was used. This method consists in replacing the variable pressure in the coefficient of the right-hand side of the piezoelectric conductivity equation with a constant pressure equal to the initial pressure in the reservoir. The compressibility factor of liquid sulfur dioxide is on the order of 10^{-9} Pa^{-1}. Then, with pressure drops in the reservoir of about 1 MPa, we have: $\beta_s(p - p_0) \ll 1$. Then sulfur dioxide can be considered a weakly compressible liquid.

§3. Self-similar solution

We introduce a self-similar variable: $\xi = x \big/ \sqrt{\chi^{(T)}t}$. For this variable based on (1.1), (2.3) and (2.4) we get solutions for pressure and temperature distribution in each layer zone:

$$p_{(1)} = p_{(n)} + \frac{\left(p_e - p_{(n)}\right) \int_{\xi}^{\xi_{(n)}} \exp\left(-\frac{\xi^2}{4\eta_{(1)}}\right)d\xi}{\int_0^{\xi_{(n)}} \exp\left(-\frac{\xi^2}{4\eta_{(1)}}\right)d\xi}, \quad 0 < \xi < \xi_{(n)},$$

$$T_{(1)} = T_{(n)} + \frac{\left(T_e - T_{(n)}\right) \int_{\xi}^{\xi_{(n)}} \exp\left(-\frac{\xi^2}{4} - X_{(1)}p_{(1)}\right)d\xi}{\int_0^{\xi_{(n)}} \exp\left(-\frac{\xi^2}{4} - X_{(1)}p_{(1)}\right)d\xi}, \quad 0 < \xi < \xi_{(n)},$$

(3.1)

$$p_{(2)}^2 = p_0^2 + \frac{\left(p_{(n)}^2 - p_0^2\right) \int_{\xi}^{\infty} \exp\left(-\frac{\xi^2}{4\eta_{(2)}}\right)d\xi}{\int_{\xi_{(n)}}^{\infty} \exp\left(-\frac{\xi^2}{4\eta_{(2)}}\right)d\xi}, \quad \xi_{(n)} < \xi < \infty,$$

$$T_{(2)} = T_0 + \frac{\left(T_{(n)} - T_0\right) \int_{\xi}^{\infty} \exp\left(-\frac{\xi^2}{4} - X_{(2)}p_{(2)}^2\right)d\xi}{\int_{\xi_{(n)}}^{\infty} \exp\left(-\frac{\xi^2}{4} - X_{(2)}p_{(2)}^2\right)d\xi}, \quad \xi_{(n)} < \xi < \infty,$$

(3.2)

where $\eta_{(j)} = \chi_{(j)}^{(p)} \big/ \chi^{(T)}, (j = 1, 2)$.

Based on the relations (2.2), taking into account the distributions for pressure and temperature (3.1) and (3.2), we obtain the relations to determine the self-similar coordinate of the hydrate formation surface $\xi_{(n)}$ and the pressure and temperature values on it:

$$\frac{\left(p_e - p_{(n)}\right) \exp\left(-\frac{\xi_{(n)}^2}{4\eta_1}\right)}{\int_0^{\xi_{(n)}} \exp\left(-\frac{\xi^2}{4\eta_{(1)}}\right)d\xi} = A_{(1)}\xi_{(n)},$$

(3.3)

$$\frac{\left(p_{(n)}^2 - p_0^2\right) \exp\left(-\frac{\xi_{(n)}^2}{4\eta_2}\right)}{\int_{\xi_{(n)}}^{\infty} \exp\left(-\frac{\xi^2}{4\eta_{(2)}}\right)d\xi} = A_{(2)}p_{(n)}\xi_{(n)},$$
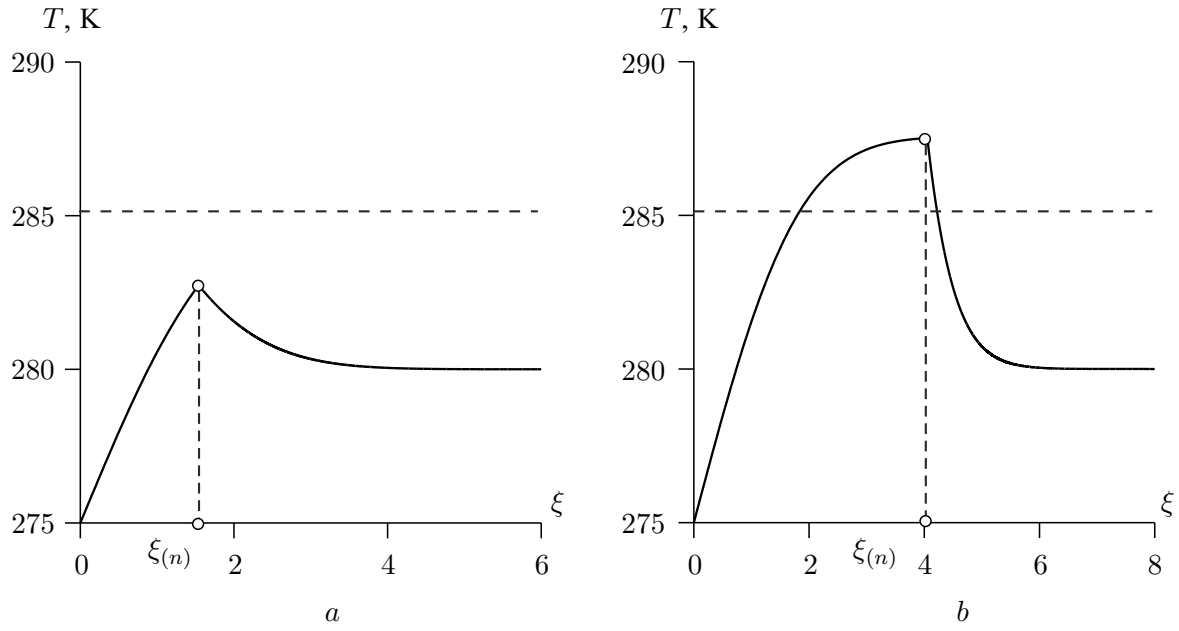
(3.4)

Fig. 2. Temperature distribution in the layer at the different injection pressures $p_e = 4.1\,(a)$ and $4.4\,(b)$ MPa. The dashed line is the temperature at the upper quadruple point

$$\frac{\left(T_{(n)} - T_e\right) \exp\left(-\dfrac{\xi_{(n)}^2}{4} - X_{(1)}p_{(n)}\right)}{\displaystyle\int_0^{\xi_{(n)}} \exp\left(-\dfrac{\xi^2}{4} - X_{(1)}p_{(1)}\right)d\xi} - \frac{\left(T_0 - T_{(n)}\right) \exp\left(-\dfrac{\xi_{(n)}^2}{4} - X_{(2)}p_{(n)}^2\right)}{\displaystyle\int_{\xi_{(n)}}^{\infty} \exp\left(-\dfrac{\xi^2}{4} - X_{(2)}p_{(2)}^2\right)d\xi} = B\xi_{(n)}, \quad (3.5)$$

where $A_{(1)} = \dfrac{m\mu_s\chi^{(T)}}{2k_s}\left(d\dfrac{\rho_h GS_h}{\rho_{0s}} + 1 - S_h\right)$, $A_{(2)} = \dfrac{m\mu_g\chi^{(T)}}{k_g}\left(1 - S_{w0}\right)$, $B = \dfrac{m\rho_h L_h S_h}{2\rho c}$.

The system of equations written in this paper was solved as follows. Having achieved from equation (3.3) the pressure value at the border of gas hydrate formation $p_{(n)}$ (as a $\xi_{(n)}$ function) and substituting this value $p_{(n)}$ into equation (3.4), we obtain a transcendent equation with one unknown $\xi_{(n)}$, which was solved by the half division method. Then we determine the pressure values $p_{(n)}$ and temperature $T_{(n)}$ at the $\xi_{(n)}$ border of gas hydrate formation from equations (3.3) and (3.5).

§4. The results of the calculations

Fig. 2 shows the temperature distributions within the layer at the different pressure values of sulfur dioxide injection $p_e = 4{,}1\,(a)$ and $4{,}4\,(b)$ MPa. The dashed line is the temperature of the upper quadruple point. For other parameters the following values are adopted: $m = 0{,}2$, $S_{w0} = 0{,}2$, $p_e = 4{,}2$ MPa, $p_0 = 4$ MPa, $T_0 = 280$ K, $T_e = 275$ K, $k_0 = 5 \cdot 10^{-15}\,\text{m}^2$, $G = 0{,}372$, $\mu_s = 3{,}68 \cdot 10^{-4}$ Pa·s, $\mu_g = 1 \cdot 10^{-4}$ Pa·s, $\beta_s = 1{,}35 \cdot 10^{-9}$ Pa^{-1}, $\lambda = 2$ W/(m·K), $\rho c = 2 \cdot 10^6$ J/(K·kg), $\rho_h = 1390\,\text{kg/m}^3$, $\rho_w = 1000\,\text{kg/m}^3$, $\rho_{0s} = 1434\,\text{kg/m}^3$, $c_s = 1350$ J/(K·kg), $L_h = 2{,}62 \cdot 10^5$ J/kg.

According to Fig. 2, the temperature at the border of sulfur dioxide gas hydrate formation is lower than the temperature at the upper quadrupole point at low sulfur dioxide injection pressure (case *a*). Therefore, in this case, the model with the frontal border of sulfur dioxide gas hydrate
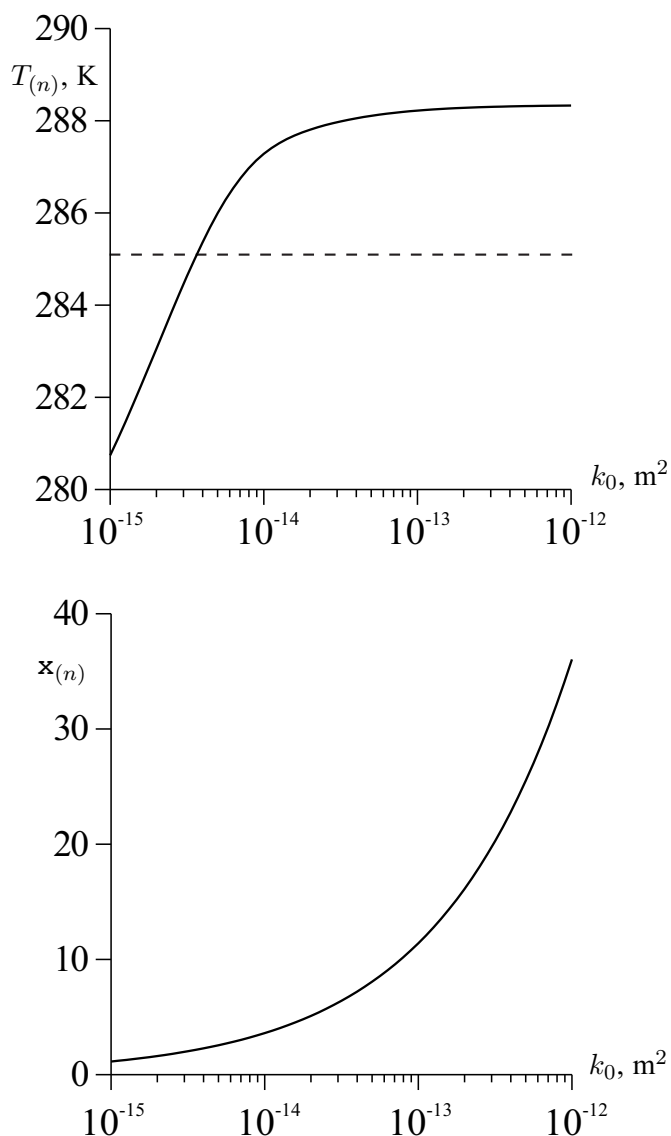
Fig. 3. The dependence of the temperature and the coordinates of the formation border of gas hydrate on the absolute permeability of the layer at $p_e = 4.2\,\text{MPa}$ and $p_0 = 4\,\text{MPa}$. The dashed line shows the temperature of the quadrupole point

formation gives an adequate mathematical description of the process. At higher pressures of sulfur dioxide injection (case *b*), the temperature at the border of sulfur dioxide gas hydrate formation rises above the temperature of the upper quadrupole point. In this case, it is necessary to use a model with an extended area of phase transitions for an adequate description of the process.

Fig. 3 shows the dependence of the temperature and the coordinates of the gas hydrate formation border on the absolute permeability of the layer. According to Fig. 3, the movement rate of the hydrate formation surface increases with increasing layer permeability. This is due to the fact that the movement of the given surface is limited by the flow rate of liquid sulfur dioxide, which according to Darcy's law increases with the growth of layer permeability. Also, Fig. 3 shows that, as the layer permeability increases, during the layer permeability increasing, the temperature of the phase transition increases on the surface. This is due to the fact that hydrate formation is accompanied by the release of latent heat of the phase transitions, and the speed of the surface of phase transitions (i. e., the intensity of hydrate formation) increases with increasing permeability. In addition, as the heat part released on the phase transitions surface is discharged through the left
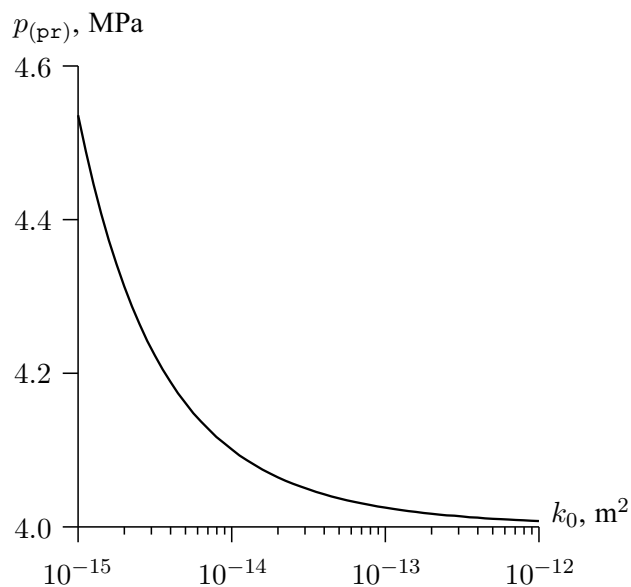
Fig. 4. The dependence of the limit pressure value on the absolute permeability

colder layer, a decrease in heat intensity removal through the left layer border takes place with increasing coordinate of the hydrate formation surface. These factors given according to Fig. 3 lead to an increase in temperature at this border with increasing layer permeability.

As a result, at sufficiently large values of layer permeability, the temperature at the hydrate formation border may exceed the equilibrium decomposition temperature of sulfur dioxide gas hydrate (dashed line), which will correspond to the appearance of an intermediate region saturated with a mixture of water, sulfur dioxide and its gas hydrate in a state of thermodynamic equilibrium. Calculations were carried out to find the limit value of the injection pressure of sulfur dioxide p_{pr}, above which there is an intermediate zone saturated with a mixture of water, sulfur dioxide and its gas hydrate, in a state of thermodynamic equilibrium.

Fig. 4 shows the dependence of the pressure limit on the layer absolute permeability. According to Fig. 4, as the layer absolute permeability increases, the value of the injection limit pressure increases. This is due to the fact that with a decrease in the layer absolute permeability, the temperature decreases on the formation surface of sulfur dioxide gas hydrate. Therefore, a low intensity of heat removal through the left layer border and a high intensity of the latent heat of hydrate formation is required to exceed the equilibrium decomposition temperature of the gas hydrate on this surface, it is realized at large values of the injection pressure and, accordingly, the velocity of the phase transitions border. Thus, the intermediate region saturated with a mixture of water, sulfur dioxide and its gas hydrate, locating in a state of thermodynamic equilibrium, occurs at high injection pressure values of layer permeability.

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М. К. Хасанов, С. Р. Кильдибаева
Математическая модель образования газогидрата диоксида серы при инжекции жидкой двуокиси серы в пласт, насыщенный метаном и водой

Представлены результаты теоретического исследования процесса образования газогидрата диоксида серы при инжекции жидкой двуокиси серы в пласт, насыщенный водой и метаном. Построены автомодельные решения прямолинейно-параллельной задачи. Исследованы зависимости температуры и координаты фронта образования газогидрата диоксида серы от проницаемости пласта. Установлено, что с увеличением проницаемости пласта происходит рост температуры на поверхности фазового перехода. Вследствие этого при достаточно больших значениях проницаемости пласта температура на границе гидратообразования может превысить равновесную температуру разложения газогидрата диоксида серы, что будет соответствовать возникновению промежуточной области, насыщенной смесью воды, диоксида серы и его газогидрата, находящихся в состоянии термодинамического равновесия. Установлено, что при достаточно высоких значениях давления инжекции и проницаемости образование газогидрата диоксида серы будет происходить в протяженной области.

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