Theoretical research of the carbon dioxide injection process into the rock saturated with ice

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Abstract. The results of the theoretical research of the carbon dioxide injection process into the reservoir initially saturated with methane and ice are presented. In the rectilinear-parallel approach the analytical solutions which describe the distributions of temperature and pressure in the reservoir were built. It is shown, that modes with different quantity of the interphase boundaries of the carbon dioxide hydrate formation are possible.

1. Introduction
Currently, the greenhouse effect is one of the global environmental problems facing mankind. The main reason for this effect is industrial gases entering the atmosphere, primarily carbon dioxide. This raises the problem of reducing the carbon dioxide concentration in the atmosphere, for example, due to its disposal in underground reservoirs [1-3]. However, at long-term storage of CO\textsubscript{2} in gaseous or liquid state, there is a danger of emission into the atmosphere [4]. Subsurface CO\textsubscript{2} storage through clathrate hydrate formation is a novel option for the reduction of atmospheric carbon content and permanent underground CO\textsubscript{2} disposal over geological periods. A number of researchers proposed the carbon dioxide injection into permafrost, because the upper boundary of the carbon dioxide hydrate stability in the permafrost begins from the depths of 100-150 meters and the bottom boundary – 500-800 meters [4]. In addition, the CO\textsubscript{2} hydrate formation in a porous medium can be used to increase the capacity of the underground reservoirs for the gas store. The fact of the matter is that in a hydrate state the same gas mass can be stored under considerably lower pressure and in the less volume [5]. Technological ideas must be confirmed by the valid theoretical researches. Therefore the construction of the mathematical model of the dioxide carbon injection process into a reservoir partially saturated with ice is the actual problem.

2. Mathematical model
Assume that a reservoir, initially filled with methane and ice, fills half-space \(x > 0\). Before the injection of gas, pressure \(p_0\) and temperature \(T_0\) in the reservoir correspond to thermodynamic conditions of the existence of methane and ice in a free state:

\[
t = 0, \ x > 0: \quad T = T_0, \quad p = p_0, \quad S = S_0. \tag{1}
\]

Assume that through the left boundary of the reservoir \((x = 0)\) the carbon dioxide is being injected. The pressure \(p_w\) and temperature \(T_w\) of the injected gas correspond to the existence conditions of the mixture of CO\textsubscript{2} and its hydrate, and are supported at this boundary at constant level:

\[
t > 0, \ x = 0: \quad T = T_w, \quad p = p_w. \tag{2}
\]
Conducted estimations show that at the CO\textsubscript{2} injection into a reservoir saturated with methane and ice the diffusion mixing can be neglected. This is because the mass transfer rate due to filtration is much greater than the mass transfer rate due to diffusion. Also, in the considered range of pressures and temperatures the viscosity of CO\textsubscript{2} is about one and a half times higher than the viscosity of CH\textsubscript{4}. Therefore in this work we consider that the gas mixing process has no effect to the stability of the displacement front of methane with carbon dioxide [6]. In this case we can assume that at the injection of carbon dioxide into a reservoir saturated with methane and ice two characteristic zones are formed. The pores in the zone \([0, x_{(n)}]\) are filled with CO\textsubscript{2} and its hydrate, and the porous medium in the zone \([x_{(n)}, \infty)\) is saturated with methane and ice (fig. 1). Thereby, \(x_{(n)}\) is the coordinate of the movable boundary of phase transitions.

\[\text{Figure 1. Scheme of the problem of the carbon dioxide injection into a porous medium taking into account the CO}_2\text{hydrate formation.}\]

We adopt several assumptions enumerated here. CO\textsubscript{2} hydrate is a two-component system with the mass concentration of gas \(-G\). We will neglect the relationship of the mass concentration of the gas in a hydrate with pressure and temperature. Suppose that porosity \(m\) is constant; rock skeleton, the hydrates of carbon dioxide and ice are all incompressible and immovable. Methane and carbon dioxide are the calorically perfect gases. In this paper we research the processes, the duration of which is considerably longer than the typical time of temperature equilibrium \(\tau \approx d^2/\chi\) (\(d\) is the typical pore dimensions, \(\chi = \lambda/\rho\chi\) is the thermal diffusivity of a porous medium). Therefore, we assume that the temperatures of the porous medium and of the saturant (carbon dioxide and its hydrate or methane and ice) are similar (one temperature process).

With consideration of the accepted assumptions the system of main equations can be written in the following form [5, 7, 8]:

\[\frac{\partial}{\partial t} (m\rho_g S_g) + \text{div} (m\rho_g S_g \vec{v}_g) = 0,\]

\[mS_g \vec{v}_g = -\frac{k_g}{\mu_g} \text{grad} p,\]

\[\frac{\partial}{\partial t} (\rho_c T) + \rho_g c_g mS_g \vec{v}_g \text{grad} T = \text{div} (\lambda \text{grad} T),\]

\[p = \rho_g R_g T, \quad \sum_{j=g,i,h} S_j = 1, \quad k_g = k_0 S_g^3,\]

\[\rho_c = (1-m)\rho_{sk} c_{sk} + m \sum_{j=g,i,h} \rho_j S_j c_j, \quad \lambda = (1-m)\lambda_{sk} + m \sum_{j=g,i,h} S_j \lambda_j.\]

Hereafter, subscripts \(sk, h, i\) and \(g\) are related to the parameters of the rock skeleton, hydrate CO\textsubscript{2}, ice and gas (methane or carbon dioxide), respectively; \(\rho_j (j = sk, h, i \text{ or } g)\) is the true density of the \(j\)-th phase, \(S_j (j = g, i, h)\) is the \(j\)-th phase saturation, \(k_0\) is the absolute reservoir permeability, \(\nu_g\) and \(\mu_g\) are
the velocity and dynamic viscosity of the gas phase, \( p \) is the pressure, \( T \) is the temperature, 
\( c_j (j = g, i, h) \) is the specific heat capacity of the \( j \)-th phase, \( \lambda_j (j = sk, g, i, h) \) is the thermal conductivity coefficient of the \( j \)-th phase, \( \rho_c \) and \( \lambda \) are the specific volumetric heat capacity and the thermal conductivity coefficient of the system «reservoir – fluid».

The temperature and pressure values at the hydrate formation surface are related by the condition of phase equilibrium [9]:

\[
T_s(p) = T_* + T_0 \ln \left( \frac{p}{p_{00}} \right),
\]

where \( p_{00} \) is the equilibrium pressure corresponding to the initial temperature \( T_0 \), \( T_* \) is the empirical parameter.

In addition, at the boundary \( x_{(a)} \) the relations, which follow from conditions of mass and heat balance, are realized [5, 8]:

\[
\left[ m \left( S_g \rho_g \left( \nu_g - \dot{x}_{(a)} \right) - S_h \rho_h G \dot{x}_{(a)} \right) \right] = 0,
\]

\[
\left[ m \left( S_h \rho_h (1 - G) + S_i \rho_i \dot{x}_{(a)} \right) \right] = 0,
\]

\[
\left[ \lambda \ \text{grad} T \right] = \left[ m L_{ph} \rho_p S_h \dot{x}_{(a)} \right].
\]

were \([\psi]\) is the jump of the parameter \( \psi \) at the boundary \( x_{(a)} \), \( L_h \) is the heat of the carbon dioxide hydrate formation, \( S_h \) is the \( \text{CO}_2 \) hydrate saturation. The dot over \( x_{(a)} \) denotes the movement velocity of this boundary. Temperature and pressure at the boundary \( x_{(a)} \) are considered to be continuous.

3. Calculation results
The system of equations (1)-(7) can be solved analytically. To do this we introduce the self-similar variable: \( \xi = x / \chi^{1/2} t \). For this variable the system of equations (3)-(5), with application of Leibenson linearization, can be presented in the form of the system of ordinary differential equations of the 2nd order:

\[
-\frac{\xi}{2} \frac{dp_{(j)}^2}{d\xi} = \eta_{(j)} \frac{dp_{(j)}^2}{d\xi}, \quad -\frac{\xi}{2} \frac{dT_{(j)}}{d\xi} = Pe_{(j)} \frac{dp_{(j)}^2}{d\xi} \frac{dT_{(j)}}{d\xi} + \frac{d}{d\xi} \left( \frac{dT_{(j)}}{d\xi} \right) \quad (j = 1, 2),
\]

\[
\eta_{(j)} = \frac{k_{(j)}}{\chi}, \quad \kappa_{(j)} = \frac{k_{(j)}}{m S_{g(j)} \mu g(j)}, \quad Pe_{(j)} = \frac{\rho_{g0} \rho_{p0} c_{g(j)} k_{(j)}}{\mu g(j)} \quad (j = 1, 2).
\]

Here, the subscript 1 in brackets refers to the parameters of the zone \([0, \xi_{(a)}], 2 - [\xi_{(a)}, \infty] \).

The piezococonductivity equation is nonlinear, because of pressure conductivity factor \( \kappa_{(j)} \) include the unknown function \( p_{(j)} \). To obtain approximate analytical solution we used the Leibenson linearization. For this purpose the variable pressure \( p_{(j)} \) in the parameter \( \kappa_{(j)} \) assumed constant and equal to the initial reservoir pressure \( p_{00} \). Note that this will not make a significant error in the solution, because in the work we consider the cases of small pressure gradients (\( \Delta p \ll p_{00} \)).

After the piezococonductivity and temperature conductivity equations (8) integration the solutions for the pressure and temperature distributions in the first and second zones can be obtained:

\[
p_{(1)}^2 = p_{(n)}^2 + \left( p_{(w)}^2 - p_{(n)}^2 \right) \int_{-\xi}^{\xi} \exp \left( -\frac{\xi^2}{4(\eta_{(1)})} \right) d\xi \int_{-\xi}^{\xi} \exp \left( -\frac{\xi^2}{4(\eta_{(1)})} \right) d\xi \quad (\xi \in [0, \xi_{(a)})],
\]

\[
T_{(1)} = T_{(n)} + \left( T_{(w)} - T_{(n)} \right) \int_{-\xi}^{\xi} \exp \left( -\frac{\xi^2}{4} - \frac{Pe_{(1)}^2 p_{(1)}^2}{2 p_{0}^2} \right) d\xi \int_{-\xi}^{\xi} \exp \left( -\frac{\xi^2}{4} - \frac{Pe_{(1)}^2 p_{(1)}^2}{2 p_{0}^2} \right) d\xi.
\]
\[
P_{(2)}^2 = p_0^2 + \left( p_{(n)}^2 - p_0^2 \right) \int_\xi^\infty \exp \left( -\frac{\xi^2}{4\eta(2)} \right) d\xi \int_\xi^\infty \exp \left( -\frac{\xi^2}{4\eta(2)} \right) d\xi \quad (\xi \in [\xi(n), \infty]).
\]

\[
T_{(2)} = T_0 + \left( T_{(n)} - T_0 \right) \int_\xi^\infty \exp \left( -\frac{\xi^2}{4} - \frac{Pe(2)}{2p_0^2} \right) d\xi \int_\xi^\infty \exp \left( -\frac{\xi^2}{4} - \frac{Pe(2)}{2p_0^2} \right) d\xi.
\]

On the basis of the conditions (7) and using the obtained solutions we can write the equations for determination of the coordinate of the phase transition boundary \(\xi(n)\) and the values of the parameters on this boundary.

When constructing the mathematical model it was assumed that the first zone saturated with CO\(_2\) hydrate and in the second zone saturated with ice. Therefore, the constructed model adequately describes the process if the local temperature in the zone \([0, \xi(n)]\) is lower than the local temperature of the carbon dioxide hydrate decomposition, and the local temperature in the zone \([\xi(n), \infty)\) is lower than 273 K (ice point). Let us call this the condition of thermodynamic consistency. The local temperature of the CO\(_2\) hydrate dissociation is determined from the formula (6) by using the obtained pressure distribution.

Fig. 2 shows the distributions of temperature and pressure for the carbon dioxide injection pressure \(p_w = 1.2 \text{ MPa}\).

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Here and on the following figures dashed lines correspond to the equilibrium temperature of CO\(_2\) hydrate formation. The following parameters were used for calculation: \(m = 0.25\), \(S_0 = 0.6\), \(p_0 = 1.15 \text{ MPa}\), \(T_0 = 271 \text{ K}\), \(T_n = 271 \text{ K}\), \(k_0 = 2 \times 10^{-15} \text{ m}^2\), \(\rho = 2.5 \times 10^6 \text{ J/(K} \cdot \text{m}^3)\), \(\lambda = 2 \text{ W/(mK)}\), \(G = 0.28\), specific gas constant for carbon dioxide \(R_{gc} = 189 \text{ J/(K} \cdot \text{kg)}\), specific gas constant for methane \(R_{gm} = 520 \text{ J/(K} \cdot \text{kg)}\), \(\rho_{h} = 1100 \text{ kg/m}^3\), \(\rho_i = 900 \text{ kg/m}^3\), specific heat of carbon dioxide \(c_{gc} = 800 \text{ J/(K} \cdot \text{kg)}\), specific heat of methane \(c_{gm} = 1560 \text{ J/(K} \cdot \text{kg)}\), coefficient of dynamic viscosity of carbon dioxide \(\mu_{gc} = 1.3 \times 10^{-5} \text{ Pa} \cdot \text{s}\), coefficient of dynamic viscosity of methane \(\mu_{gm} = 10^{-5} \text{ Pa} \cdot \text{s}\), \(L_h = 1.6 \times 10^5 \text{ J/kg}\), \(T_{eih} = 19 \text{ K}\), \(T_{eih} = 7.6 \text{ K}\), \(p_0 = 1.02 \text{ MPa}\) [6, 8, 10].

Fig. 2 shows that at the relatively low pressure of the carbon dioxide injection the reservoir temperature in the zone \([0, \xi(n)]\) is below the equilibrium CO\(_2\) hydrate decomposition temperature, and in the zone \([\xi(n), \infty)\) is below the ice point. Therefore, in this case, the solution with the frontal boundary of phase transitions provides adequate mathematical description of the process.

Fig. 3 shows that a further increase of \(p_w\) leads to increasing the reservoir temperature, on a certain stretch after the phase transition boundary (in the zone \([\xi(n), \infty)\) above 273 K, and ice is overheating in this zone. Consequently, in this case, it is necessary to introduce a second phase-transition boundary of the ice melting. And the third (intermediate) zone is appearing in the reservoir, which is saturated with methane and water.
The pressure and temperature depending on the self-similar coordinate $\xi$, $p_w = 1.25 \text{ MPa}$.

Fig. 4 shows that at the higher value of the injection pressure of carbon dioxide the reservoir temperature on a certain stretch of the zone $[0, \xi(n)]$ becomes higher the equilibrium temperature of the CO$_2$ hydrate decomposition. This corresponds to the overheating of the mixture of carbon dioxide and its hydrate at this region. Consequently, in this case, it is necessary to introduce the third boundary of phase transitions, because the zone, which is saturated with carbon dioxide and water, is appearing in the reservoir. This zone is located between zones “CO$_2$ + CO$_2$ hydrate” and “CH$_4$ + water”.

The pressure and temperature depending on the self-similar coordinate $\xi$, $p_w = 1.35 \text{ MPa}$.

4. Conclusions
The mathematical model of the carbon dioxide injection process into the reservoir, which is initially saturated with methane and ice, was presented in this work. This model takes into account the CO$_2$ hydrate formation. The self-similar solutions of the one-dimensional problem were built. These solutions describe the distributions of main parameters in each of the allocated zones of the reservoir. On the basis of obtained solutions it was shown that different situations can exist at the carbon dioxide hydrate formation, notably with the one, two or three interphase boundaries.

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