SIMULATION OF CH₄ RECOVERY FROM HYDRATE DEPOSITS BY INJECTION OF CO₂

by

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The paper presents a mathematical model of CH₄ recovery from gas hydrate deposits via injection of liquid CO₂. The process of CH₄ recovery is supposed to occur on the moving frontal boundary separating the deposit into two domains. The near domain is saturated with liquid CO₂ and its hydrate while the far one is saturated with CH₄ and its hydrate. Self-similar solutions describing the temperature and pressure fields were obtained. The effect of main parameters on the dynamics of the process under study was explored. It was revealed that at low temperatures of the CO₂ being injected the temperature in the far domain did not exceed that of equilibrium for decomposition of CH₄ gas hydrate. It was also found that with increasing pressure at which CO₂ was injected into the gas hydrate domain, the extension of the region saturated with CO₂ hydrate was increasing.

Keywords: hydrate, CH₄ recovery, CO₂ injection

Introduction

Recently, a rather serious alternative to traditional sources of natural gas has become gas hydrates. It is known that quite large volumes of CH₄ gas are concentrated in gas hydrate deposits located in permafrost zones and under the seafloor [1, 2]. Regarding to this, creating various technologies for extracting hydrocarbon gas from gas hydrate deposits is becoming urgent. Conventional methods of extracting CH₄ gas from hydrates are either heating or depressurization which is a rather complex technical problem under negative temperature conditions. Another problem not related to the extraction of natural gas from hydrates is constant emission of large amounts of CO₂ into the Earth’s atmosphere [3, 4]. Consequently, the challenge is to seek for a fundamentally possible and promising method of CO₂ utilization. One of such methods is replacing CH₄ in its gas hydrate with liquid CO₂ [5-8]. Such a technology would allow both CH₄ to be recovered and CO₂ to be utilized. It is known that CO₂ hydrate is more stable than that of CH₄. Therefore, the process of replacing CO₂ molecules in its hydrate with CH₄ ones becomes possible [6].

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Experimental studies of the process of replacing CH₄ with CO₂ in its gas hydrate are discussed in [6-8]. In addition, in [8] the process of CO₂ hydrate formation is studied in a range of positive and negative temperatures. According to these, CH₄ replacement in its hydrate with liquid CO₂ will occur at temperatures and pressures that meet the conditions of stable hydrate [6, 7].

Mathematical models for formation and decomposition of gas hydrates when injecting the same gas which saturated the hydrate area in its initial state are considered in [9-13]. The papers [14, 15] present a mathematical model for injection of liquid CO₂ into a porous medium saturated with CH₄ and its gas hydrate.

The purpose of this work is to build a mathematical model of the process of CH₄ recovery from gas hydrate deposits via injection of liquid CO₂.

**Problem statement and governing equations**

Let a horizontal area at its initial time be saturated with a hydrate-forming mixture \( S_{h0} \) (that of snow and CH₄) and CH₄ \( S_{g0} \) at a negative temperature of, \( T_0 \), and a pressure of, \( p_0 \), that correspond to the stable state of CH₄ gas hydrate. We assume that liquid CO₂ is injected through the boundary \( x = 0 \) at the temperature, \( T_e \), and pressure, \( p_e \), that correspond to the stable state of CO₂ gas hydrate and are maintained constant on this boundary. The phase equilibrium diagram of the system is shown in fig. 1. To determine the dependence of the equilibrium temperature, \( T_e(p) \), on the current pressure value, we apply the relation:

\[
T_e(p) = T_{(0)} + T_0 \ln \left( \frac{p}{p_{(0)}} \right)
\]

where \( T_{(0)}, p_{(0)} \) are the equilibrium temperature and pressure, respectively, and \( T_0 \) – the empirical parameter.

Given the assumptions, we write down a system of governing equations describing the processes of filtration and heat transfer in a gas-hydrate area for a 1-D flow. The process of replacement takes place on the front surface of \( x(s) \) which divides the area into two domains. The near domain is saturated with liquid CO₂ and its hydrate. The far domain is saturated with CH₄ and its hydrate. Lower indices \( i = d \) and \( i = m \) correspond to the near domain, \( 0 < x < x(s) \), and the far one, \( x(s) < x < \infty \), for CO₂ and CH₄, respectively.

We write the mass conservation equations for each domain:

\[
\frac{\partial}{\partial t}(\rho_i S_i) + \frac{\partial}{\partial x}(\rho_i v_i) = 0
\]

where \( \rho_i \) is the true density, \( S_i \) – the saturation, and \( v_i \) – the velocity of the \( i^{th} \) phase.

The energy conservation equations are written:
\[ \rho c_i \frac{\partial T_i}{\partial t} + \rho_i c_i S_{\nu_i} \frac{\partial T_i}{\partial x} = \lambda_i \frac{\partial^2 T_i}{\partial x^2} \]  

(3)

where \( c_i \) is the specific mass heat capacity of the \( i^{th} \) phase, \( \rho c \) – the specific volume heat capacity, and \( \lambda \) – the thermal conductivity of the system.

For \( \nu \) the filtration process Darcy's law can be written:

\[ S_{\nu_i} = -\frac{k_i}{\mu_i} \frac{\partial p_i}{\partial x} \]  

(4)

where \( \mu_i \) is the gas dynamic viscosity and \( k_i \) is the gas permeability coefficient.

For \( \text{CH}_4 \) the Mendeleev-Clapeyron equation is written:

\[ \rho_m = \frac{p_m}{R_T} \]  

For the liquid phase the equation of state is:

\[ \beta_l = \beta_{(0,4)} \exp\left( \frac{\beta_l(p_d - p_{(0,4)})}{\rho_{(0,4)}} \right) \]

where \( \beta \) is the volume compression ratio of liquid \( \text{CO}_2 \).

Taking into account the conditions of mass and heat balance on the boundary between the two domains, the following relations are satisfied:

\[ -\frac{k_i}{\mu_i} \frac{\partial p_i}{\partial x} = \left( S_m - \frac{\rho_m G_m S_m}{\rho_m} \right) \dot{x}_s \]  

(5)

\[ S_{\text{ad}} \rho_{\text{ad}} (1 - G_a) \dot{x}_s = S_m \rho_m (1 - G_m) \dot{x}_s \]  

(6)

\[ \frac{\lambda}{\lambda_m} \frac{\partial T_d}{\partial x} - \frac{\lambda_m}{\lambda_m} \frac{\partial T_m}{\partial x} = (\rho_{\text{ad}} S_{\text{ad}} l_{\text{ad}} - \rho_m S_m l_m) \dot{x} \]  

(7)

where \( \rho_{\text{ad}} \) is the specific heat of hydrate formation for the \( i^{th} \) phase and \( \dot{x}_s \) is the interface velocity.

The value of hydrate saturation in the \( \text{CO}_2 \) zone can be found from eq. (6) which is a condition of the hydrate-bound \( \text{CO}_2 \) mass balance:

\[ S_{\text{ad}} = \frac{S_m \rho_m (1 - G_m)}{\rho_{\text{ad}} (1 - G_a)} \]  

(8)

Let us introduce dimensionless quantities \( P_d \) and \( P_m \) in the following forms:

\[ P_d = \frac{P_d}{\rho_{(0,4)}} = \exp\left( \beta(p_d - p_{(0,4)}) \right), \quad P_m = \frac{P_m^2}{P_0^2} \]  

(9)

Based on eqs. (2)-(4), the equations of piezoconductivity and thermal diffusivity are written:

\[ \frac{\partial}{\partial t} \left( \chi \frac{\partial P_i}{\partial x} \right) = \chi \frac{\partial^2 P_i}{\partial x^2} \]  

(10)

\[ \frac{\partial T_d}{\partial t} = \chi T \frac{\partial P_d}{\partial x} \frac{\partial T_d}{\partial x} + \chi^2 \frac{\partial^2 T_d}{\partial x^2} \]  

(11)
where

\[
\text{Pe}_d = \frac{\rho_d c_d \kappa_d}{\lambda \mu_d \beta}, \quad \text{Pe}_m = \frac{\rho_m c_m k_m p_0}{2 \lambda \mu_m}, \quad \chi_0^m = \frac{\kappa_m}{S_{m0} \mu_m \beta},
\]

\[
\chi_0^p = \frac{k_{pm} p_{m0}}{S_{pm0} \mu_{pm0}}, \quad \varphi = \frac{\chi'}{4 \chi_0}, \quad \chi' = \frac{\lambda}{\rho_c}
\]

This system is augmented with the following initial and boundary conditions:

\[
t = 0 \quad (x \geq 0): S_e = S_{e0}, \quad S_h = S_{h0}, \quad T = T_0, \quad p = p_0
\]

\[
x = 0 \quad (t > 0): T = T_0, \quad p = p_e
\]

\[
x = \infty \quad (t > 0): T = T_0, \quad p = p_0
\]

Since the pressure at the interface between the domains is assumed to be continuous, the values of \(P_{sd}\) and \(P_{sm}\) are related by the ratio:

\[
(12)
\]

**Self-similar solution**

Let us introduce the self-similar variable \(\xi\):

\[
\xi = \frac{x}{2\sqrt{\chi'_0} t}
\]

The equations of pisoconductivity eq. (10) and thermal diffusivity eq. (11) for this variable are written:

\[
-\xi^2 \frac{d^2 P_d}{d \xi^2} = \frac{\chi'_0}{2 \chi'_0} \frac{d^2 P_d}{d \xi^2}, \quad -\xi^2 \frac{d^2 P_m}{d \xi^2} = \frac{1}{2} \frac{d^2 P_m}{d \xi^2}
\]

\[
-\xi^2 \frac{d^2 T_d}{d \xi^2} = 2 \text{Pe}_d \varphi \frac{d^2 T_d}{d \xi^2} + 2 \varphi \frac{d^2 T_d}{d \xi^2}
\]

On integrating eqs. (14) and (15), we can write the solution for the pressure and temperature distributions in each domain:

\[
(16)
\]

\[
(17)
\]

where

\[
\eta = \frac{\chi'_0}{\chi_0^m}
\]
Based on the conditions eqs. (5)-(7) and taking into account the solutions eqs. (16) and (17), we obtain equations for determining the displacement front co-ordinate, $\xi$, and the values of $p_0$ and $T_0$ on it:

$$\frac{(P_s - P_{sd}) \exp \left( -\frac{\xi^2}{\eta} \right)}{\int_0^\xi \exp \left( -\frac{\xi^2}{\eta} \right) d\xi} = A_0 \xi P_d$$

(18)

$$\frac{(P_m - 1) \exp (-\xi^2)}{\int_0^\xi \exp (-\xi^2) d\xi} = A_m \sqrt{P_m \xi},$$

(19)

$$\frac{(T_s - T_d) \exp \left( -\frac{\xi^2}{4\varphi} - Pe P_d \right)}{\int_0^\xi \exp \left( -\frac{\xi^2}{4\varphi} - Pe P_d \right) d\xi} = (T_0 - T_d) \exp \left( -\frac{\xi^2}{4\varphi} - Pe P_d \right) \int_0^\xi \exp \left( -\frac{\xi^2}{4\varphi} - Pe P_d \right) d\xi = B \xi,$$

(20)

where

$$A_0 = \frac{\chi^e \mu \beta}{k_i} \left( 1 - S_{md} + \frac{\rho_m G S_{md}}{\rho_d} \right), \quad A_m = \frac{2 \chi^e \mu \beta}{p_0 k_m} \left( 1 - S_{lm} + \frac{\rho_m G_m S_{lm}}{\rho_m} \right),$$

$$B = \frac{2 \chi^e \mu \beta}{\lambda} (\rho_m S_{md} l_{md} - \rho_m S_{lm} l_{lm}).$$

Expressing the quantity of $P_{sm}$ from eq. (18) and substituting it into the ratio eq. (12), we find $P_{sd}$ as a function of $\xi$. Substituting $P_{sd}(\xi)$ into eq. (18), we result in a transcendental equation with one unknown $\xi$, which is solved by the bisection method. From eqs. (12), (18), and (20) we obtain the values of pressure, $P_0$, and temperature, $T_0$, on the boundary $x_{s0}$.

### Results of numerical analysis

For the thermophysical parameters, gas, CO$_2$, and hydrate the following values were taken: $G_m = 0.12$, $G_d = 0.28$, $R_g = 520$ [Jkg$^{-1}$K$^{-1}$], $\rho_{md} = 890$ [kgm$^{-3}$], $\rho_m = 900$ [kgm$^{-3}$], $\rho_{bd} = 1100$ [kgm$^{-3}$], $k_0 = 10^{-6}$ [m$^2$], $c_{em} = 1560$ [Jkg$^{-1}$K$^{-1}$], $c_{bd} = 2600$ [Jkg$^{-1}$K$^{-1}$], $c_{hm} = 2500$ [Jkg$^{-1}$K$^{-1}$], $\mu_d = 10^{-4}$ [Pa s], $\mu_m = 10^{-5}$ [Pa s], $\lambda_{hm} = 0.5$ [Wm$^{-1}$K$^{-1}$], $\beta = 10^{-8}$ [Pa$^{-1}$], $l_{md} = 1.5 \times 10^{-2}$ [Jkg$^{-1}$] (at the $T < 0$ °C), $l_{lm} = 1.45 \times 10^{-1}$ [Jkg$^{-1}$] (at the $T < 0$ °C).

For the equilibrium temperature and the corresponding pressure, as well as the empirical parameter included in the eq. (1), the following values were taken: the phase equilibrium condition for CH$_4$ - $T_{(s0)} = 263$ [K], $p_{(s0)} = 1.86$ [MPa], $T_s = 30$ [K], the phase equilibrium condition for CO$_2$ - $T_{(s0)} = 263$ [K], $p_{(s0)} = 0.67$ [MPa], $T_s = 16$ [K]. In the graphs, the equilibrium hydrate formation curve eq. (1) is indicated by a dash-dotted line.

For the CH$_4$ hydrate temperature, pressure, and saturation characterizing the initial state of the gas-CH$_4$ hydrate system, the following values were taken, respectively, $T_0 = 233$ [K], $p_0 = 1.5$ [MPa], and $S_{lm} = 0.3$.

Figure 2(a) illustrates the temperature and fig. 2(c) pressure field distributions in the computation domain at different pressure values of the liquid CO$_2$ being injected $p_s$, with scaled-up fragments of the temperature, 2(b), and pressure, 2(d), distributions being located on the right. In the figure, the dash-dotted line shows the values of the moving boundary $\xi$, for the corresponding pressure values of the CO$_2$ being injected. At the pressure values of
\(p_{e} = 2 \text{ [MPa]}, p_{e} = 3 \text{ [MPa]}, p_{e} = 5 \text{ [MPa]},\) the moving boundary takes the values of \(\zeta_{s} = 0.034,\) \(\zeta_{s} = 0.084,\) \(\zeta_{s} = 0.166,\) respectively. It can be seen from the graphs that with increasing the pressure at which \(\text{CO}_{2}\) is injected into the gas hydrate domain, the extension of the area saturated with \(\text{CO}_{2}\) hydrate is increasing.

![Graphs showing temperature and pressure distributions](image)

**Figure 2.** Temperature (a), (b) and pressure (c), (d) distributions in the domain at different pressures, \(p_{e}\) of the liquid \(\text{CO}_{2}\) being injected depending on the dimensionless self-similar variable, \(\zeta;\)

1 - at \(p_{e} = 2 \text{ [MPa]},\) 2 - at \(p_{e} = 3 \text{ [MPa]},\) and 3 - at \(p_{e} = 5 \text{ [MPa]}\)

Figure 3(a) shows the temperature and fig. 3(c) pressure field distribution in the computation domain at different temperatures of the liquid \(\text{CO}_{2}\) being injected \(T_{e},\) with scaled-up fragments of the temperature, 3(b), and pressure, 3(d), distributions being located on the right. At different temperatures of the \(\text{CO}_{2}\) being injected the boundary coordinate \(\zeta_{s}\) takes the value of \(\zeta_{s} = 0.034.\) It can be seen from the graphs that if \(\text{CO}_{2}\) is injected at a temperature that is lower than the initial one in the gas hydrate domain, the temperature rises to its initial value in the domain.
A numerical analysis of the process of replacing CH$_4$ with liquid CO$_2$ in the gas hydrate domain at negative temperatures was conducted. Self-similar solutions describing the temperature and pressure fields were constructed. The impact of the main and initial parameters on the dynamics of the process under study was investigated. It was shown that at low temperatures of the CO$_2$ being injected, the temperature in the far domain did not exceed the equilibrium decomposition temperature for CH$_4$ gas hydrate. It was found that with increasing pressure at which CO$_2$ was injected into the gas hydrate domain, the extension of the region saturated with CO$_2$ hydrate was increasing.

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Nomenclature

c – specific mass heat, [Jkg⁻¹K⁻¹]
\(G\) – mass content of the phase in the hydrate
k – permeability coefficient, [m²]
l – specific heat of hydrate formation, [Jkg⁻¹]
p – pressure, [Pa]
R – reduced gas constant, [Jkg⁻¹K⁻¹]
S – volume saturation of the phase
T – temperature, [K]
t – time
x – co-ordinate, [m]

\(\mu\) – dynamic viscosity, [Pa·s]
\(\dot{c}\) – dimensionless self-similar variable
\(\rho\) – true density, [kgm⁻³]

Subscripts

0 – initial value of the parameter
d – liquid CO₂
e – value at the discharge boundary
g – gas phase
h – hydrate phase
i – phases corresponding to the areas of liquid CO₂ and CH₄
s – mobile frontal boundary between the areas of CO₂ and CH₄

Greek symbols

\(\beta\) – coefficient of volume compression of liquid CO₂, [Pa⁻¹]
\(\lambda\) – coefficient of thermal conductivity of the system, [Wm⁻¹K⁻¹]

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