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Numerical simulation of injection process of warm carbon dioxide into layer saturated with methane and its hydrate

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Abstract. In this article, in a flat-one-dimensional approximation, a mathematical model is presented for injecting warm carbon dioxide into a methane hydrate formation of finite length. It is established that the model of formation of hydrate of carbon dioxide in the absence of an area saturated with methane and water, under certain parameters, leads to thermodynamic contradiction. The mathematical model of carbon dioxide injection with formation of the region saturated with methane and water is constructed.

1. Introduction

Gas hydrates are crystalline compounds formed from water and natural gas (more often from methane) at high pressures and relatively low temperatures conditions. Methane hydrates represent a highly concentrated form of methane: 1 m³ of methane hydrate contains 0.8 m³ of water and more than 160 m³ of methane at standard temperature and pressure.

One of the methods of extracting gas from gas hydrates, in addition to heating, depressing and injecting inhibitors [1], is the injection of carbon dioxide into depleted gas hydrate deposits [2]. Such process, in addition to releasing methane, allows effectively sequestering carbon dioxide, which is a greenhouse gas [3-5]. Theoretical models of injection of CO₂ into methane hydrate formations are examined in [6, 7].

In this paper, a mathematical model for the injection of warm carbon dioxide into a methane hydrate formation of finite length is presented in a plane-one-dimensional approximation, taking into account the real properties of gases, Joule-Thomson effects and adiabatic expansion of gases.

2. Mathematical model

Let us consider a porous layer of length L saturated at the initial instant of time with methane and its hydrate, the volume fraction of which is equal to v. In this case, the initial pressure p₀ and temperature T₀ satisfy the conditions for the stable existence of CH₄ and its hydrate. We assume that a warm (with a temperature higher than the initial one) carbon dioxide is pumped through the left boundary of the formation, the pressure pₑ and temperature Tₑ of which satisfy the conditions for the existence of CO₂ and its hydrate. As a result of this process, two areas are formed in the formation. In the near, adjacent to the left border of the reservoir in the pores are CO₂ and its hydrate, and in the pores of the far – CH₄ and its hydrate. This creates a stable mobile boundary of the phase transition, which separates these regions and moves deep into the formation. The stability of this boundary is due, firstly, to the fact that the flow in the porous medium is laminar, and secondly, because the viscosity of CO₂ is higher than...
the viscosity of CH₄.

In describing the process of heat and mass transfer accompanied by the replacement of hydrate CH₄ with CO₂ hydrate, let us adopt the following assumptions: the porosity of the reservoir is constant, the hydrates CO₂ and CH₄ are two-component systems with a mass fraction of gas G_d and G_m, accordingly. Let us also assume that the temperature of the porous medium and the substance that saturates it is the same.

Taking into account the above-mentioned assumptions, the system of basic equations, including the equations of continuity and heat inflow, as well as the Darcy law and the equation of state of the real gas under the above-mentioned assumptions are [6, 7]:

\[
\frac{\partial}{\partial t}(\rho \phi S_e) + \frac{\partial}{\partial x}(\rho \phi S_e v_e) = 0,
\]

\[
\rho C \frac{\partial T}{\partial t} + \rho \phi C_g \phi S_e v_e \left( \frac{\partial T}{\partial x} + \varepsilon_g \frac{\partial p}{\partial x} \right) - \frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) - \rho \phi C_g \phi S_e \frac{\partial p}{\partial t} = 0,
\]

\[
\phi S_e v_e = -\frac{k_g}{\mu_g} \frac{\partial p}{\partial x}, \quad \rho_g = \frac{p}{\rho_g C_g}, \quad \eta_g = \frac{1}{\rho_g C_g} - \varepsilon_g,
\]

\[
\rho = (1 - \phi) \rho_{sk} \phi + \phi \sum_{j=g,h,l} S_j \rho_j C_j, \quad \lambda = (1 - \phi) \lambda_{sk} + \phi \sum_{j=g,h,l} \lambda_j.
\]

Here, \( \phi \) – porosity; \( \rho \) – 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 \( j \)-th phase \((g – \text{gas}, h – \text{gas hydrate}, l – \text{water})\); \( v_e, k_g, R_g, \mu_g, \varepsilon_g, \eta_g \) \((g = c, m)\) – speed, permeability, gas constant, dynamic viscosity, throttling factor and adiabatic coefficient of the \( g \)-th gas phase \((c – \text{carbon dioxide}, m – \text{methane})\); \( \rho_{sk}, \lambda_{sk} \) 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 permeability coefficient of the \( g \)-th gas phase on the current gas saturation will be determined on the basis of the Kozeni formula [8]:

\[
k_g = k_{0g} S_e^3 \ (g = c, m).
\]

The supercompressibility coefficient for methane will be found on the basis of the Latonov-Gurevich equation [9]:

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

here \( T_c \) and \( p_c \) are empirical critical parameters for the gas.

For the coefficient of supercompressibility of carbon dioxide, let us use a linear approximation [10]:

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

Since there is no gas mixing and there is a stable displacement front \( x = x_{(n)} \), the conditions for the balance of mass (gases and water contained in hydrates) and heat look like [7]:

\[
\begin{align*}
\phi \rho_c S_e (v_e - \dot{x}_{(n)}) &= \phi \rho_{hc} S_{hc} G_c \dot{x}_{(n)}, \\
\phi \rho_{m} S_{m} (v_m - \dot{x}_{(n)}) &= \phi \rho_{hm} S_{hm} G_m \dot{x}_{(n)}, \\
\phi \rho_c \left( 1 - G_c \right) S_{hc} \dot{x}_{(n)} &= \phi \rho_m \left( 1 - G_m \right) S_{hm} \dot{x}_{(n)},
\end{align*}
\]

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. Pressure and temperature at the border will be considered as continuous values.

Since \( S_{hm} = v \), from (3), for the value of hydration of the near region, let us obtain the equation:

\[
S_{hc} = \rho_{hm} \left( 1 - G_m \right) \left( \rho_{hc} \left( 1 - G_c \right) \right)^{-1} v.
\]
Acquiring the Darcy’s law to (2), the conditions for the balance of mass of gas and heat are given in the form:

\[
\frac{k_w}{\mu_w} \frac{\partial p_m}{\partial x} = \phi \frac{\partial \bar{X}(x)}{\partial x} \left( \frac{S_m^1 + \rho_m G_m S_m^2}{\rho_m} \right),
\]

\[
\frac{k_m}{\mu_m} \frac{\partial p_m}{\partial x} = \phi \frac{\partial \bar{X}(x)}{\partial x} \left( \frac{S_m^1 + \rho_m G_m S_m^2}{\rho_m} \right),
\]

\[
\lambda \frac{\partial T_m}{\partial x} - \lambda \frac{\partial T_m}{\partial x} = \phi \left( \rho_m \frac{\partial S_m}{\partial x} \right),
\]

(4)

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

Applying to (1) Darcy’s law, equations piezoconductivity and conductivity can be represented in the form:

\[
\frac{1}{z(T)} \frac{\partial p(x)}{\partial t} = \chi^{(p)} \frac{\partial}{\partial x} \left( \frac{p(x)}{z(T)} \frac{\partial p(x)}{\partial x} \right),
\]

(5)

\[
\frac{\partial T(x)}{\partial t} = \chi^{(T)} \frac{\partial}{\partial x} \left( \frac{\partial T(x)}{\partial x} + \rho \frac{\partial p(x)}{\partial x} \right) + \chi^{(T)} \frac{\partial}{\partial x} \left( \frac{\partial T(x)}{\partial x} + \rho \frac{\partial p(x)}{\partial x} \right) + Y(x) \frac{p(x)}{z(T)} \frac{\partial p(x)}{\partial x},
\]

(6)

in which \( \chi^{(p)} = k / \left( \mu \phi (1 - S_{hc}) \right) \), \( \chi^{(T)} = k / \left( \mu \phi (1 - \nu) \right) \), \( X(1) = C_k / k \), \( \lambda R / (\mu \ell) \), \( X(2) = C_m k_m / \left( \lambda R / (\mu \ell) \right) \), \( Y(1) = \phi C_s \), \( \phi \), \( C_m / \left( \lambda R / (\mu \ell) \right) \), \( Y(2) = \phi C_m S_{hc} / \left( \lambda R / (\mu \ell) \right) \), \( \chi^{(T)} = \lambda / \rho C \). Here and below, the subscripts in parentheses \( i = 1, 2 \) refer to the parameters of the first and second regions accordingly.

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

\[
t = 0: \quad p = p_0, \quad T = T_0 \quad (0 \leq x \leq L);
\]

(7)

\[
x = 0: \quad p = p_0, \quad T = T_c \quad (t > 0);
\]

(8)

\[
x = L: \quad p = p_0, \quad \frac{\partial T}{\partial x} = 0 \quad (t > 0).
\]

(9)

To solve the problems (5), (6) with initial and boundary conditions (7) – (9) and conditions (4) on the boundary of the phase transition, the method of catching the front into the node of the spatial grid [6] is in combination with the iteration method and the sweep algorithm.

3. Calculations results

Figure 1 for time \( t = 150 \) days shows the distribution of temperature and pressure in the formation when carbon dioxide is injected at a temperature of \( T_c = 280 \) K into the formation of length \( L = 100 \) m. For other parameters characterizing the system, the following values are assumed: \( \phi = 0.1, \nu = 0.22 \), \( \lambda = 2 \) W / (m·K), \( k_0 = 10^{-15} \) m², \( p_0 = 3 \) MPa, \( T_0 = 274 \) K, \( \rho C = 2.5 \cdot 10^8 \) J/(K·m³), \( G_c = 0.28, \ G_m = 0.13, \ R_c = 189 \) J / (kg·K), \( R_m = 520 \) J/(kg·K), \( \mu_c = 1.3 \cdot 10^{-5} \) Pa·s, \( \mu_m = 10^{-5} \) Pa·s, \( \rho_{hc} = 900 \) kg/m³, \( L_{hc} = 4.1 \cdot 10^3 \) J/kg, \( L_{hm} = 4.5 \cdot 10^3 \) J/kg, \( C_c = 800 \) J/(kg·K), \( C_m = 1560 \) J/(kg·K). For the Joule-Thomson coefficients of gases, values \( c_c = 13.9 \) K/MPa, \( c_m = 4.5 \) K/MPa [11]. The solutions obtained were tested for thermodynamic consistency. This means that the local temperature in the region of existence of methane and its hydrate \( T_{hm} \) should be lower than the equilibrium temperature of system «gas-hydrate-water» \( T_{eq} \) determined from the equation [12]:

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

Here \( T_0 \) and \( p_{eq} \) – empirical parameters, depending on the type of gas hydrate. In particular, for methane hydrate \( T_0 = 10 \) K, \( p_{eq} = 2.87 \) MPa.
Figure 1. Distribution of temperature and pressure in the reservoir at time \( t = 150 \) days, at
\[ p_e = 3.3 \text{ MPa} \] \( a \); \( p_e = 3.1 \text{ MPa} \) \( b \).

The dashed line is the equilibrium temperature of methane hydrate.

It follows from the figure that when the carbon dioxide is injected at a pressure of \( p_e = 3.3 \text{ MPa} \), the solution of the problem is thermodynamically consistent. In this case, the process of formation of the hydrate of CO\(_2\) occurs without the formation of a region saturated with methane and water. When the gas is injected at a pressure \( p_e = 3.1 \text{ MPa} \), the temperature in the region containing methane and its hydrate rises above equilibrium; in this case, the formation of carbon dioxide hydrate occurs with the formation of a region saturated with methane and water. This is explained by the fact that with a decrease in the pressure of the injected gas, the velocity of the boundary of the phase transition, which is limited by the intensity of the entry of CO\(_2\) to the boundary of the phase transition, also decreases. In this case, the effect of the heated left boundary of the formation is significant.

It is established that the main parameters determining the modes of hydrate formation are both the permeability of the reservoir and the parameters of the pumped gas, and the initial parameters of the system.

4. Model with the formation of a region saturated with methane and hydrate

The process of injecting CO\(_2\) into the methane hydrate formation is examined. Let us assume that in this case, three areas are formed in the formation. In the near one, CO\(_2\) and its hydrate are adjacent to the left border of the reservoir in the pores, and in the pores of the farther one – methane and its hydrate. The intermediate region, which separates the nearest and the furthest areas, contains methane and water in a free state. There are two moving boundaries. Boundary \( x = x_{(d)} \) divides the near and intermediate areas, and boundary \( x = x_{(d)} \) is the intermediate and further one.
The system of basic equations has the form (1). The conditions at the near boundary of phase transition \( x = x_{(n)} \), where the formation of the hydrate of CO\(_2\) from the gas and water takes place, have the form:

\[
\phi S_d \rho_d \left( v_d - \dot{x}_{(n)} \right) = \phi S_m G_d \rho_d \dot{x}_{(n)} , \quad \phi S_m \rho_m \left( v_m - \dot{x}_{(n)} \right) = 0 ,
\]

\[
\phi \rho_{ld} \left( 1 - G_d \right) S_{ld} \dot{x}_{(n)} = \phi \rho_l S_l \dot{x}_{(n)} , \quad \lambda \frac{\partial T}{\partial x} - \lambda \frac{\partial T}{\partial x} = \phi \rho_{ld} S_{ld} L_{ld} \dot{x}_{(n)} .
\]

Here, \( S_l \) – the water saturation of the intermediate region, \( \rho_l = 1000 \text{ kg/m}^3 \) is the water density.

Analogically, the conditions on boundary \( x = x_{(d)} \), where the decomposition process of methane hydrate to gas and water occurs, have the form:

\[
\phi S_m \rho_m \left( v_m - \dot{x}_{(d)} \right) = \phi S_m G_m \rho_m \dot{x}_{(d)} , \quad \phi \rho_m \left( 1 - G_m \right) \nu \dot{x}_{(d)} = \phi \rho_m S_m \dot{x}_{(d)} \frac{\partial T}{\partial x} - \lambda \frac{\partial T}{\partial x} = - \phi \rho_m S_m L_{md} \dot{x}_{(d)} .
\]

The initial and boundary conditions have the form (7) - (9).

Fig. 2 for time \( t = 150 \) days shows the temperature and pressure distributions when the gas is injected at a pressure of \( p_e = 3.1 \) MPa. As follows from the figure, with an increase in the temperature of the injected gas, the extent of the area containing methane and water increases. This is explained by the fact that the rate of decomposition of the gas hydrate is determined by the intensity of the supply of heat to it. Therefore, the rate of decomposition of methane gas hydrate increases with the temperature of the injected gas.

**Figure 2.** Temperature and pressure distribution for time \( t = 150 \) days at \( T_e = 280 \) K - a and \( T_e = 276 \) K - b.
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