Numerical study of the process of injection carbon dioxide into a porous formation saturated with methane and its hydrate

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Abstract. In this article, in a planar one-dimensional approximation, we examine the problem of injecting gaseous carbon dioxide into a porous formation saturated in its initial state with methane and its hydrate. On the basis of the equations of multiphase systems mechanics, a mathematical model of the formation of CO\textsubscript{2} hydrate from methane gas hydrate is constructed, acknowledging the real properties of gases. It is shown that the formation of carbon dioxide hydrate can occur in two regimes: 1) with the formation of an area saturated with methane and water, or 2) without water at all. It has been established that the main parameters determining the hydrate formation regimes are: the formation permeability, the parameters of the injected gas, and the initial parameters of the system. Here, we construct and analyze critical diagrams separating these two modes.

1. Introduction
Gas hydrates are solid crystalline compounds formed from gas and water (ice) at certain pressures and temperatures. The huge reserves of natural gas, concentrated in hydrates, make them an almost inexhaustible source of energy, the fuel of the future. Another aspect of their research is associated with the sequestration of greenhouse gases into the hydrate phase. A number of researchers have suggested an idea regarding the injection of CO\textsubscript{2} into gas hydrate formations in order to extract natural gas from them and the carbon dioxide compound into the hydrate form [1].

This is possible due to the fact that carbon dioxide hydrate, other conditions being equal, is more stable than methane hydrate. Laboratory experiments on the effect of CO\textsubscript{2} (in the liquid or gaseous phase) on methane hydrate are examined, in particular, in [2-4]. It is shown that the proportion of methane substituted in this way from the hydrate composition can make up to 70\% [2, 3]. Theoretical models of injecting CO\textsubscript{2} into methane hydrate formations are examined in [5, 6]. In this paper, we present a mathematical model of the substitution of CH\textsubscript{4} for CO\textsubscript{2} in the methane hydrate formation during the carbon dioxide injection, taking into account the finite extent of the formation, the real gas properties, the Joule-Thomson effect, and the adiabatic expansion of the gas.

2. Mathematical model
We examine a homogeneous porous medium of length $L$, the roof and sole of which are impermeable and thermally insulated. We assume that at the initial moment the reservoir is completely saturated with methane and its hydrate, the pressure $p_0$ and temperature $T_0$ of which correspond to the conditions for their stable existence. Let us suppose that carbon dioxide is pumped through the left boundary of
the formation (x = 0), the pressure \( p_r \) and the temperature \( T_e \) correspond to the conditions for the stable existence of a mixture of CO\(_2\) and its hydrate. As a result of this injection of CO\(_2\) in the formation, two areas are formed. Thus, the pores of the near area adjacent to the left border of the formation contain carbon dioxide and its hydrate; the pores of the far field are filled with methane and its hydrate. In this case, a stable mobile boundary arises that moves into the depth of the reservoir over time and separates the above-mentioned regions. Its stability comes from the fact that flows in porous media are laminar, and also greater, in comparison with methane, viscosity of carbon dioxide. In describing the processes of heat and mass transfer in porous media, we accept the following assumptions: the porosity is constant; the skeleton of the porous medium, hydrate and water are incompressible and immobile; the temperature of the porous medium and the saturating substance is the same. In this case, we assume that methane and carbon dioxide hydrates are two-component systems with mass concentration of gas \( G_m \) and \( G_c \).

The system of basic equations describing the processes of filtration and heat transfer in a porous medium and representing the laws of conservation of masses and energy, the Darcy law and the equation of state, in the rectilinear parallel case with the assumptions noted above in each of the regions has the form:

\[
\begin{align*}
\frac{\partial}{\partial t} (\rho_g \phi \rho S_g) + \frac{\partial}{\partial x} \left( \rho_g \phi \rho S_g v_g \right) &= 0, \\
\rho C \frac{\partial T}{\partial t} + \rho_g C_g \phi \rho S_g v_g \left( \frac{\partial T}{\partial x} + \epsilon_g \frac{\partial p}{\partial x} \right) - \frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) - \rho_g C_g \phi \rho S_g \eta_g \frac{\partial p}{\partial t} &= 0, \\
\phi S_g v_g &= -\frac{k_g}{\mu_g} \frac{\partial p}{\partial x}, \quad \rho_g = \frac{p}{z_g R_g T}, \quad \eta_g = \frac{1}{\rho_g C_g} - \epsilon_g, \\
\rho C = (1 - \phi) \rho_{sk} C_{sk} + \phi \sum_{j = g, h, l} S_j \rho_j C_j, \quad \lambda = (1 - \phi) \lambda_{sk} + \phi \sum_{j = g, h, l} S_j \lambda_j
\end{align*}
\]

Here, \( \phi \) – porosity; \( p \) – pressure; \( T \) – temperature; \( S_j, \rho_j, C_j \) and \( \lambda_j \) (\( j = g, h, l \)) – pore density, density, specific mass heat capacity and thermal conductivity of the \( j \) phase (\( g \) – gas, \( h \) – gas hydrate, \( l \) – water); \( v_g, k_g, R_g, \mu_g, \epsilon_g, \eta_g \) (\( g = c, m \)) – speed, permeability, gas constant, dynamic viscosity, throttling factor and adiabatic coefficient of the \( g \)-th gas phase (\( c \) – carbon dioxide, \( m \) – methane); \( \rho_{sk}, \lambda_{sk} \) and \( C_{sk} \) – density, thermal conductivity and specific heat of the skeleton of the porous medium; \( \rho C \) and \( \lambda \) – specific volume heat capacity and coefficient of thermal conductivity of the «porous medium-saturating fluid» system.

The dependence of the phase permeability coefficient for the gas \( k_g \) on the gas saturation \( S_g \) and the absolute permeability \( k_0 \) is given in the following way [7]:

\[
k_g = k_0 S_g^{3} \quad (g = c, m).
\]

The supercompressibility coefficient for methane will be found on the basis of the Latonov-Gurevich equation [8]:

\[
z_m = \left(0.17376 \cdot \ln(T/T_e) + 0.73\right)^{p/p_e} + 0.1 \cdot p/p_e,
\]

here \( T_e \) and \( p_e \) are empirical critical parameters for the gas.

For the coefficient of supercompressibility of carbon dioxide, we will use a linear approximation [9]:

\[
z_c = -0.006 p/10^6 + 0.998
\]

From the system (1) it is possible to obtain the equations of piezoconductivity and thermal diffusivity:
\[
\frac{1}{z_{1}(T)} \frac{\partial p_{1}(t)}{\partial t} = \chi_{1}(p) \frac{\partial}{\partial x} \left( \frac{p_{1}(t)}{z_{1}(T)} \frac{\partial p_{1}(t)}{\partial x} \right),
\]
\[
\frac{\partial T_{1}(t)}{\partial t} = \chi^{(T)}(X_{1}(x_{1})) \frac{\partial}{\partial x} \left( \frac{\partial T_{1}(t)}{\partial x} \right) + \left( \frac{\partial}{\partial x} \right) \left( \frac{\partial T_{1}(t)}{\partial x} \right) + Y_{1}(x_{1}) \frac{\partial p_{1}(t)}{\partial t},
\]

in which \( \chi_{1}(p) = k_{c} \left( \mu_{c} \phi \left( 1 - S_{hc} \right) \right)^{-1} \), \( \chi^{(T)}(X_{1}(x_{1})) = C_{v} \left( \lambda R_{\mu} \mu_{c} \right)^{-1} \), \( X_{1}(x_{1}) = C_{c} k_{c} \lambda R_{\mu} \mu_{c} \)^{-1}, \( Y_{1} = \phi C_{s} \left( R_{c} \rho C \right)^{-1} \), \( Y_{2} = \phi C_{s} \left( R_{c} \rho C \right)^{-1} \), \( \chi^{(T)} = \lambda \rho C^{-1} \). Here and below, the subscripts in parentheses \( i = 1, 2 \) refer to the parameters of the first and second regions accordingly.

As noted above, when injecting CO\(_2\) into the methane hydrate formation, two areas and the mobile boundary of the phase transition \( x = x \) \((n)\) separating them appear. Therefore, the conditions for the conservation of masses of gases and water on it have the form [5, 6]:

\[
\phi \rho_{c} S_{c} \left( \nu_{c} - \dot{x}_{(n)} \right) = \phi \rho_{m} S_{m} \dot{x}_{(n)} \), \quad \phi \rho_{m} S_{m} \left( \nu_{m} - \dot{x}_{(n)} \right) = \phi \rho_{m} S_{m} \dot{x}_{(n)} \).
\]

Here \( S_{hc} \) and \( S_{hm} \) - pore saturation with hydrate of carbon dioxide and methane, accordingly; \( \dot{x}_{(n)} \) – the velocity of the boundary of the phase transition.

Since the volume saturation of the methane hydrate equals \( \nu \) \((S_{hm} = \nu)\), from the last equation of the system (4) for volume saturation with hydrate CO\(_2\), we get:

\[
S_{hc} = \rho_{hm} \left( 1 - G_{m} \right) \left( \rho_{c} \left( 1 - G_{c} \right) \right)^{-1} \nu.
\]

Applying Darcy’s law to the first two equations of system (4), the conditions for the mass balance of gas and heat on the mobile boundary of the phase transition \( x = x_{(n)} \) can be represented as:

\[
- \frac{k_{c}}{\mu_{c}} \frac{\partial p_{c}}{\partial x} = \phi \dot{x}_{(n)} \left( S_{c} + \frac{\rho_{c} G S_{hc}}{\rho_{c}} \right),
\]
\[
- \frac{k_{m}}{\mu_{m}} \frac{\partial p_{m}}{\partial x} = \phi \dot{x}_{(n)} \left( S_{m} + \frac{\rho_{m} G_{m} \nu}{\rho_{m}} \right),
\]
\[
\lambda \frac{\partial T_{c}}{\partial x} - \lambda \frac{\partial T_{m}}{\partial x} = \phi \left( \rho_{c} S_{c} L_{hc} - \rho_{m} \nu L_{hm} \right) \dot{x}_{(n)}.
\]

Here \( L_{hc} \) and \( L_{hm} \) – accordingly, are the specific heats of formation of carbon dioxide and methane hydrates.

The initial conditions, as well as the conditions at the boundaries of the formation, can be represented as:

\[
t = 0: \quad p = p_{0}, \quad T = T_{0}, \quad (0 \leq x \leq L);
\]
\[
x = 0: \quad p = p_{c}, \quad T = T_{c}, \quad (t > 0);
\]
\[
x = L: \quad p = p_{0}, \quad \frac{\partial T}{\partial x} = 0, \quad (t > 0).
\]

To solve the problem (2), (3) with initial and boundary conditions (6) and conditions (5) on the moving boundary of the phase transition, the original equations are represented in an implicit finite-difference form. To solve such a system, the method of catching the front in a spatial mesh node was used [5, 6], in combination with the sweep algorithm and the iteration method.

3. Calculations results

In Figure 1, for the time \( t = 200 \) days, the temperature and pressure distributions in the formation are shown when carbon dioxide is injected with temperature \( T_{c} = 280 \) K. For other parameters characterizing the system, the following values are assumed: \( L = 100 \) m, \( \phi = 0.1 \), \( \nu = 0.2 \).
\( \lambda = 2 \text{ W/(m·K)} \), \( k_0 = 10^{-15} \text{ m}^2 \), \( p_0 = 3 \text{ MPa} \), \( T_0 = 274 \text{ K} \), \( \rho C = 2,5 \times 10^6 \text{ J/(kg·K)} \), \( G_c = 0.28 \), \( G_m = 0.13 \), \( R_c = 189 \text{ J/(kg·K)} \), \( R_m = 520 \text{ J/(kg·K)} \), \( \mu_c = 1.3 \times 10^{-5} \text{ Pa·s} \), \( \mu_m = 10^{-5} \text{ Pa·s} \), \( \rho_{sd} = 1100 \text{ kg/m}^3 \), \( \rho_{hd} = 1100 \text{ kg/m}^3 \), \( \rho_{hm} = 900 \text{ kg/m}^3 \), \( L_{hc} = 4.1 \times 10^5 \text{ J/kg} \), \( L_{hm} = 4.5 \times 10^5 \text{ J/kg} \), \( C_c = 800 \text{ J/(kg·K)} \), \( C_m = 1560 \text{ J/(kg·K)} \). For the Joule-Thomson coefficients of gases, the values \( \varepsilon_c = 13.9 \text{ K/MPa} \), \( \varepsilon_m = 4.5 \text{ K/MPa} \).

In Fig. 1 it is stated that for various parameters of the injected gas, the formation of a carbon dioxide hydrate can occur both with the dissociation of methane hydrate into gas and water, and without it. In Fig. 1a the temperature is shown to be in the area saturated with methane and its hydrate is below the equilibrium temperature, which is well described by a curve of the form [10]:

\[
T_{(1)} = T_0 + T \ln \left( \frac{p}{p_{t_0}} \right).
\]

Here \( T \) and \( p_{t_0} \) – empirical parameters, depending on the type of gas hydrate. In particular, for methane hydrate \( T = 10 \text{ K} \), \( p_{t_0} = 2.87 \text{ MPa} \). Consequently, in this case, the decomposition of methane into gas and water does not occur. At lower values of the pressure of the injected gas, as followed from fig. 1b, the temperature in the region of methane and its hydrate rises above the equilibrium temperature. In this case, it is necessary to enter the area containing methane and water in the free state; the formation of the hydrate of CO$_2$ now occurs from gas and water.

In fig. 2 for the instant \( t = 200 \text{ days} \), the temperature dependences \( T_{(i)} \) at the boundary of the phase transition on the injection gas pressure \( p_0 \), the absolute permeability \( k_0 \) of the formation, and the initial pressure \( p_{i0} \) of the system are shown. From fig. 2 follows the fact that an increase in both the initial pressure of the system and a decrease in the permeability of the formation and the pressure of the injected gas in comparison with the parameters corresponding to fig. 1 lead to the fact that the velocity of the front of the phase transition, which is limited by the intensity of the supply of CO$_2$ to it,
decreases. In this case, the effect of a higher temperature on the well, which results in the temperature in the area containing methane and hydrate rising above the equilibrium temperature, is indeed significant.

Figure 2. Dependences of the temperature at the boundary of the phase transition and its coordinates as a function of the pressure of the injected gas – a; absolute permeability of the formation – b; the initial pressure in the system is c. The dashed line is the equilibrium temperature of methane hydrate.

In fig. 3 for the time \( t = 20 \) days, the dependence of the critical temperature is shown, above which the regime with methane hydrate decomposition into gas and water is realized, from the initial pressure \( p_0 \) and the pressure of the injected gas, \( p_e \).

Figure 3. The dependence of the critical temperature on
a – the initial pressure of the system: \( k_0 = 10^{-15} \text{ m}^2 \cdot 1 \), \( k_0 = 7 \cdot 10^{-16} \text{ m}^2 \cdot 2 \);

b – discharge gas pressure: \( \nu = 0,2 \cdot 1 \); \( \nu = 0,25 \cdot 2 \)

As follows from the fig. 3, the value of the critical temperature drops, as the initial pressure increases and the permeability of the formation decreases. This is due to the fact that the velocity of the boundary of the phase transition is limited by the rate of supply of \( \text{CO}_2 \), which, in turn, depends on the pressure drop in the formation. Similarly, the increase in the critical temperature is observed with an increase in the pressure of the injected gas. At the same time, with a decrease in the initial hydration of the reservoir at relatively high values of the pressure of the injected gas, the value of the critical temperature increases. This is true due to the fact that with decreasing hydratonsaturations, gas saturation increases, therefore increasing the intensity of carbon dioxide intake to the boundary of the phase transition.

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