Injection of liquid carbon dioxide into a gas hydrate reservoir

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Abstract. This paper presents the results of mathematical modeling of liquid carbon dioxide injection into a porous reservoir of a finite length, initially saturated with methane and its hydrate. Calculations show that when forming the carbon dioxide hydrate, different situations are possible: an area is formed, saturated with water and methane; and such area is absent in a porous medium. It has been established that the main parameters determining the different hydrate formation regimes are the temperature and pressure of the injected carbon dioxide, as well as the reservoir permeability.

1. Introduction

Natural gas hydrates are crystalline compounds formed from water and gas (most often methane) under certain thermobaric conditions. Hydrates attract special attention, because they accumulated huge reserves of natural gas. At the same time, use of traditional methods of gas production from gas hydrate deposits (reduction of pressure at the production well bottom, heating of the reservoir, or injection of inhibitors [1, 2]) is often not economically rational, and may also have an adverse environmental impact. In this connection, a new method of natural gas extraction was proposed, consisting in injecting carbon dioxide (liquid or gaseous) into methane hydrate reservoirs. This method is due to the fact that the CO₂ hydrate is thermodynamically more stable than the CH₄ hydrate [3]. Therefore, carbon dioxide can replace methane in its hydrate. At the same time, along with the extraction of natural gas, the problem of utilization of carbon dioxide, which significantly contributes to the greenhouse effect, is being solved.

The results of experimental studies on the replacement of methane in gas hydrate with liquid and gaseous carbon dioxide are given in particular in [4-8]. Mathematical models of gas extraction from the hydrate saturated reservoir are presented in a number of works, for example in [9-14]. The results of mathematical modeling of the process of the liquid carbon dioxide injection into a semi-infinite porous reservoir are presented in [9, 10]. For such reservoirs, the influence of the right boundary on the heat and mass transfer process is inessential. However, for a more detailed description of the processes occurring in porous media during the injection of liquid carbon dioxide, it is necessary to take into account the finite length of the hydrate saturated reservoirs. In this paper, we present the results of numerical modeling of the liquid carbon dioxide injection into a porous reservoir of finite length, initially saturated with methane and its hydrate.
2. Mathematical model

Consider a porous layer of a length $L$, whose top and bottom are impermeable and thermally insulated. Suppose that the reservoir is initially saturated with methane and its hydrate, the reservoir pressure $p_0$ and temperature $T_0$ correspond to the conditions for their stable existence. Let liquid carbon dioxide be pumped through the left boundary ($x = 0$). The pressure $p_c$ and the temperature $T_c$ of the injected fluid correspond to the conditions for the stable existence of liquid carbon dioxide and its hydrate. Two regions are formed in the reservoir: the near (first) region containing liquid carbon dioxide and its hydrate, and the pores of the far (the second) region containing methane and its hydrate. The boundary between the regions $x = x_0$ is characterized by the CH$_4$-CO$_2$ replacement process. This boundary moves deeper into the reservoir.

When describing the heat and mass transfer process, we take the following assumptions: the porous medium skeleton and hydrate are incompressible and immobile; the porosity is constant; the temperature of porous medium and its saturating matters is constant. Hydrates CO$_2$ and CH$_4$ are two-component systems with mass concentration of gas $G_i$ and $G_m$, respectively. The gas (methane) is considered to be calorically perfect, and the liquid (carbon dioxide) is an elastic liquid.

The system of basic equations, representing the equations of conservation of mass and energy, the Darcy law, the equation of state of a calorically perfect gas and an elastic fluid, in the flat-one-dimensional approximation with the noted assumptions has the form [9, 10, 15]:

\[
\frac{\partial}{\partial t} (\phi_i S_i) + \frac{\partial}{\partial x} (\phi_i S_i v_i) = 0, \quad (i = c, m)
\]

\[
\rho_C \frac{\partial T}{\partial t} + \rho_i C_i \frac{\partial T}{\partial x} = \lambda \frac{\partial}{\partial x} \left( \frac{\partial T}{\partial x} \right),
\]

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

\[
\rho_c = \rho_{c0} \exp(\beta(p - p_0)),
\]

\[
p_m = \rho_m R_{gm} T.
\]

Here $\phi$ is the porosity; $t$ is the time; $p$ is the pressure; $T$ is the temperature; $S_i$, $\rho_i$, $C_i$, $v_i$, $\mu_i$ and $k_i$ ($i = c, m$) are the saturation, density, specific heat, velocity, dynamic viscosity, and permeability of the $i$-th phase ($c$ – carbon dioxide, $m$ – methane), respectively; $R_{gm}$ is the reduced gas constant for methane; $\rho_{c0}$ and $\beta$ are the true density of carbon dioxide at the pressure $p_0$ and the coefficient of volume compression of liquid carbon dioxide; $\rho C$ and $\lambda$ are the specific volume heat capacity and thermal conductivity of the system “reservoir – saturating matter”.

The dependence of the permeability coefficient $k_i$ on the saturation $S_i$ and absolute permeability $k_0$ is given as follows:

\[
k_i = k_0 S_i^3.
\]

The conditions of the mass conservation at the moving boundary of the phase transition $x = x_0$ have the form [9, 10, 15]:

\[
-k_c \frac{\partial p(1)}{\partial x} = \phi S_c \left( 1 + \frac{G_c \rho_{hc}}{\rho_c} \right) \dot{x}(n), \quad -k_m \frac{\partial p(2)}{\partial x} = \phi S_m \left( 1 + \frac{G_m \rho_{hm}}{\rho_m} \right) \dot{x}(n)
\]

\[
\phi \rho_{hc} (1 - G_c) S_{hc} \dot{x}(n) = \phi \rho_{hm} (1 - G_m) S_{hm} \dot{x}(n),
\]

\[
\frac{\lambda}{\partial T(1)} - \frac{\lambda}{\partial T(2)} = \phi \left( \rho_{hc} S_{hc} L_{hc} - \rho_{hm} S_{hm} L_{hm} \right) \dot{x}(n).
\]
Here $S_{hc}$ ($i = c, m$) is the pore saturation with hydrate; $\rho_0$ and $L_0$ ($i = c, m$) are the density and the gas hydrate formation specific heat; $\dot{x}_m$ is the velocity of the phase transition boundary; the subscripts in brackets $j = 1, 2$ refer to the parameters of the first or second region.

Let the initial volume saturation of pores with methane hydrate be $S_{hm} = \nu$, then from the third equation of the system (2) for the pores volume saturation with the CO$_2$ hydrate, we obtain:

$$S_{hc} = \frac{\rho_{hm}(1-G_m)\nu}{(1-G_c)\rho_{hc}}.$$  

The initial and boundary conditions have the form:

$$t = 0, 0 \leq x \leq L: \quad T = T_0, \quad p = p_0, \quad S_{hm} = \nu, \quad S_m = 1 - \nu,$$  

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

$$t > 0, x = L: \quad p = p_0, \quad \frac{\partial T}{\partial x} = 0.$$  

Substituting in the first equation of system (1) Darcy law, the state equations of a calorically perfect gas and an elastic fluid, we obtain the pressure conductivity equations describing the pressure distributions in the near and far regions:

$$\frac{\partial p_1}{\partial t} = \frac{k_c}{\phi S_c \beta \mu_c \exp(\beta(p_1 - p_0))} \frac{\partial}{\partial x} \left( \exp(\beta(p_1 - p_0)) \frac{\partial p_1}{\partial x} \right),$$  

$$\frac{\partial p_2}{\partial t} = \frac{k_m}{\phi S_m \mu_m} \frac{\partial}{\partial x} \left( \frac{p_2}{\partial x} \right).$$  

Similarly, for the thermal diffusivity equations, we can write:

$$\frac{\partial T_1}{\partial t} = \frac{\partial}{\partial x} \left( \frac{\lambda}{\rho C \mu_c} \frac{\partial T_1}{\partial x} \right) + \frac{\rho_c C_c k_c}{\rho C \mu_c} \frac{\partial p_1}{\partial x} \frac{\partial T_1}{\partial x},$$  

$$\frac{\partial T_2}{\partial t} = \frac{\partial}{\partial x} \left( \frac{\lambda}{\rho C \mu_m} \frac{\partial T_2}{\partial x} \right) + \frac{\rho_m C_m k_m}{\rho C \mu_m} \frac{\partial p_2}{\partial x} \frac{\partial T_2}{\partial x}.$$  

The resulting system of equations (4)-(7) with initial and boundary conditions (3), and also conditions on the moving boundary of phase transitions (2), is closed. To solve this system, we used the method of catching the front in a node of a spatial grid. In this case, the original equations were represented in an implicit finite-difference form. The resulting system of algebraic equations was solved by the sweep method in combination with the iteration method.

3. Calculations results

Figure 1 shows the distributions of temperature and pressure in the reservoir at the liquid carbon dioxide injection at the pressure $p_c = 4.1$ MPa for the time $t = 25$ days. For other parameters characterizing the system, the following values are accepted [1, 9, 16-19]: $\phi = 0.2, \ k_0 = 10^{-16}$ m$^2$, $v = 0.2, \ p_0 = 3.5$ MPa, $T_0 = 274$ K, $\rho C = 2.5 \cdot 10^6$ J/(K-m$^3$), $\lambda = 2$ W/(m-K), $G_e = 0.28, \ G_m = 0.13$, $R_{hm} = 520$ J/(K-kg), $\beta = 10^8$ Pa$^{-1}$, $\rho_{hc} = 1100$ kg/m$^3$, $\rho_{hm} = 900$ kg/m$^3$, $\rho_e = 890$ kg/m$^3$, $\mu_e = 10^4$ Pa-s, $\mu_m = 10^5$ Pa-s, $L_{hc} = 3.54 \cdot 10^5$ J/kg, $L_{hm} = 4.5 \cdot 10^5$ J/kg, $C_e = 800$ J/(K-kg), $C_m = 1560$ J/(K-kg), $L = 100$ m.
Figure 1. The distributions of temperature and pressure along the $x$-coordinate. $T_c = 279$ K ($a$) и 281 K ($b$).

It follows from Fig. 1a that at a relatively low temperature of the injected carbon dioxide, the temperature in the region containing methane and its hydrate is below the equilibrium temperature of the CH$_4$ hydrate decomposition (dashed line), which is determined by the expression [16]:

$$\ln p = A - B / T,$$

where $A = 29.112$, $B = 7694.30$.

Consequently, in this case the solution with a single boundary of phase transition is thermodynamically consistent. As the temperature of the injected carbon dioxide increases (Fig. 1b), the temperature in the region containing methane hydrate rises above a certain value of the equilibrium temperature of the CH$_4$ hydrate decomposition. In this case the solution with a single moving boundary of phase transition does not allow us to construct a thermodynamically consistent solution. Therefore, it is necessary to introduce another region containing the dissociation products of the hydrate (water and methane) in a free state.

Figure 2 shows (for the time $t = 10$ days) the dependence of the critical temperature value of the injected carbon dioxide (above which the regime with the dissociation region of the CH$_4$ hydrate is realized) on the pressure at the left boundary $p_e$. As follows from the figure, with increasing injection pressure, the critical temperature also increases, the faster the higher the reservoir permeability. At low
pressures of the injected gas, close to the initial reservoir pressure, and also at low reservoir permeability, the critical temperature tends to the equilibrium decomposition temperature of the CH₄ hydrate. This is due to the fact that as the injected gas pressure approaches to the initial pressure and the permeability decreases, the velocity of the phase transition boundary decreases (since it is limited by the rate of the carbon dioxide filtration). In this case, the value of the temperature at the phase transition boundary approaches to the temperature at the reservoir left boundary (i.e., to the temperature of the injected carbon dioxide).

![Figure 2. Dependence of the critical temperature on the injected gas pressure for the different values of reservoir permeability $k_0$. Lines 1 and 2 correspond to $k_0 = 10^{-17}$ and $10^{-16}$ m². The dashed line is the equilibrium decomposition temperature of the CH₄ hydrate.](image)

4. Conclusions
Mathematical model of the warm liquid carbon dioxide injection into a porous medium of finite length saturated with methane and its hydrate is presented. The calculation results showed that depending on the temperature and pressure of the injected carbon dioxide, as well as the reservoir permeability, the replacement of CH₄ with CO₂ in the gas hydrate or the decomposition of methane hydrate into gas and water can occur. The methane hydrate decomposition regime is realized at high temperatures of the injected carbon dioxide, as well as low injection pressures, and low reservoir permeability.

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