Modelling of process of displacement of methane from gas hydrate reservoir at dioxide carbon injection

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Abstract. The paper presents a mathematical model for describing the process of displacing methane with carbon dioxide from a reservoir saturated with methane and its hydrate. For gas substitution kinetics, a scheme has been proposed in which the intensity of the process is defined by the diffusion of carbon dioxide through the hydrate layer formed between the gas mixture flow and methane hydrate. The numerical research of influence of main parameters on dynamics of process is conducted. Influence of coefficient of diffusion mixing of the gas mixture and permeability for the time of complete gas-replacement in reservoir is studied.

1. Introduction
Nowadays much attention is paid to the problem of search and development of alternative energy sources. One of these sources is natural gas hydrates, where the potential reserves of methane exceed value $1.6 \cdot 10^{16} \text{ m}^3$ \cite{1–3}. One of the last innovative ways of extraction of methane of composition of hydrate is its replacement with carbon dioxide in gas hydrate \cite{4–6}. The advantages of this method are the possibility simultaneous extraction of methane from the reservoir and the preservation of carbon dioxide in the hydrate state, the possibility of partial conservation of energy consumption in connection with the release of heat due to a phase transition, the possibility of preserving the mechanical strength of the rock as a result of gas substitution \cite{4, 5}.

2. Mathematical model
2.1. Main equations
Let us consider in the flat-one-dimensional approximation the process of the gaseous carbon dioxide injection into a hydrate reservoir. Since carbon dioxide hydrate is more stable than methane hydrate, under certain conditions, methane molecules will be replaced by carbon dioxide molecules in gas hydrate without the release of free water \cite{4, 6}. In this paper it is assumed that the replacement process will occur in the stable existence of the methane and carbon dioxide hydrates as well as the existence of CO\textsubscript{2} in a gaseous state. Let the hydrate reservoir initially consist of three components, namely, from a solid skeleton that does not participate in the physico-chemical transformation, methane and its hydrate. The porous medium skeleton, gas hydrate (of methane and carbon dioxide) is assumed to be immobile and incompressible. Let us write the equations of mass conservation for carbon dioxide and methane filtered through the
reservoir:
\[
\frac{\partial}{\partial t} \left( \varphi S_g \rho^0_{g(c)} \right) + \frac{\partial}{\partial x} \left( \varphi S_g v_g(c) \rho^0_{g(c)} \right) = -J_g(c),
\]
\[
\frac{\partial}{\partial t} \left( \varphi S_g \rho^0_{g(m)} \right) + \frac{\partial}{\partial x} \left( \varphi S_g v_g(m) \rho^0_{g(m)} \right) = J_g(m).
\]  
(1)

Here and below subscripts \(sk\), \(h\) and \(g\) refer to the parameters of the skeleton, hydrate and gas, respectively, the subscripts in brackets \(i = c, m\) refer to the parameters of carbon dioxide and methane, respectively; \(\varphi\) is the reservoir porosity (for the volume occupied by gas and hydrate); \(S_g\) is the gas saturation; \(\rho^0_{g(i)}\) and \(v_g(i)\) \((i = c, m)\) are the partial densities and velocities of the gas mixture components; \(J_g(c)\) and \(J_g(m)\) are the intensities of the carbon dioxide transition to the hydrate and the methane displacement from the hydrate. We will assume that the gas hydrate consists of two components: methane hydrate and carbon dioxide hydrate. Then the volume hydrate saturation can be represented as:
\[
S_h = S_{h(c)} + S_{h(m)}, \quad S_g + S_h = 1,
\]

where \(S_{h(i)}\) is the saturation of pores with the carbon dioxide hydrate \((i = c)\) and the methane hydrate \((i = m)\).

Since the gas hydrate is immobile, the equations of mass conservation for the gas in the gas hydrate state can be written in the form:
\[
\frac{\partial}{\partial t} \left( \varphi S_{h(i)} G(i) \rho^0_{h(i)} \right) = J_g(i), \quad \frac{\partial}{\partial t} \left( \varphi S_{h(m)} G(m) \rho^0_{h(m)} \right) = -J_g(m),
\]  
(2)

\(\rho^0_{h(i)}\) and \(G(i)\) \((i = c, m)\) are the hydrate density and the gas mass content in the hydrate.

The most common structure of the hydrates of methane and carbon dioxide is \(sI\); in this structure in the equilibrium state of the surrounding gas hydrate system there are one molecule of gas per about six water molecules. Average mass content of carbon dioxide and methane in the hydrate is assumed to be equal, respectively \(G_{(c)} = 0.29\) and \(G_{(m)} = 0.13\). Therefore, the following relation is satisfied with good accuracy:
\[
(1 - G_{(c)}) \rho^0_{h(c)} = (1 - G_{(m)}) \rho^0_{h(m)}.
\]  
(3)

This condition also means that the unit volume of the hydrate of carbon dioxide and methane contains the same mass of water. Taking into account the above facts we assume that the number of molecules of methane leaving the hydrate is equal to the number of molecules of carbon dioxide passing into the hydrate. Those the process of the CH\(_4\)-CO\(_2\) replacement occurs without the release of water from the gas hydrate composition [4,6]. Hence, for the intensities \(J_g(c)\) and \(J_g(m)\), the following relation holds:
\[
\frac{J_g(c)}{M_{(c)}} = \frac{J_g(m)}{M_{(m)}},
\]  
(4)

where \(M_{(i)}\) \((i = c, m)\) is the gas molar mass. For the filtration and diffusion mixing of the gas mixture we shall adopt, respectively, the Darcy’s law and Fick’s law:
\[
\phi S_g v_g = -\frac{k_g}{\mu_g} \frac{\partial p}{\partial x},
\]  
(5)

\[
\rho^0_{g(c)} w_{g(c)} = -\rho^0_{g(m)} w_{g(m)} = D_g \frac{\partial \rho^0_{g(m)}}{\partial x},
\]  
(6)

\(w_{g(c)} = v_g(c) - v_g\), \(w_{g(m)} = v_g(m) - v_g m\).
where $D_g$ is the diffusion mixing coefficient of the mixture of methane and carbon dioxide; $w_{g(i)}$ ($i = c, m$) is the diffusion rate of the gas mixture components.

We will assume that the gas mixture is calorically perfect and obeys Dalton’s law:

$$
p_{g(c)} = p_{0}^{0}R_{(c)}T, \quad p_{g(m)} = p_{0}^{0}R_{(m)}T, \quad p = p_{g(c)} + p_{g(m)},
$$

$R_{(i)}$ ($i = c, m$) is the specific gas constant.

Assuming that the temperatures of the porous medium skeleton and substances that saturate it coincide ($T_{sk} = T_{h} = T_{g} = T$), we write the equation for changing the internal energy of the system consisting of the porous medium skeleton and the saturating it substances:

$$
\rho \frac{\partial T}{\partial t} + \varphi S_{g} \rho_{g} \frac{\partial T}{\partial x} = \frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) + \varphi \left( \rho_{h(c)}^{0} l_{h(c)} \frac{\partial S_{h(c)}}{\partial t} + \rho_{h(m)}^{0} l_{h(m)} \frac{\partial S_{h(m)}}{\partial t} \right),
$$

where $c_j$ and $\lambda_j$ ($j = g, h$) are the specific heat and thermal conductivity of the j-th phase; $l_{h(m)}$ and $l_{h(c)}$ are the specific heat of the methane hydrate decomposition and the carbon dioxide hydrate formation per unit mass; $\rho c$ and $\lambda$ are the specific volume heat capacity and thermal conductivity of the system.

The system of equations (1-8) is supplemented by the following boundary and initial conditions:

$$
x = 0, \quad t > 0 : \quad p = p_{e}, \quad p_{g(c)} = p_{g(c)e}, \quad T = T_{e},
$$

$$
x = L, \quad t > 0 : \quad p = p_{0}, \quad \partial T / \partial x = 0,
$$

$$
0 < x < L, \quad t = 0 : \quad p = p_{0}, \quad p_{g(c)} = 0, \quad T = T_{0},
$$

where $p_{0}$ and $T_{0}$ are the initial reservoir pressure and temperature; $p_{e}$ and $T_{e}$ are the pressure and temperature of the carbon dioxide injected into the reservoir; $L$ is the porous reservoir length.

### 2.2. Diffusion kinetics in the hydrate

We will assume that the rate of replacement of methane molecules by carbon dioxide molecules is determined by the diffusion of carbon dioxide through the carbon dioxide hydrate layer formed between the gas and methane hydrate. To construct analytical expressions for the kinetics of the carbon dioxide hydrate formation (or the replacement of methane molecules by carbon dioxide molecules), we consider the following limiting scheme. The porous medium (skeleton) is schematically represented as a system of cylindrical channels of radius $a$. We assume that the methane hydrate completely covers the porous channels walls. According to the scheme under consideration, the methane hydrate will be in the annular layer between $r = a$ and $r = a_{c}$, carbon dioxide hydrate in the layer between $r = a_{c}$ and $r = a_{g}$, and the gas mixture of carbon dioxide and methane moves in the channel of radius $r = a g$. Within the framework of the adopted scheme, the introduced linear dimensions and relative phase saturations will be related as follows:

$$
S_{h(m)} = 1 - \left( \frac{a_{c}}{a} \right)^{2}, \quad S_{h(c)} = \left( \frac{a_{c}}{a} \right)^{2} - \left( \frac{a_{g}}{a} \right)^{2}, \quad S_{g} = \left( \frac{a_{g}}{a} \right)^{2}.
$$

For the diffusion gas transfer through the carbon dioxide hydrate layer, we write the diffusion equation, see [7, 8]:

$$
\frac{\partial p_{g(c)}}{\partial t} = D_{h(c)} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial p_{g(c)}}{\partial r} \right), \quad a_{g} < r < a_{c},
$$

where $p_{g(c)}$ is the average density of the carbon dioxide dissolved in CO$_2$ hydrate (but not in the hydrate state); $D_{h(c)}$ is the diffusion coefficient of the carbon dioxide in CO$_2$ hydrate.
Under the boundary conditions:

\[ r = a_g : \rho_{g(c)} = \rho_{g(c)s} \quad r = a_c : \rho_{g(c)} = 0. \]  

(12)

The expression for the mass flow of the mobile carbon dioxide to the contact surface between the carbon dioxide and methane hydrates, per unit area, can be written as follows:

\[ j_{g(c)} = -D_{h(c)} \left( \frac{\partial \rho_{g(c)}}{\partial r} \right)_{a(c)}. \]  

(13)

The carbon dioxide consumption intensity \( J_{g(c)} \) is related to the flow \( j_{g(c)} \): \( J_{g(c)} = A_h j_{g(c)} \).

Let us determine the total area \( A_h \) of the contact surface per unit volume of the porous medium (the specific contact surface) between the hydrates CO\(_2\) and CH\(_4\). Within the framework of the adopted scheme for this area it is possible to write down:

\[ A_h = 2\pi a(c)n(c), \quad n(c) = \frac{\varphi (1 - S_{h(m)})}{\pi a^2(c)}, \]  

(14)

where \( n(c) \) is the number of the channels with radius \( a(c) \) in the porous medium volume unit.

Use the quasistationary solution of equation (11) with boundary conditions (12), expressions (13), (14), we can write:

\[ J_{g(c)} = 2\varphi (1 - S_{h(m)}) \frac{\rho_{g(c)s} D_{h(c)} a^2(c)}{a^2(c) \ln(a(c)/a_g)}. \]  

(15)

Note that \( \rho_{g(c)s} \) and \( D_{h(c)} \) are unknown empirical parameters. In the formula (15) these parameters enter as a product. Therefore, let us introduce one empirical parameter (the reduced diffusion coefficient for CO\(_2\)), which, in view of the above assumptions, response for the CO\(_2\) hydrate formation kinetics:

\[ D = \frac{\rho_{g(c)s} D_{h(c)}}{P_{g(c)}}. \]

The values of the gas diffusion coefficient through the hydrate layer given in different articles vary greatly. For example, references [9–11] mentions the values of the gas diffusion coefficient in hydrate from \( 10^{-15} \) m\(^2\)/s to \( 10^{-12} \div 10^{-10} \) m\(^2\)/s. It should be noted that many factors can affect the intensity of the hydrate formation and decomposition, such as the state of hydrate-forming constituents and the content of impurities in them, the introduction of various surfactants, inhibitors and nano-additives [12], impact of the electromagnetic and shock waves [13, 14] and much more.

3. Analysis of results

The following main values are accepted: \( p_0 = 3 \) MPa; \( T_0 = T_e = 273 \) K; \( p_e = 3.4 \) MPa; \( S_{h(m)0} = 0.2 \); \( L = 50 \) m, \( \varphi = 0.1 \); \( k = 5 \times 10^{-12} \) m\(^2\); \( D_g = 10^{-5} \) m\(^2\)/s; \( D = 5 \times 10^{-15} \) m\(^2\)/s.

Figure 1 shows the distributions of parameters along the reservoir length at different time moments. It can be seen that due to the CO\(_2\) injection into the reservoir the partial pressure of carbon dioxide in the porous medium increases and the process of methane replacement with carbon dioxide in the gas hydrate begins. Note that in the present case, the process of displacing free methane from the reservoir and the process of replacing methane with carbon dioxide go almost evenly on time. The gas substitution process in the reservoir ends in about an hour, then the remaining methane obtained from gas hydrate is displaced from the reservoir. The process of CH\(_4\)-CO\(_2\) replacement in the methane hydrate is accompanied by an increase in temperature (approximately 1 K).
Figure 1. Evolution of the carbon dioxide partial pressure fields (a) and methane (b), temperature (c) and carbon dioxide hydrate saturations (d).

Figure 2 shows the dependencies of the time of complete substitution of methane in hydrate for carbon dioxide in the whole reservoir on the values of absolute permeability taking into account (curve 1) and excluding (curve 2) diffusion mixing of the gas mixture with diffusion coefficient \( D = 5 \cdot 10^{-14} m^2/s \). It can be seen that diffusion mixing affects the total replacement time in the entire formation only in the case of low-permeable porous media, i.e. at low values of filtration mass transfer intensity.

Figure 2. The influence of diffusion mixing of the gas mixture at the time of complete gas substitution in the composition of the hydrate in the entire reservoir, depending on the permeability \((1 - D_g=10^{-5} m^2/s, 2 - 0)\).
4. Conclusion
We have numerically analyzed the process of replacing methane with carbon dioxide in a gas hydrate when carbon dioxide is injected into a porous media, which is initially saturated with methane and its hydrate, with allowance for diffusion kinetics. The study identified three characteristic stages of the process. The initial stage of the process is characterized by the displacement of free methane from the reservoir and the beginning of the process of gas substitution in the composition of the hydrate. At the second stage, methane is obtained, resulting from the replacement of methane with carbon dioxide in the hydrate composition. The third stage is characterized by the complete transition of methane hydrate to carbon dioxide hydrate and the complete extraction of methane from the gas hydrate reservoir. It was revealed that diffusion mixing of methane and carbon dioxide affects the time of complete substitution in the entire reservoir only in the case of low-permeability media.

Acknowledgments
This work was supported by the Russian Science Foundation (Grant No. 17-79-20001).

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