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Formation of CO$_2$ hydrate in a porous reservoir at the liquid carbon dioxide injection taking into account its boiling

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Abstract. The theoretical study results of the CO$_2$ hydrate formation process at the liquid carbon dioxide injection into the porous reservoir initially saturated with methane and water are presented. In the rectilinear-parallel approach the analytical solutions which describe the distributions of main parameters in the reservoir were built. On the basis of the obtained solutions, it is shown that, depending on the injection pressure of carbon dioxide, it is necessary to consider the frontal surface or the extended zone of the gas hydrate formation.

1. Introduction
A number of researchers identify the greenhouse effect among the main causes leading to climate change and global warming. Moreover, with the development of technology, the number of sources that provide the greenhouse effect in the atmosphere increases every year. The strategy to combat the intensification of the greenhouse effect should be to adopt a set of various measures. One of such measures is to reduce the concentration of carbon dioxide by the regular removal of CO$_2$ from the atmosphere and storing it in porous reservoirs, in particular, in depleted hydrocarbon deposits [1-5]. At long-term storage of CO$_2$ in gaseous or liquid state, there is a danger of its emission into the atmosphere. Therefore in a number of works the potential possibility of the CO$_2$ underground burial in a solid gas hydrate form is studied [6-9]. The main argument in favor of such disposal of carbon dioxide is the ability of hydrates to bind a significant amount of gas in a small volume and at a relatively low pressure [10].

In the presented work the mathematical model of the CO$_2$ hydrate formation at the liquid carbon dioxide injection into a reservoir taking into account the carbon dioxide boiling is studied.

2. Mathematical model
Assume that a reservoir, initially filled with methane and water with the initially saturation $S_{w0}$, occupy the half-space $x > 0$. The values of pressure $p_0$ and temperature $T_0$ in the reservoir at the initial time moment (before the liquid carbon dioxide injection) in the phase diagram are in the region of existence of carbon dioxide and its hydrate, and also in the region of existence of methane and water in the free (not gas hydrate) state:

$t = 0, x > 0: \quad T = T_0, \quad p = p_0, \quad S_w = S_{w0}, \quad S_m = 1 - S_{w0}$.

Here and below, the subscript $i = l, w, c, m, h$ corresponds to the parameters of the $i$-th phase ($l$ is liquid carbon dioxide, $w$ is water, $c$ is gaseous carbon dioxide, $m$ is methane, and $h$ is the hydrate of carbon dioxide).
Assume that through the left boundary of the reservoir \((x = 0)\) the carbon dioxide is being injected. The pressure \(p_e\) and the temperature \(T_e\) of the injected fluid correspond to the conditions of the CO\(_2\) existence in the liquid state and they are constant at this boundary:

\[
 t > 0, \ x = 0: \quad T = T_e, \quad p = p_e.
\]

We will assume that the injection of liquid carbon dioxide is accompanied by its boiling and further formation of CO\(_2\) hydrate.

In the considered problem, due to the continuous injection of carbon dioxide into the reservoir, the intensity of mass transfer caused by filtration in the permeable porous medium is significantly higher than the intensity of mass transfer caused by diffusion. Therefore, we shall neglect the diffusion mixing of carbon dioxide and methane. We also consider the front of the displacement of methane by carbon dioxide to be stable.

In the considered problem the fluid parameters at the left boundary of the reservoir and the pressure and temperature values in the porous medium at the initial time moment correspond to the conditions of the carbon dioxide hydrate formation. Therefore, it can be assumed that the formation of CO\(_2\) hydrate occurs at the boundary of the displacement of methane by carbon dioxide. Consequently, three characteristic zones are formed in the reservoir. In the first (near) zone the pores are saturated with liquid carbon dioxide and CO\(_2\) hydrate; in the second (intermediate) zone the gaseous carbon dioxide and CO\(_2\) hydrate are present, and in the third (far) zone the pores are saturated with methane and water (fig.1).

![Figure 1. Scheme of the problem of the liquid carbon dioxide injection into a porous medium.](image)

We adopt the following assumptions to describe the processes of heat and mass transfer when the carbon dioxide injection into a porous reservoir. The rock skeleton, water and hydrate are incompressible, the porosity \(\phi\) is constant. The methane and carbon dioxide are the calorically perfect gases, and the liquid carbon dioxide is the elastic and slightly compressible liquid. Since in the considered cases the value of the initial water saturation does not exceed 0.2, the water will be assumed to be immobile. The porous medium skeleton and hydrate are also immobile.

The system of main equations describing, in the one-dimensional case, the processes of filtration and heat transfer in a porous medium is the laws of conservation of masses and energy, the Darcy law and the equation of gas state [11-15]:

\[
 \frac{\partial}{\partial t} (\phi \rho \mathbf{S}_i) + \frac{\partial}{\partial x} (\phi \rho \mathbf{S}_i \mathbf{V}_i) = 0, \quad (i = l, c, m)
\]

\[
 \rho C_v \frac{\partial T_i}{\partial t} + \rho c_i \phi S_i \mathbf{V}_i \frac{\partial T_i}{\partial x} = \lambda \frac{\partial}{\partial x} \left( \frac{\partial T_i}{\partial x} \right),
\]

\[
 \phi S_i \mathbf{V}_i = -\frac{k_i}{\mu_i} \frac{\partial p_i}{\partial x},
\]

(1)
\[ \rho_i = \rho_{i0} \left( 1 + \beta (p_i - p_0) \right), \quad \rho_i = p_i / R_{ge} T_i, \quad (i = c, m) \]

where \( t \) is the time; \( x \) is the coordinate; \( S_i, \rho_i, v_i, k_i, C_i \) and \( \mu_i \) (\( i = l, c, m \)) are the pore saturation, density, velocity, relative permeability, mass heat capacity and the mobile fluid dynamic viscosity; \( R_{ge} \) and \( R_{gm} \) are the specific gas constants for carbon dioxide and methane; \( \beta \) is the coefficient of the volume compression of liquid carbon dioxide; \( \rho_{i0} \) is the true specific density of liquid carbon dioxide which is correspond to the pressure \( p_0 \); \( \rho C \) and \( \lambda \) are the specific volumetric heat capacity and the coefficient of the thermal conductivity of the system. Since the main contribution to the values of \( \rho C \) and \( \lambda \) is made by the corresponding parameters of the porous medium skeleton we shall consider them to be constant quantities.

Taking into account the Darcy law and the equation of state, the conditions for the balance of mass and heat at the boundary between the first and second zones (the boiling front) can be written in the following form:

\[ -\frac{\rho_{i0} k_i}{\mu_i} \frac{\partial p_i}{\partial x} + \frac{k_c}{2 \mu_c R_{ge} T_0} \frac{\partial^2 p_c}{\partial x^2} = \phi (1 - S_h) \left( 1 + \beta (p_n - p_0) - \frac{p_n}{\rho_{i0} R_{ge} T_0} \right) x_{(n)}, \quad (2) \]

\[ \frac{\lambda}{\lambda} \frac{\partial T_c}{\partial x} - \frac{\lambda}{\lambda} \frac{\partial T_l}{\partial x} = \rho_{i0} \left( 1 + \beta (p_n - p_0) \right) L_l \left( -\frac{k_l}{\mu_l} \frac{\partial p_l}{\partial x} - \phi (1 - S_h) \right) x_{(n)}. \]

Here \( L_l \) is the specific mass heat of evaporation of CO\(_2\); \( x_{(n)} \) is the velocity of the moving of the carbon dioxide boiling boundary. The temperature and pressure at this boundary are assumed to be continuous.

The relationship between pressure and temperature at the boiling boundary in the case of small temperature differences can be represented in the form of the Clausius-Clapeyron curve approximation:

\[ p_{(n)} = p_{c0} \left( \frac{\theta}{T_{c0}} - \frac{\theta}{T_{(n)}} \right), \quad (3) \]

where \( p_{c0} \) is the equilibrium boiling pressure corresponding to the temperature \( T_{c0} \); \( \theta \) is the empirical parameter.

Taking into account the Darcy law and the equation of state, the balance and heat conditions at the boundary between the second and third zones can be written in the form:

\[ -\frac{k_c}{\mu_c} \frac{\partial p_c}{\partial x} = \phi \left( \frac{\rho_h}{\rho_c} S_h G + S_c \right) \hat{x}_{(d)}, \quad (4) \]

\[ -\frac{k_m}{\mu_m} \frac{\partial p_m}{\partial x} = \phi S_m \hat{x}_{(d)}, \]

\[ \phi S_h \rho_h (1 - G) \hat{x}_{(d)} = \phi S_w \rho_w \hat{x}_{(d)}, \]

\[ \frac{\lambda}{\lambda} \frac{\partial T_c}{\partial x} - \frac{\lambda}{\lambda} \frac{\partial T_h}{\partial x} = \phi S_h \rho_h L_h \hat{x}_{(d)}, \]

where \( L_h \) is the specific mass heat of formation of carbon dioxide hydrate; \( \rho_w \) and \( \rho_h \) are the density of water and gas hydrate; \( S_w \) and \( S_h \) are water and hydrate pore saturation; \( G \) is the relative mass concentration of carbon dioxide in its hydrate; \( \hat{x}_{(d)} \) is the speed of movement of the hydrate formation boundary. The temperature and pressure at this boundary are assumed to be continuous.
3. Calculation results

Fig. 2 shows the distributions of temperature and pressure in the reservoir three days after the start of the liquid carbon dioxide injection. For the parameters characterizing the system, the following values are assumed: \( \phi = 0.1 \), \( S_{\phi} = 0.2 \), \( p_0 = 3.0 \) MPa, \( T_c = 260 \) K, \( T_0 = 279 \) K, \( k = 5 \times 10^{-16} \) m\(^2\), \( G = 0.28 \), \( \lambda = 2.1 \) W/(m·K), \( pC = 2 \times 10^5 \) J/(K·m\(^3\)), \( \rho_h = 1100 \) kg/m\(^3\), \( \rho_l = 1000 \) kg/m\(^3\), \( \rho_0 = 890 \) kg/m\(^3\), \( C_l = 2800 \) J/(K·kg), \( C_c = 800 \) J/(K·kg), \( C_m = 1560 \) J/(K·kg), \( R_{gc} = 189 \) J/(K·kg), \( R_{gm} = 520 \) J/(K·kg), \( \mu_l = 10^{-4} \) Pa·s, \( \mu_c = 1.3 \times 10^{-5} \) Pa·s, \( \mu_m = 6 \times 10^{-5} \) Pa·s, \( L_h = 4 \times 10^5 \) J/kg, \( L_l = 2.25 \times 10^5 \) J/kg, \( \theta = 1610 \) K, \( T_{co} = 274 \) K, \( p_{co} = 3.56 \) MPa [7, 9, 14, 16].

![Figure 2](image.png)

**Figure 2.** The temperature and pressure distributions at injection pressure \( p_c = 3.2 \) (a), 3.6 (b) and 4.2 (c) MPa. The dashed line is the equilibrium temperature of the carbon dioxide hydrate decomposition.

The process of hydrate formation is accompanied by the release of latent heat of phase transitions. In this connection, the temperature in the regions saturated with carbon dioxide hydrate can rise above the equilibrium temperature of its dissociation. Fig. 2 shows that for the small value of the injection pressure of carbon dioxide \( p_c = 3.2 \) MPa (case a), the reservoir temperature in the regions saturated with hydrate is below the equilibrium dissociation temperature. This is due to the fact that in this case the gas hydrate zone is located close to the left boundary of the reservoir, the temperature of which is lower than the initial reservoir temperature \( T_0 \). Therefore, through this boundary, an efficient removal of the heat released during hydrate formation is ensured.

At the higher pressure \( p_c = 3.6 \) MPa (case b), the reservoir temperature in a portion of the region saturated with hydrate (immediately beyond the hydrate formation front) rises above the equilibrium temperature of its decomposition. This is due to the fact that in this case the hydrate formation front is already located far enough from the left boundary of the reservoir. Therefore, the efficiency of the heat
removal through this boundary is reduced. This situation corresponds to the "overheating" of the gas hydrate. In this case it is necessary to consider the CO2 hydrate formation not at the frontal surface, but in the extended (volumetric) region.

At even higher pressure of the carbon dioxide injection $p_e = 4.2$ MPa (case c), the temperature of the reservoir behind the hydrate formation front again drops below the equilibrium temperature of its dissociation. This is due to the fact that in this case the distance between the hydrate formation front and the boiling front is very small (fig. 2c). And since boiling is accompanied by absorption of latent heat of vaporization, this leads to cooling of the sections of the reservoir located near the boiling front. Consequently, in this case (as with the parameters corresponding to fig. 2a), the model with the frontal boundary of hydrate formation gives an adequate mathematical description of the process.

4. Conclusions

The mathematical model of the liquid carbon dioxide injection into the porous reservoir initially saturated with methane and water, taking into account the carbon dioxide boiling, was presented in this work. The features of this process were studied. It is established that, in a certain pressure range, for an adequate mathematical description of the process it is necessary to introduce an extended region of the formation of carbon dioxide hydrate in order to avoid the situation of the gas hydrate "overheating". It is shown that this situation is not realized in those cases when the hydrate formation front is located close enough either to the left boundary of the reservoir or to the carbon dioxide boiling front.

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